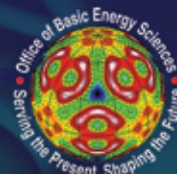


Basic Research Needs for
**Materials
under
Extreme
Environments**

Report of the Basic Energy
Sciences Workshop on
Materials under
Extreme Environments

June 11-13, 2007



On the cover:

The cover illustration depicts a diamond-anvil cell that can exert pressures of hundreds of gigapascals. Adapted from an image from A. Correa, Lawrence Livermore National Laboratory.*

*R. J. Hemley, A pressing matter, *Phys. World* **19**, 26–30 (2006).

BASIC RESEARCH NEEDS FOR MATERIALS UNDER EXTREME ENVIRONMENTS

Report of the Basic Energy Sciences Workshop for Materials under Extreme Environments

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ACRONYM LIST

AFM	atomic force microscopy
CVD	chemical vapor deposit
DFT	density functional theory
FIB	focused ion beam
HDAL	high-density amorphous liquids
HDL	high-density liquids
IACS	International Annealed Copper Standard
LCLS	Linac Coherent Light Source
LDAL	low-density amorphous liquids
LDL	low-density liquids
MD	molecular dynamics
MEMS	microelectromechanical
NIF	National Ignition Facility
PRA	primary recoil atoms
PRD	Priority Research Direction
SCC	stress corrosion cracking
SEM	scanning electron microscope
SIA	self-interstitial atom
SNS	Spallation Neutron Source
STEM	scanning transmission electron microscopy
TEAM	transmission electron aberration-corrected microscopes
TEM	transmission electron microscope
XLPE	cross-linked polyethylene

EXECUTIVE SUMMARY

EXECUTIVE SUMMARY

Never has the world been so acutely aware of the inextricably linked issues of energy, environment, economy, and security. As the economies of developing countries boom, so does their demand for energy. Today nearly a quarter of the world does not have electrical power, yet the demand for electricity is projected to more than double over the next two decades. Increased demand for energy to power factories, transport commodities and people, and heat/cool homes also results in increased CO₂ emissions. In 2007 China, a major consumer of coal, surpassed the United States in overall carbon dioxide emissions. As global CO₂ emissions grow, the urgency grows to produce energy from carbon-based sources more efficiently in the near term and to move to non-carbon-based energy sources, such as solar, hydrogen, or nuclear, in the longer term. As we look toward the future, two points are very clear: (1) the economy and security of this nation is critically dependent on a readily available, clean and affordable energy supply; and (2) no one energy solution will meet all future energy demands, requiring investments in development of multiple energy technologies.

Materials are central to every energy technology, and future energy technologies will place increasing demands on materials performance with respect to extremes in stress, strain, temperature, pressure, chemical reactivity, photon or radiation flux, and electric or magnetic fields. For example, today's state-of-the-art coal-fired power plants operate at about 35% efficiency. Increasing this efficiency to 60% using supercritical steam requires raising operating temperatures by nearly 50% and essentially doubling the operating pressures. These operating conditions require new materials that can reliably withstand these extreme thermal and pressure environments. To lower fuel consumption in transportation, future vehicles will demand lighter weight components with high strength. Next-generation nuclear fission reactors require materials capable of withstanding higher temperatures and higher radiation flux in highly corrosive environments for long periods of time without failure. These increasingly extreme operating environments accelerate the aging process in materials, leading to reduced performance and eventually to failure. If one extreme is harmful, two or more can be devastating. High temperature, for example, not only weakens chemical bonds, it also speeds up the chemical reactions of corrosion.

Often materials fail at one-tenth or less of their intrinsic limits, and we do not understand why. This failure of materials is a principal bottleneck for developing future energy technologies that require placing materials under increasingly extreme conditions. Reaching the intrinsic limit of materials performance requires understanding the atomic and molecular origins of this failure. This knowledge would enable an increase in materials performance of order of magnitude or more. Further, understanding how these extreme environments affect the physical and chemical processes that occur in the bulk material and at its surface would open the door to employing these conditions to make entirely new classes of materials with greatly enhanced performance for future energy technologies. This knowledge will not be achieved by incremental advances in materials science. Indeed, this knowledge will only be gained by innovative basic research that will unlock the fundamentals of how extremes environments interact with materials and how these interactions can be controlled to reach

the intrinsic limits of materials performance and to develop revolutionary new materials. These new materials would have enormous impact for the development of future energy technologies: extending lifetimes, increasing efficiencies, providing novel capabilities, and lowering costs. Beyond energy applications, these new materials would have a huge impact on other areas of importance to this nation, including national security, industry, and other areas where robust, reliable materials are required.

This report summarizes the research directions identified by a Basic Energy Sciences Workshop on Basic Research Needs for Materials under Extreme Environments, held in June 2007. More than 140 invited scientists and engineers from academia, industry, and the national laboratories attended the workshop, along with representatives from other offices within the Department of Energy, including the National Nuclear Security Administration, the Office of Nuclear Energy, the Office of Energy Efficiency and Renewable Energy, and the Office of Fossil Energy. Prior to the workshop, a technology resource document, *Technology and Applied R&D Needs for Materials under Extreme Environments*, was prepared that provided the participants with an overview of current and future materials needs for energy technologies. The workshop began with a plenary session that outlined the technology needs and the state of the art in research of materials under extreme conditions. The workshop was then divided into four panels, focusing on specific types of extreme environments: Energetic Flux Extremes, Chemical Reactive Extremes, Thermomechanical Extremes, and Electromagnetic Extremes. The four panels were asked to assess the current status of research in each of these four areas and identify the most promising research directions that would bridge the current knowledge gaps in understanding how these four extreme environments impact materials at the atomic and molecular levels. The goal was to outline specific Priority Research Directions (PRDs) that would ultimately lead to the development of vastly improved materials across a broad range of future energy technologies. During the course of the workshop, a number of common themes emerged across these four panels and a fifth panel was charged to identify these cross-cutting research areas.

Photons and energetic particles can cause damage to materials that occurs over broad time and length scales. While initiation, characterized by localized melting and re-crystallization, may occur in fractions of a picosecond, this process can produce cascades of point defects that diffuse and agglomerate into larger clusters. These nanoscale clusters can eventually reach macroscopic dimensions, leading to decreased performance and failure. The panel on energetic flux extremes noted that this degradation and failure is a key barrier to achieving more efficient energy generation systems and limits the lifetime of materials used in photovoltaics, solar collectors, nuclear reactors, optics, electronics and other energy and security systems used in extreme flux environments. The panel concluded that the ability to prevent this degradation from extreme fluxes is critically dependent on being able to elucidate the atomic- and molecular-level mechanisms of defect production and damage evolution triggered by single and multiple energetic particles and photons interacting with materials. Advances in characterization and computational tools have the potential to provide an unprecedented opportunity to elucidate these key mechanisms. In particular, ultrafast and ultra-high spatial resolution characterization tools will allow the initial atomic-scale damage events to be observed. Further, advanced computational capabilities have the potential to

capture multiscale damage evolution from atomic to macroscopic dimensions. Elucidation of these mechanisms would allow the complex pathways of damage evolution from the atomic to the macroscopic scale to be understood. This knowledge would ultimately allow atomic and molecular structures to be manipulated in a predictable manner to create new materials that have extraordinary tolerance and can function within an extreme environment without property degradation. Further, it would provide revolutionary capabilities for synthesizing materials with novel structures or, alternatively, to force chemical reactions that normally result in damage to proceed along selected pathways that are either benign or self-repair damage initiation.

Chemically reactive extreme environments are found in many advanced energy systems, including fuel cells, nuclear reactors, and batteries, among others. These conditions include aqueous and non-aqueous liquids (such as mineral acids, alcohols, and ionic liquids) and gaseous environments (such as hydrogen, ammonia, and steam). The panel evaluating extreme chemical environments concluded there is a lack of fundamental understanding of thermodynamic and kinetic processes that occur at the atomic level under these important reactive environments. The chemically induced degradation of materials is initiated at the interface of a material with its environment. Chemical stability in these environments is often controlled by protective surfaces, either self-healing, stable films that form on a surface (such as oxides) or by coatings that are applied to a surface. Besides providing surface stability, these films must also prevent facile mass transport of reactive species into the bulk of the material. While some films can have long lifetimes, increasing severity of environments can cause the films to break down, leading to costly materials failure. A major challenge therefore is to develop a new generation of surface layers that are extremely robust under aggressive chemical conditions. Before this can be accomplished, however, it is critical to understand the equilibrium and non-equilibrium thermodynamics and reaction kinetics that occur at the atomic level at the interface of the protective film with its environment. The stability of the film can be further complicated by differences in the material's morphology, structure, and defects. It is critical that these complex and interrelated chemical and physical processes be understood at the nanoscale using new capabilities in materials characterization and theory, modeling, and simulation. Armed with this information, it will be possible to develop a new generation of robust surface films to protect materials in extreme chemical environments. Further, this understanding will provide insight into developing films that can self-heal and to synthesizing new classes of materials that have unimaginable stability to aggressive chemical environments.

The need for materials that can withstand thermomechanical extremes—high pressure and stress, strain and strain rate, and high and low temperature—is found across a broad range of energy technologies, such as efficient steam turbines and heat exchangers, fuel-efficient vehicles, and strong wind turbine blades. Failures of materials under thermomechanical extremes can be catastrophic and costly. The panel on thermomechanical extremes concluded that designing new materials with properties specifically tailored to withstand thermomechanical extremes must begin with understanding the fundamental chemical and physical processes involved in materials failure, extending from the nanoscale to the collective behavior at the macroscale. Further, the behavior of materials must be understood under static, quasistatic, and dynamic thermomechanical extremes. This requires learning

how atoms and electrons move within a material under extremes to provide insight into defect production and eventual evolution into microstructural components, such as dislocations, voids, and grain boundaries. This will require advanced analytical tools that can study materials in situ as these defects originate and evolve. Once these processes are understood, it will be possible to predict responses of materials under thermomechanical extremes using advanced computation tools. Further, this fundamental knowledge will open new avenues for designing and synthesizing materials with unique properties. Using these thermomechanical extremes will allow the very nature of chemical bonds to be tuned to produce revolutionary new materials, such as ultrahard materials.

As electrical energy demand grows, perhaps by greater than 70% over the next 50 years, so does the need to develop materials capable of operating at extreme electric and magnetic fields. To develop future electrical energy technologies, new materials are needed for magnets capable of operating at higher fields in generators and motors, insulators resistant to higher electric fields and field gradients, and conductors/superconductors capable of carrying higher current at lower voltage. The panel on electromagnetic extremes concluded that the discovery and understanding of this broad range of new materials requires revealing and controlling the defects that occur at the nanoscale. Defects are responsible for breakdown of insulators, yet defects are needed within local structures of superconductors to trap magnetic vortices. The ability to observe these defects as materials interact with electromagnetic extremes is just becoming available with advances in characterization tools with increased spatial and time resolution. Understanding how these nanoscale defects evolve to affect the macroscale behavior of materials is a grand challenge, and advances in multiscale modeling are required to understand the behavior of materials under these extremes. Once the behavior of defects in materials is understood, then materials could be designed to prevent dielectric breakdown or to enhance magnetic behavior. For example, composite materials having appropriate structures and properties could be tailored using nanoscale self-assembly techniques. The panel projected that understanding how electric and magnetic fields affect materials at the atomic and molecular level could lead to the ability to control materials properties and synthesis. Such control would lead to a new generation of materials that is just emerging today—such as electrooptic materials that can be switched between transparency and opacity through application of electric fields. Beyond energy applications, these tailored materials could have enormous importance in security, computing, electronics, and other applications.

During the course of the workshop, four recurring science issues emerged as important themes: (1) *Achieving the Limits of Performance*; (2) *Exploiting Extreme Environments for Materials Design and Synthesis*; (3) *Characterization on the Scale of Fundamental Interactions*; and (4) *Predicting and Modeling Materials Performance*. All four of the workshop panels identified the need to understand the complex and interrelated physical and chemical processes that control the various performance limits of materials subjected to extreme conditions as the major technical bottleneck in meeting future energy needs. Most of these processes involve understanding the cascade of events that is initiated at atomic-level defects and progresses through macroscopic materials properties. By understanding various mechanisms by which materials fail, for example, it may be possible to increase the

performance and lifetime limits of materials by an order of magnitude or more and thereby achieve the true limits of materials performance.

Understanding the atomic and molecular basis of the interaction of extreme environments with materials provides an exciting and unique opportunity to produce entirely new classes of materials. Today materials are made primarily by changing temperature, composition, and sometimes, pressure. The panels concluded that extreme conditions—in the form of high temperatures, pressures, strain rate, radiation fluxes, or external fields, alone or in combination—can potentially be used as new “knobs” that can be manipulated for the synthesis of revolutionary new materials. All four of the extreme environments offer new strategies for controlling the atomic- and molecular-level structure in unprecedented ways to produce materials with tailored functionalities.

To achieve the breakthroughs needed to understand the atomic and molecular processes that occur within the bulk and at surfaces in materials in extreme environments will require advances in the final two cross-cutting areas, characterization and computation. Elucidating changes in structure and dynamics over broad timescales (femtoseconds to many seconds) and length scales (nanoscale to macroscale) is critical to realizing the revolutionary materials required for future energy technologies. Advances in characterization tools, including diffraction, scattering, spectroscopy, microscopy, and imaging, can provide this critical information. Of particular importance is the need to combine two or more of these characterization tools to permit so-called “multi-dimensional” analysis of materials and surfaces in situ. These advances will enable the elucidation of fundamental chemical and physical mechanisms that are at the heart of materials performance (and failure) and catalyze the discovery of new materials required for the next generation of energy technologies.

Complementing these characterization techniques are computational techniques required for modeling and predicting materials behavior under extreme conditions. Recent advances in theory and algorithms, coupled with enormous and growing computational power and ever more sophisticated experimental methods, are opening up exciting new possibilities for taking advantage of predictive theory and simulation to design and predict the properties and performance of new materials required for extreme environments. New theoretical tools are needed to describe new phenomena and processes that occur under extreme conditions. These various tools need to be integrated across broad length scales—atomic to macroscopic—to model and predict the properties of real materials in response to extreme environments. Together with advanced synthesis and characterization techniques, these new capabilities in theory and modeling offer exciting new capabilities to accelerate scientific discovery and shorten the development cycle from discovery to application.

In concluding the workshop, the panelists were confident that today’s gaps in materials performance under extreme conditions could be bridged if the physical and chemical changes that occur in bulk materials and at the interface with the extreme environment could be understood from the atomic to macroscopic scale. These complex and interrelated phenomena can be unraveled as advances are realized in characterization and computational tools. These advances will allow structural changes, including defects, to be observed in real time and then modeled so the response of materials can be predicted. The concept of

exploiting these extreme environments to create revolutionary new materials was viewed to be particularly exciting. Adding these parameters to the toolkit of materials synthesis opens unimaginable possibilities for developing materials with tailored properties. The knowledge needed for bridging these technology gaps requires significant investment in basic research, and this research needs to be coupled closely with the applied research and technology communities and industry that will drive future energy technologies. These investments in fundamental research of materials under extreme conditions will have a major impact on the development of technologies that can meet future requirements for abundant, affordable, and clean energy. However, this research will enable the development of materials that will have a much broader impact in other applications that are critical to the security and economy of this nation.

INTRODUCTION

BASIC RESEARCH NEEDS FOR MATERIALS UNDER EXTREME ENVIRONMENTS

INTRODUCTION

The global energy situation has never been more precarious. The demand for energy is expected to increase by 50% or more by 2030, with over 70% of that growth coming from countries with emerging economies. China alone is projected to account for more than 30% of this global energy demand increase over the next two decades. Worldwide demand is projected to grow further, perhaps doubling or even tripling, by 2050 as economies and populations continue to grow. Interestingly, this demand grows in spite of high energy prices. Limited oil supplies, coupled with increased demand, have resulted in oil prices hovering closer to \$100 per barrel in 2007, compared with \$60 per barrel in mid-2005—yet consumption has increased. These increased costs and decreased supplies of oil are projected to result in increased demand for electricity. Today electrical power is not available to nearly one-quarter of the world's population, and demand is expected to more than double over the next two decades. These increasing demands for energy have placed enormous pressure on the environment as atmospheric levels of carbon dioxide continue to increase. In fact, China has surpassed the United States in total carbon dioxide emissions. In addition to environmental concerns, this burgeoning demand for energy has enormous implications for the global economy and security.

Meeting the increases in global energy demand while minimizing the impact on the environment will not be possible without major investments in new energy technologies. There is no one solution to meeting these energy challenges, and it is certain that a portfolio of energy technologies will be needed: solar, advanced nuclear, hydrogen, among others. However, there is one common need to all future energy technologies: improved materials. At every step, from production to distribution to consumption, energy technologies are subject to materials problems critical to engineering or economic feasibility. Specifically, future energy production and use require materials that can perform and survive in extreme conditions. These extreme “environments” provide qualitative changes in a material's capability to endure stresses and strains, high or low temperatures, corrosive or oxidizing atmospheres, strong magnetic and electric fields, and intense photon or radiation flux. These environments are made more extreme by having two or more of these conditions exist simultaneously, as is the case in nearly every energy technology.

Design choices of materials are based on what is known about both specific materials and the environments in which they must function; limitations of our knowledge constrain those choices, often dramatically reducing the usefulness of materials and the efficiency of systems. Better understanding of materials under extreme environments would have a tremendous impact for future energy technologies, such as the following:

- Automobiles and airplanes that are lighter with engines that operate at higher temperatures, resulting in improved efficiency.
- Electrical energy storage devices, such as batteries, that are far more efficient and have much longer lifetimes.

- Electricity transmission and distribution systems that are more reliable and efficient.
- Fission reactors, conventional boilers, and stationary turbines that are more efficient, operating at higher temperatures with longer lifetimes.
- Distribution pipelines for natural gas, hydrogen, ethanol, or other liquid or gaseous fuels that are not subject to failures resulting from corrosion or other chemical reactions.
- Materials, both structural and functional, that can respond to environmental changes and can self-heal and even sense and warn before materials fail, for whatever reason.

This report summarizes the results and conclusions of the Department of Energy (DOE) Workshop on Basic Research Needs for Materials under Extreme Environments, held in Bethesda, Maryland, June 11–13, 2007. This workshop was convened specifically to evaluate the potential for developing revolutionary new materials that will meet demanding future energy requirements that expose materials to environmental extremes. The invited workshop attendees, numbering more than 140, included representatives from universities (42), national laboratories (70), government agencies (20), industries (3), and other nations (6). The workshop program and attendee list are provided in Appendices B and C, respectively. Participants were provided with a technology perspectives resource document in advance of the workshop describing the technology and applied R&D needs for materials under extreme environments. This document is included in Appendix A. Following a plenary session on technology needs and basic research challenges for materials under extreme environments, the workshop was divided into the following four topical panels: Energetic Flux Extremes, Chemically Reactive Extremes, Thermomechanical Extremes, and Electromagnetic Extremes. In addition, a Cross-cut panel identified areas of synergy across the four topical panels. Each panel was composed of research leaders in the relevant field from universities, national laboratories, and industry. Prior to the workshop, the organizers noted that while the next generation of energy technologies demands extreme environments, these types of conditions are also highly relevant to materials performances within the national security mission of DOE, and these issues were also highlighted at the workshop.

Over the last several decades, improvements in materials have occurred in a range of incremental ways. The workshop concluded that major technology breakthroughs will require fundamental understanding of the effects of extreme environments on materials. By understanding the demands placed on materials by extreme environments, particularly at the atomic and molecular level, we can push our knowledge of the behavior of materials beyond evolutionary thinking into regimes where truly exciting discovery and breakthroughs can occur that are revolutionary in nature. The workshop panels all noted that for the first time in history we have available to us a combination of experimental and computational tools that have remarkable power and uniqueness suitable for exploring the characteristics of materials at length and time scales necessary to understand performance in extremes. Among them are high-intensity synchrotron radiation sources, high-flux neutron sources (accelerator and reactor based), high-intensity and ultrafast lasers, advanced microscopies (including electron microscopes and scanning probes), high magnetic fields, and ultrascale computers, combined with modeling, simulation, and visualization tools needed to take advantage of their power.

These existing and emerging capabilities provide us with unprecedented opportunities to explore and exploit an extraordinary range of extreme conditions and allow us to detect and

measure the properties of materials under extreme environments at the appropriate length and time scales. This knowledge will allow us to make accurate predictions of the behavior of materials across a full range of extreme conditions. Importantly, this knowledge will provide the opportunity to develop and apply new methods of synthesis and processing to make materials with revolutionary capabilities to perform in extreme environments. Further, the panels noted that these extreme conditions may provide a new dimension to materials synthesis and processing, opening the door to whole new types of materials with designed functionality. Finally, the workshop panels concluded that we can no longer wait to solve our energy problems; we must begin now to realize the revolutionary breakthroughs that will enable future energy technologies. These breakthroughs will catalyze economic growth in the United States while enhancing its security.

BASIC RESEARCH NEEDS FOR MATERIALS UNDER EXTREME ENVIRONMENTS

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ENERGETIC FLUX EXTREMES

Current Status

Materials that function in extreme environments of energetic particle and photon fluxes are essential to a diverse range of technologies that provide safe, economic, and reliable energy and that ensure our security. These applications include nuclear fission and fusion reactors, long-lived radiation waste forms, nuclear stockpile materials, photovoltaic systems, solar collectors, laser applications, and nanoscale electronics for computers and communication. The performance of these systems is limited by the damage and degradation of materials under energetic particle and photon fluxes. For example, the bottleneck for producing lasers with higher photon fluxes is not the generation of the photon flux itself but the lack of transparent optical materials that are capable of transmitting and directing these higher fluxes. The operating temperature and efficiency of nuclear reactors is limited by the structural materials that can withstand neutron damage at high temperatures in highly corrosive environments. Solar photovoltaics must withstand the harsh environment of direct sunlight for decades without degrading their high surface absorbance, losing their photoelectric conversion functionality, or cracking due to severe thermal stresses.

Materials subjected to energetic particles and photons typically fail at fluxes by a factor of 10 or more below their intrinsic limits. Particle fluxes, for example, damage materials through the creation of nanoscale defects that subsequently evolve by migration and clustering, ultimately leading to failure. Next-generation nuclear reactors require materials that are able to withstand greater than an order-of-magnitude-higher neutron and particle fluences than is now possible. Perfect SiO₂ optical material can withstand energies of 200 J cm⁻³ without damage. Actual SiO₂, however, fails at far lower energies of 20 J cm⁻³ because of runaway absorbance of photon energy at nanoscale defects that usually exist on the surface of the material.

The failure of materials far below their intrinsic capability is a severe limitation, as well as a promising opportunity. Early failure is the primary constraint limiting the performance of energy and other fundamental technologies. It is an opportunity, however, because the reasons for early failure are not intrinsic and thus can be overcome with sufficient knowledge and understanding of their causes. Finding the root causes of early failure and realizing improvement in materials performance by an order of magnitude or more will enable broad new horizons for next-generation energy and security technologies. A further opportunity that may be gained from this knowledge is the possibility of using extreme photon and particle fluxes to make new classes of materials that will have improved performance for energy and security applications.

The major roadblock to bridging the gap in functional materials performance is unraveling the complex evolution of damage originating in atomic and nanoscale defect formation and culminating in macroscopic materials failure. These changes occur over broad time and length scales (Figure 1). Two independent scientific revolutions are under way that hold considerable promise for removing this roadblock. One is the developing advances in

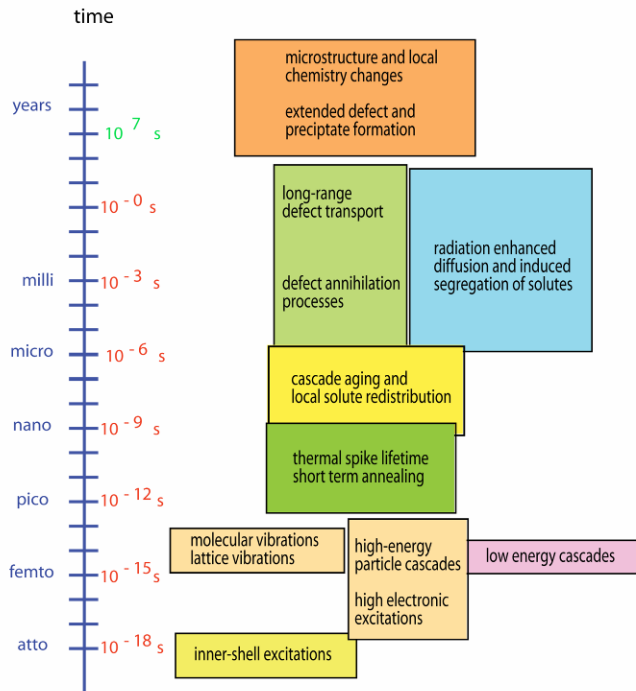


Figure 1. Exposure to fluxes initiates a cascade of events over a range of timescales, originating from point defects and leading to materials failure.

remarkable opportunity to understand, for the first time, the hidden pathways of material damage from energetic photon and particle fluxes that lead ultimately to performance degradation and failure. This knowledge will enable the design of new classes of materials to meet future energy and security needs.

Defect structures evolve through a sequence of stages in their lifetimes, from creation as point defects by a radiation field through relaxation by migration and interaction with other defects to assembly into large clusters. These clusters ultimately degrade materials performance at the macroscopic level and may lead to materials failure. Each of these stages can be tracked by the transfer of energy among the electronic, atomic, vibrational, and structural systems of the crystal, and by the time and length scales required for each transfer (Figure 1).

In the case of intense light sources, such as a laser pulse, photons can excite the electronic states of an individual atom in timescales of attoseconds (10^{-18} s), the time required for light to cross the diameter of a typical atom. This electronic excitation energy is transferred to the lattice vibrations, raising the local lattice temperature as high as 10,000 K. This high temperature melts the crystal locally and, upon recrystallization, leaves a damaged area that can grow on repeated photon absorption to a few hundred micrometers in diameter (Figure 2). This damage is produced in approximately a second, the time required to establish thermal equilibrium following the initial absorption of energy by electronic excitation.

ultra-fast and ultra-high spatial resolution characterization tools that will allow us to observe initial atomic-scale damage events as they occur. The other is advances in computer simulation of materials using high-performance computers, multi-node computer clusters and powerful computational algorithms, such as density functional theory for electronic structure and excitations and molecular dynamics for atomic interactions and dynamics. These powerful numerical approaches have the potential to capture the multiscale damage evolution from atomic to macroscopic dimensions. The convergence of these two rapidly advancing scientific frontiers presents a

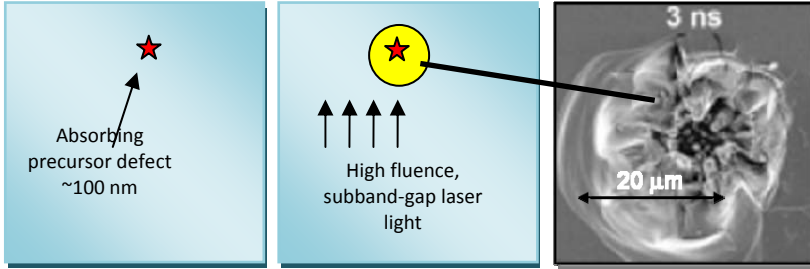


Figure 2. Intense photon beams damage optical materials by depositing energy at surface defects (left). With continued irradiation, the damage area grows (center) and the optical material must be replaced (right). Lack of understanding of the damage initiation and evolution limits the operation capacity of optical materials by a factor of 10. Overcoming this damage would reduce the cost and size and increase the output power of lasers.

The damage produced by swift heavy ions traveling at relativistic velocities follows a similar sequence (see sidebar, Swift Heavy Ions), starting with massive electronic excitation of many atoms along the linear trajectory of the heavy ion as it passes through the crystal. This excitation energy is transferred to lattice vibrations and melts the

crystal locally, leaving a line of disorder as the crystal re-solidifies. The relativistic ion may travel many micrometers through the crystal, leaving a track of damage that may be only a few tens of nanometers in diameter. The damage tracks are remarkable for their high aspect ratio, as high as 10^4 , and much higher than can be produced by photons or slower particles. The disordered material in the tracks can be etched to produce nanopore templates for assembly of biomolecules or nanowires (Figure 3). The timescales for track production start with attoseconds for electronic excitation and end with seconds for thermal equilibrium, as for photons.

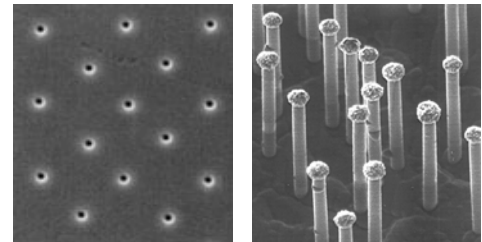
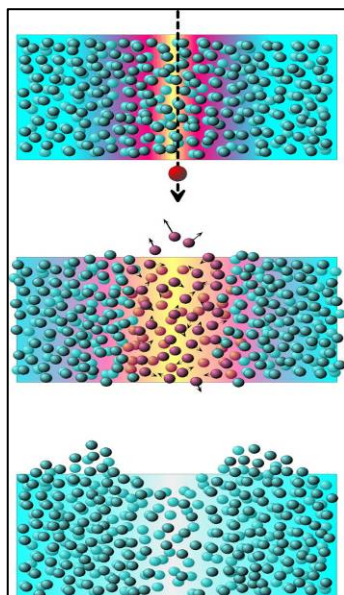


Figure 3. (a) Nanopores created by etching track centers and (b) nanorods created by filling nanopores and removing the matrix.

For lower energy particles, the times of interest are from hundredths of a picosecond for energy transfer from the incident particle to atomic displacements, through tens of picoseconds for the energy transfer to the lattice vibrations that produce local melting and recrystallization, leaving a displacement cascade of point defects comprising vacancies and interstitial atoms near the impact site. In a few microseconds, some of the point defects diffuse and agglomerate into larger clusters, while others annihilate at sinks that pre-existed or were created by the impact. These larger clusters associated with single ion events then interact with other clusters created by other impacts and eventually reach macroscopic dimensions that can degrade materials performance or cause failure. The timescales for these cluster-cluster interactions are seconds to years; in the case of nuclear waste that creates new displacement cascades continuously from radioactive decay, the timescale can reach millennia. In all cases, the important length scales range from atoms, associated with the initial creation of point defects, through micrometers as the defects accumulate, to meters as components and devices fail. It is perhaps surprising that nanoscale defects are ultimately responsible for failure of macroscopic components ranging from electronic devices to large pressure vessels (see sidebar, From Nanoscale Defects to Macroscale Property Changes).

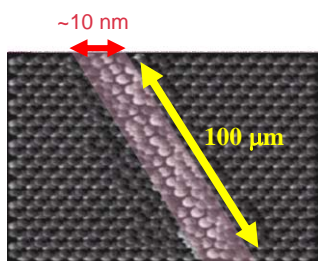
Swift Heavy Ions



high electronic
excitation in
 10^{-17} to 10^{-13} s,
at 20 eV/atom

heating and particle
emission in
 10^{-13} to 10^{-11} s

frozen-in atomic
rearrangements in
 $>10^3$ s, with
10-nm diameter



Energetic particles lose energy to either the atomic or electronic system of the target material. The partition between the two systems depends on the ion energy and mass, with the fraction deposited in the electronic system increasing with increasing ion energy. In the energy range applicable for swift heavy ions (MeV and GeV), the primary energy loss mechanism is to the electrons of the target material. This causes electronic excitation and ionization along the ion track and occurs on a timescale of 10^{-17} to 10^{-13} s (top and middle). This energy is transferred to the atomic system either through an explosion-like repulsion of the ionized atoms or through electron-phonon coupling and lattice heating. The atoms along the track have high mobility because of the temperature increase and the reduction in density. The damage state is frozen in place as indicated in the cartoon (bottom) because of the rapid transfer of energy away from the hot region into the surrounding lattice. Consequently, a tube of damage with a narrow diameter, ~ 10 nm, extending hundreds of micrometers into the solid is created (lower micrograph). The aspect ratio of the track is several orders of magnitude greater than can be obtained by other methods.

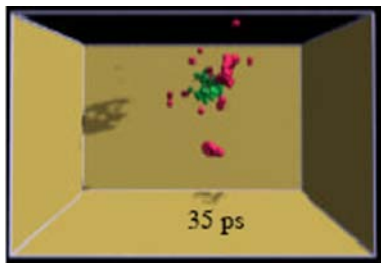
Source: K. Schwartz, C. Trautmann, T. Steckenreiter, O. Geiss, and M. Kramer, "Damage and track morphology in LiF crystals irradiated GeV ions," *Physical Review B* **58**(17), 11232–11240 (1998).

Multiscale experiments and models. Advances in computer simulation and experimental characterization have the potential of bridging the gap between the time and length scales that each can access. This confluence of capabilities will dramatically impact our understanding of the interaction of energetic photons and particles with materials at the atomic level. Until recently, limitations in computer speed and performance restricted numerical simulations of materials to short timescales and small numbers of atoms, while experimental probes operated at long times and macroscopic dimensions. Advances in computer technologies—both hardware and algorithms—are dramatically expanding the time and space domains accessible to materials simulation. Similarly, the development of new characterization tools, especially the advent of intense sources of electrons, neutrons, and photons from lasers and synchrotrons, is dramatically lowering the time and length scales of physical phenomena that can be studied. The combination of experiment and theory holds the promise of being able to predict, measure, and interpret new physical and chemical phenomena and represents unprecedented capabilities for understanding the full range of defect creation, damage evolution, and materials performance over all time and length scales.

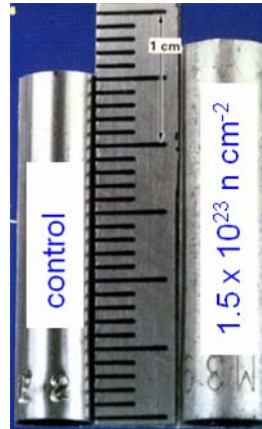
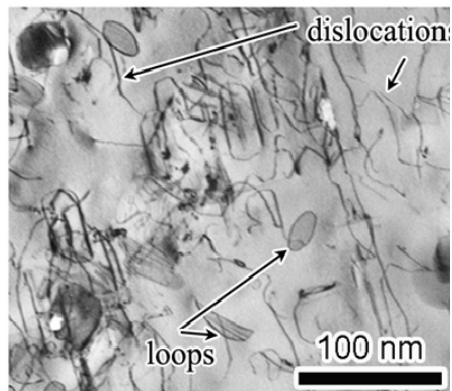
From Nanoscale Defects to Macroscopic Property Changes



Formation of defects in a displacement cascade



Displacement cascades grow to microstructural defects . . .



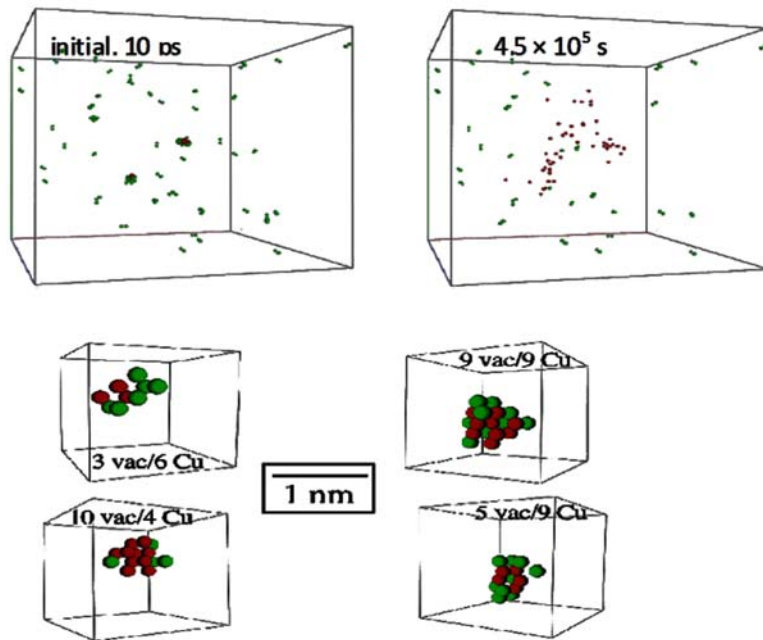
Energetic ions impart energy and momentum to atoms in a solid. When the distance between successive collisions is approximately equal to the atomic spacing, all of the atoms are displaced (top). The timescale for these displacements is on the order of tens of picoseconds (10^{-12} s) and the length scale is nanometers (10^{-9} m). The vacancy and interstitial defects produced can aggregate to produce larger defects such as dislocation loops and voids (bottom left). These defects can change the macroscale properties by causing swelling or other dimensional instability of the material, as shown in the figure at the bottom right. This is an example of the extreme variation in dimensions that can occur in materials such as Type 316 austenitic stainless steel following exposure to fast neutrons.

Source: J. L. Straalsund, R. W. Powell, and B. A. Chin, "An overview of neutron irradiation effects in LMFBR materials," *Journal of Nuclear Materials* **108&109**, 299–305 (1982).

For example, the advent of molecular dynamics computer simulations have significantly revised our understanding of damage in metals caused by exposure to energetic particles. Simulations have revealed that the origin of vacancy loops (see sidebar, Aging of Displacement Cascades) is intimately related to the local melting and recrystallization that accompanies a collision of an ion with a crystal. On recrystallization, vacancies are driven ahead of the solidification front towards the center of the damage area where they assemble into a loop. While molecular dynamics can follow the early evolution of cascades in metals, it is far less applicable to studying such events in ionic materials, such as oxides. This is another example of a gap that blocks progress in understanding damage creation and repair in ionic solids.

Aging of Displacement Cascades

Radiation damage begins with the creation of energetic primary recoil atoms (PRA) by nuclear or atomic interactions with a flux of bombarding particles. High-energy PRAs quickly lose kinetic energy by atomic collisions, down to an atomic displacement threshold. The hot displacement cascade region is several nanometers in extent and contains a very large concentration of vacancy and self-interstitial atom (SIA) defects and cools in less than 100 ps. This phase of radiation damage has been extensively modeled and is reasonably well understood in metals, with similar initial damage production in a wide range of metals and alloys. Thermal migration of SIAs and vacancy defects, solutes, and cluster complexes results in the spatially and temporally correlated evolution of cascade structures—cascade aging—over much longer times. An intriguing “self-healing” consequence of this long timescale evolution is that while the vacancy solute complexes exist, they promote defect recombination, which can greatly reduce the negative effects of radiation damage.



Kinetic lattice Monte Carlo simulation snapshots of cascade aging in an Fe-0.3%Cu alloy at 300°C showing the initial configuration of vacancies (red) compared with the configuration at 4.5×10^5 s. The diffusion of vacancies and vacancy clusters results in the formation vacancy—copper atoms complexes (green). The last vacancy leaves the cascade region at $\sim 10^7$ s, leaving residual copper clusters.

Courtesy of Simon Phillpot, the University of Florida.

The number of developing experimental techniques that push to faster timescales and shorter length scales is especially exciting. Femtosecond laser pulses allow characterization of the very rapid process of particle formation and phase transformation during ejection of material from a substrate by laser ablation. Core-level photoemission spectroscopy can provide local chemical information of a thin surface layer as it ablates into vacuum, while x-ray absorption spectroscopy of thin foils can provide complementary information on the entire laser-heated area. Grazing incidence reflectivity at x-ray wavelengths can probe the initial structural evolution following a particle or photon absorption, determining the timescale for roughness to form on nanometer length scales. Electron microscopy, with its advances in aberration correction and energy filtering, is enabling mapping the locations of individual impurity atoms in a host structure. Microelectromechanical (MEMS) devices and microlithographic processing allow test platforms to be miniaturized and used in the electron microscope so that the dynamic response can be observed at atomic resolution while concurrently measuring the

macroscopic response. Coupling lasers with electron microscopes is ushering in unprecedented opportunities to probe reactions, such as phase transformations and solidification, with nanosecond time resolution. Advances like these set the stage for the first comprehensive experimental picture of defect production and multiscale damage evolution in materials exposed to energetic photon and particle fluxes. The challenge is to develop the wide range of tools and instrumentation needed to exploit the faster timescales and shorter length scales that are now within experimental reach.

Materials modification by energetic fluxes: surface and bulk re-organization. If the processes by which particles and photons interact with materials were understood, the door would be opened to harness these processes to make new classes of materials. For example, controlling surface morphology by ion irradiation provides a pathway to explore non-equilibrium processes at surfaces, a central challenge for thin film and surface science. Surfaces exposed to environments of low-energy ion irradiation are subjected to self-rearrangement, including surface roughening and nanoparticle formation. The nature of the roughening pattern is sensitive to the material, the ion beam parameters such as the ion mass, energy, and beam direction, and to the processing conditions. The final surface pattern is a result of interplay between surface kinetics and defects near the surface. Although linear instability models can account for the initial surface roughening and nonlinear models for the late stages, there are essential features that cannot be accounted for by either approach. For example, these models cannot describe the close packing structure of quantum dots on semiconductor surfaces. Potentially rich applications of quantum dots in photovoltaic energy conversion, solid state lighting, digital electronics, and quantum computing are blocked by our inability to predict the variation in sputtering conditions that govern quantum dot formation for different materials, and for their easier formation on compound than on simple semiconductors.

An example of ripple pattern and nanoparticle formation caused by ion irradiation of $\text{Cd}_2\text{Nb}_2\text{O}_7$ is shown in Figure 4. The irradiation was conducted with 30-keV Ga^+ ions from a focused ion beam (FIB) instrument. The zigzag arrow in Figure 4(a) shows the FIB scanning direction and the straight arrow the projected direction of the incident ion beam. The scanning electron microscope (SEM) images show the ripple pattern that forms under ion irradiation, with characteristic wavelength varying from a few nanometers to sub-micrometer scale depending on irradiation conditions. Close inspection of the surface shows that nanoparticles of pure cadmium with a surprisingly uniform diameter of ~ 5 nm form within the ripple features as a consequence of irradiation-induced phase decomposition [1]. This approach could provide a unique opportunity for spatially placing specified patterns of nanoparticles on substrates. Surface roughening, pattern formation, and nanoparticle segregation are potentially powerful nanofabrication techniques, but the guiding principles that govern their operation are still unknown. A related area that may have more impact but is even less well understood is bombardment with ion clusters containing a few thousands atoms and energies of order 10 keV. Such ion clusters produce dramatically higher yields of sputtered species per event than that produced by irradiation with atoms, especially where the emitted species are large molecular complexes. The reasons for the large yield must lie in the very different collision dynamics for ion clusters versus single ions, though little is understood about the details [2].

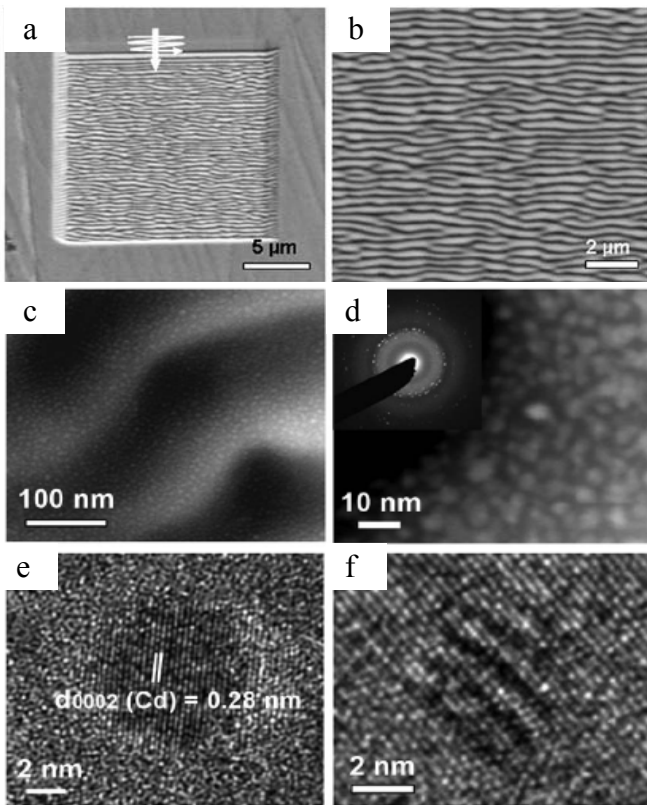


Figure 4. (a) Scanning electron microscope (SEM) images of ripples on the surface of $\text{Cd}_2\text{Nb}_2\text{O}_7$ created by 30 keV Ga^+ focused ion beam bombardment. (b) and (c) Enlarged views showing the high degree of texture aligned with the scanning and incident beam directions indicated by the arrows in (a). (d) Nanoparticles of the host material created by the ion bombardment and embedded in the ripple structure. (e) and (f) High-resolution images of nanoparticles in the amorphous region and on top of the crystalline substrate, respectively.

wavelengths in the infrared where pure silicon is transparent. Such surfaces have promise for applications as photovoltaic devices.

Further, the use of photons to ablate materials from a surface is also an attractive materials synthesis technique because it is easily applied to a wide range of materials. This approach is applicable to even polymers and biomolecules, which can be vaporized intact and deposited on a substrate while retaining their structure and functionality. In order to exploit the full potential of photons for producing new materials, it is critical to gain a basic atomic- and molecular-level understanding of the complex physical and chemical processes that occur when light interacts with materials. This knowledge could provide revolutionary new capabilities for the design of new materials—from treatment of surfaces that would protect materials from damage arising from radiation effects or corrosion to the creation of thin films of materials for photovoltaics and light-emitting diodes.

Intense light sources are widely used in metals processing, semiconductor manufacturing, optoelectronics, medicine, and biotechnology. Intense photon flux can be used to modify materials morphology and size at a fixed composition (e.g., drilling, welding, annealing, recrystallization, and polishing) and for inducing chemical reactions that alter composition (e.g., patterning, coating, and physicochemical modification). However, new means of using photons to make new materials is just beginning to emerge. For example, exposing a surface to photon irradiation in combination with another environment has the potential to produce exciting new materials with novel structures. Exposure of silicon to the plasma generated by femto-second laser irradiation in a SF_6 environment has been shown to produce conical structures in which a highly nonequilibrium phase exists in the near-surface region (Figure 5). The surface is rich in S (>1 atomic %), a chemical change that creates “black” silicon [3] that is remarkably absorbing over nearly the full optical spectrum, even at

Basic Science Challenges and Opportunities

Point defects created in a solid on exposure to energetic fluxes degrade the properties of materials to the extent that they can fail catastrophically. This degradation and failure is a key

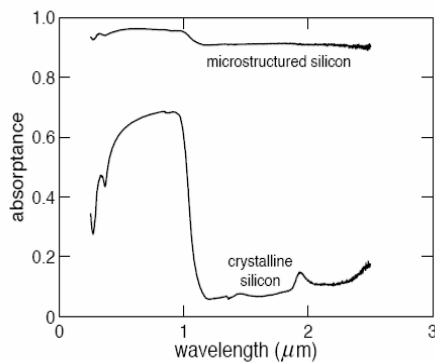
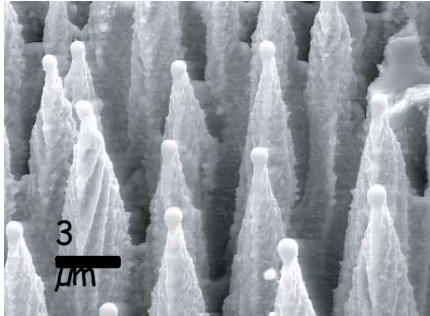


Figure 5. Silicon exposed to a plasma generated by a femtosecond laser in the presence of a chalcogen-rich environment produces “black silicon.” This black silicon has a conical structure with spherical balls at the ends of the column. The optoelectronic properties of black silicon compared with crystalline silicon at infrared wavelengths of light are shown.

barrier to achieving more efficient energy generation systems and limits the lifetime of materials used in photovoltaics, solar collectors, nuclear reactors, optics, detectors, electronics, and other energy and security systems employed in extreme flux environments. These energetic fluxes can be harnessed, either separately or in conjunction with another stimulus, to manipulate the surface and internal structure of materials, enabling exploration and utilization of conditions that are far from equilibrium and therefore inaccessible by other means to make revolutionary new materials. Achieving major advances in our ability to minimize or eliminate the degradation caused by energetic flux interactions with solids or to capitalize on our ability to fashion new materials using energetic fluxes depends critically on

evolution triggered by single and multiple energetic particles and photons interacting with solids. This will require fundamental studies of materials using a range of extreme photon and particle fluxes, including advanced photon and particle-beam sources, coupled with structural and functional characterization techniques, such as those based on scattering of electrons, neutrons, x-rays, and others. The increasing spatial resolution and the pulsed time structure of intense sources such as the Spallation Neutron Source (SNS) and the Linac Coherent Light Source (LCLS) allow unprecedented opportunities to image the formation of atomic and nanoscale defects as they are created. Using a variety of characterization techniques matched to the time and length scales of the defect structure as it evolves, a full picture of the damage development from nanoscale origins to macroscopic materials degradation and failure can be experimentally established. Such a comprehensive picture of damage evolution caused by particle and photon fluxes would enable two new strategic objectives for materials under extreme environments: preventing materials failure and performance degradation by interrupting of the nano-to-macro chain of damage evolution,

manipulating atomic and molecular structures, in a predictable manner, to create materials that can function within an extreme environment without property degradation and synthesizing new structures with novel and exotic properties, or to force chemical reactions to proceed along selected pathways.

- manipulating atomic and molecular structures, in a predictable manner, to create materials that can function within an extreme environment without property degradation and
- synthesizing new structures with novel and exotic properties, or to force chemical reactions to proceed along selected pathways.

These advances will only be achieved by elucidating the atomic- and molecular-level mechanisms of defect production and damage

and exploiting the structural modifications triggered by energetic fluxes to create new materials with enhanced properties that are not accessible by any other synthesis or modification route.

As our knowledge of the response of atoms and molecules under energetic flux bombardment advances, it will become possible to manipulate and control these phenomena across wide time and length scales. Such control explores the limits of current understanding of defects, structure-property relationships, and of optical and energetic beam technologies. The wealth of experimental data and insights produced from these targeted experiments will enable sophisticated multiscale models of material response over the relevant time and length scales and thus begin to codify and quantify the many effects—cumulative, synergistic, transient and emergent—of photon- and particle-beam irradiation of materials. Through understanding how irradiation *produces* damage, it will become possible to use energetic particles or photons to *repair* damage produced by an earlier irradiation. For example, photons have been used to stimulate recovery of ion implantation damage in semiconductors, and high-energy particles that deposit energy in the electronic system have been used to aid the repair of damage in oxides [4]. Quite apart from advancing our understanding of the fundamental physics and chemistry of bulk matter—and of surfaces and interfaces—such investigations will point the way to concepts that will provide breakthrough capabilities for future energy and security technologies: to *design* the synthesis of materials with tailored characteristics and to *construct* physically based predictive models that would not only guide the development of new systems but would also enable accurate lifetime prediction of materials in extreme environments.

A parallel and equally important need is the development of high-fidelity models to describe the dynamic response of materials in energetic flux environments accurately. This may involve validation of the models at each length scale, from the electronic and atomic-level dynamics in single crystals, to the mesoscopic interactions between grains, and finally to the bulk polycrystalline response of complex engineering materials. Experimental validation from the nano- to micro-scales is required to predict material properties. Here we must be prepared to evaluate the foundations on which current models are based as new processes and reaction rates are identified by advances in time-resolved experiments.

Modeling energetic particle-beam interactions with matter holds many challenges associated with multiscale modeling. Present models do not include electronic interactions, stopping effects, and thermal transport mechanisms. There is a strong need for the development of interatomic potentials for ionics of much higher fidelity, and to implement the paradigm of self-consistent charge equilibration. Although there is considerable understanding of the first 100 ps of radiation cascade development in metals, this is just the beginning of a much more complex and physically rich cascade story that has been just recently studied using a combination of molecular dynamics and kinetic lattice Monte Carlo tools (see sidebar, Aging of Displacement Cascades). Multiple defects such as vacancies and interstitials are typically created, each with its own complex diffusional kinetics. Moreover, large local stresses created around each defect can greatly modify the kinetic barriers so that defect diffusion around the cascade in the early stages can differ greatly from transport closer to equilibrium. Despite advances in conceptual understanding that reveal the importance of these

fundamental effects, the details of cascade aging in metals, especially alloys, remain largely unexplored. Other challenges include identifying and incorporating, in a physically realistic and computationally tractable manner, the microstructural features encountered in real materials. For example, the long-range stress field of dislocations and other microstructural features strongly affects impurity segregation and has important consequences on microstructure and microchemical evolution under irradiation. Extension from the processes that are complete in the microsecond time frame to the prediction of the properties of materials in the second and year time frames requires advances in our ability to develop models that span the many spatial and temporal levels relevant to controlling morphology in nanostructures and other patterned structures to the prediction of the properties of materials.

Explaining the mechanisms of energy absorption from intense laser pulses to a transparent optical solid and the resulting material modifications is a challenging problem of nonlinear optics and defect physics in dielectrics. The fundamental mechanisms behind extrinsic damage in optical materials remain poorly understood due to the difficulty in identifying which defects lead to damage, the small volume occupied by these defects, and their scarcity. There is also little known about the accumulation of nanoscale damage or photochemical modification resulting from prolonged high average power exposure. Basic research is needed to understand the dynamics of optical damage, including methods to model and probe nanoscale defect-assisted energy deposition and the basic material response during a damage event in which the resulting plasma temperatures exceed 10,000 K. This could be facilitated, for example, using multi-scale modeling, in which ab initio techniques provide models for energy deposition that are then used in molecular dynamics or hydrodynamics simulations to address the material response, combined with high-resolution optical pump-probe schemes to image the extrinsic damage events.

Materials synthesis, modification, and repair. Advances in sources of energetic particle and photon flux provide unprecedented opportunities to design a material with unique chemistries and structures that are inaccessible by other processing routes, to manipulate particles and molecules to create unique structures, to control transformation pathways and chemical scheme that extends beyond the traditional time, temperature, and deformation processing variables by introducing ion flux as an additional external driving force as the system undergoes thermal relaxation. Further, recent advances in high-density plasma arc-based photon sources have permitted the controlled manipulation of materials on the atomic scale. These sources have large areas (up to $\sim 1000 \text{ cm}^2$) and can provide controlled heat fluxes (up to $20,000 \text{ W/cm}^2$) with pulse rates down to 1 millisecond to material surfaces with heating and cooling rates on the order of 10^4 to 10^5 K/sec . Because of the large illumination area, it is believed that a one-dimensional thermal field is established unlike the three-dimensional thermal field associated with lasers. Also, the spectral output ranges from 0.2 to 1.4 microns unlike the single wavelength associated with lasers. These capabilities allow rapid controlled annealing (at different temperatures), which will allow for a unique opportunity to “freeze” specific microstructures, allowing for direct measurements of nucleation and growth rates as a function of time and temperature [5]. Adding this and other sources of particles and photon flux to the traditional synthesis and processing tool set have tremendous promise for accelerating the development of new materials, such as high-efficiency and ultrastable photovoltaics and extreme radiation-resistant or hardened materials. It may even possible to

design materials that “self-report” fatigue and impending failure and/or self-repair (see sidebar, Manipulating Matter with Photons). All of these capabilities will not be realized, however, without a detailed knowledge of the chemical and physical processes that occur during the interaction of photon and particle fluxes with materials.

Conclusion

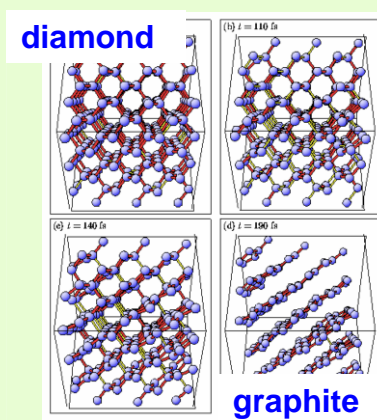
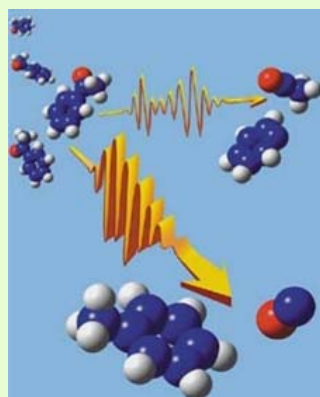
Materials in energetic particle and photon fluxes typically fail at fluences that are an order of magnitude or more below their intrinsic limits. This early failure can be traced to structural defects that originate at atomic (or nanoscale) dimensions and grow by interaction with the host material and with each other until they dominate the bulk behavior. The evolution of this damage spans many decades of length and timescales, thus presenting a fundamental barrier that obscures the cause-and-effect relationship between atomic and nanoscale defect production and macroscopic materials failure. Like waves on the ocean that are orders of magnitude larger in size than the molecules they comprise, the structure at one scale is lost at the other.

Emerging breakthroughs in experimental characterization and theoretical modeling provide an unprecedented opportunity to capture the multiscale character of defect creation and damage evolution. Intense sources of electrons, neutrons, and photons from synchrotrons and lasers now enable formerly invisible phenomena operating at ultrafast time and ultra-small length scales to be resolved experimentally. Simultaneously, advances in computation are pushing the limits of numerical simulation to larger time and length scales. The growing synergies of characterization and numerical modeling tools enables creating comprehensive and predictive models of damage evolution, inspired and validated by experimentation at each time and length scale, that connect the defects created by energetic photon and particle fluxes at the atomic and nanoscale to materials performance and failure at the macroscale.

Once understood, the complex pathways of damage evolution can be intentionally interrupted at strategic points to prevent the early failure of materials an order of magnitude or more below their intrinsic limits. Achieving improvement in performance by at least a factor of 10 is not only desirable for extending the lifetime, increasing the efficiency, and lowering the cost of today’s energy and security technologies but is also essential if we are to implement next-generation technologies in fission, fusion, and megawatt lasers. The primary roadblock to realizing these technologies is materials performance. We know the operating principles and design parameters that will produce dramatic gains in capacity and efficiency, but we lack the materials that can perform in the extreme environments of photon and particle flux required to achieve these gains. Breaking through these barriers in materials performance will only be achieved by reactions, or to initiate repair of the damage in situ. For example, ion beams can be employed to modify the sub-surface structure and chemistry of binary alloys, giving rise to a processing fundamental research, which will produce major advances required for future energy and security technologies.

Beyond improvements in performance, understanding the atomic to macroscale response of materials in energetic fluxes opens powerful new directions for materials synthesis and modification. Particle and photon fluxes deliver significant energy to materials, creating configurations of atoms and molecules that are far from their normal equilibrium structures.

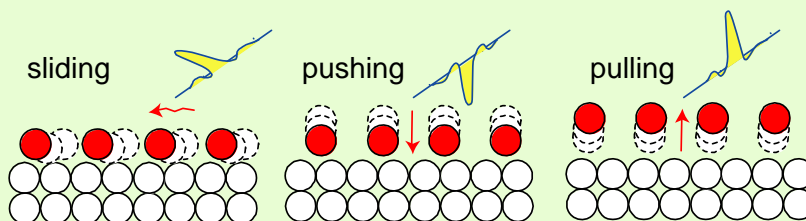
Manipulating Matter with Photons



Because atoms and molecules interact with their environment entirely by means of electromagnetic fields, it may be feasible to “design” a pulse of light that, when incident on an atom or molecule, can precisely control its position and orientation in a desired way. For example, amplitude and phase control of intense light allows placing and orienting of simple molecular systems to dictate reaction pathways. In condensed matter, ions can be repositioned by tailored light pulses to promote targeted phase transformations. Computer simulations suggest, for example, the possibility of converting diamond to graphite using this approach. This provides a tremendous opportunity for tailoring material properties, exploiting the complexity and emergent behavior of intense light-matter interactions.

The frequency, amplitude, and polarization of light pulses can be tailored with ultrafast lasers to distort the structure of complex molecules in controlled ways (upper left). Such distortions can be used to drive phase transformations, for example from diamond to graphite (upper right). Atoms on surfaces can likewise be driven laterally, up, or down to make or break bonds with the substrate (below). Such coherent control of atomic and molecular positions and orientations enables delicate coherent control of the chemical reactions and phase transformations of materials.

Collective Manipulation with THz radiation



Source: T. Brixner, N. H. Damrauer, P. Niklaus, and G. Gerber, “Photoselective adaptive femtosecond quantum control in the liquid phase,” *Nature* **414** (6859), 57–60 (2001).

Understanding the fundamental physical and chemical processes that occur when a particle or photon beam interacts with a material will allow tuning a specific electronic or vibrational mode to displace a specific atom or molecule. The ability to selectively alter specific atomic arrangements allows not only synthesis of new materials but also repair of damaged materials while they remain in operation. The ability to target selected atomic or molecular species within a material and to drive them into far-from-equilibrium configurations using energetic particle and photon fluxes creates qualitatively new approaches to materials synthesis and modification that cannot be achieved by conventional near-equilibrium routes.

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CHEMICAL EXTREMES

Current Status

Chemically reactive extreme environments are found in numerous advanced power systems, such as fuel cells, nuclear reactors, and batteries, which are critical to realizing a future in which society benefits from secure, affordable energy with minimal adverse environmental impacts. Next-generation energy systems will require materials that perform reliably under increasingly extreme conditions that include exposure to aqueous and nonaqueous liquid and gaseous environments. Overcoming the barriers caused by the inability of today's materials to function reliably in these extremes of chemical reactivity is a major challenge to meeting future energy needs. Incremental advances in reducing the reactivity of materials in both aqueous and non-aqueous liquid and gaseous environments have occurred but not nearly to the level needed to meet the future challenges imposed by these aggressive environments. This is because there is a lack of a fundamental understanding of thermodynamic and kinetic processes that occur at the atomic level under reactive environments. However, an emerging confluence of new computational and experimental tools presents an exceptional opportunity to understanding the fundamental processes involved in the degradation of materials in extreme chemical environments. For example, understanding how materials respond to an extreme chemical environment at the nanoscale will provide the necessary foundation for designing next-generation materials to meet future energy requirements for extreme chemical environments. This understanding of chemistry under extreme conditions will also lead to opportunities for the synthesis of new materials with, for example, enhanced strength, hardness, chemical inertness, conductivity, flux resistance, and energy storage capacity.

Chemical reactive environments are encountered in a wide array of situations. In many cases, the *extreme* reactivity of a material, whether solid, liquid, or gas, derives from elevated temperature and/or pressure (e.g., supercritical steam) and/or an impressed or induced electrical potential. In other cases, the nature of the reactant species itself (e.g., elemental sulfur, a mineral acid, or a mixture of reactants) presents an extreme over wide ranges of environmental variables. Furthermore, spatial confinement can lead to extremes under somewhat benign macroscopic conditions. Examples of the extreme environments encountered in advanced energy systems (see Resource Document, *Technology and Applied R&D Needs for Materials under Extreme Environments*, Appendix A) include the following:

- Aqueous fluids in “ultrasupercritical” fossil and nuclear power plants, hydrogen fuel cells for transportation, advanced batteries, nuclear waste processing and geological disposal, and hydrogen production via water splitting
- Reactive and nonreactive gases at extreme temperatures and pressures, including gas turbines, gas-cooled nuclear reactors, solid oxide fuel cells, and gaseous H₂ transmission and storage
- Molten salts and non-ionic liquids as heat-transfer or tritium-breeding media in advanced fission and fusion systems and thermochemical hydrogen production schemes
- Ionic liquids for fuel cell and battery applications
- Steam, gases, and hydrocarbons produced during in situ oil shale processing and coal and biomass liquefaction and gasification

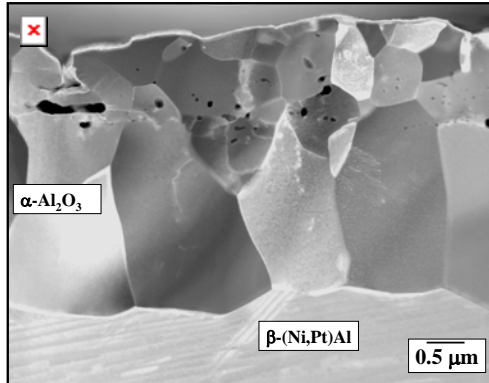
Chemical-induced surface degradation occurs, or at least initiates, at the interface of a material with its environment. Many materials are utilized in environments that render them thermodynamically unstable. Chemical stability in these environments is therefore controlled by protective surfaces, either self-healing, chemically stable films (such as oxides that form on a surface) or engineered films applied to the surface (coatings), that must also form stable surfaces upon exposure in the appropriate environment. Besides their stability, these surface films (whether on the bulk material or an applied coating) must prevent facile mass transport of reactive species from the environment into the bulk of the material; that is, they must be permeation barriers and stay attached to the underlying material (see sidebar, Protective Surface Layers in Reactive Environments). The stability and permeation resistance of these films are a function of the temperature, pressure, type, and concentration of chemical species in the environment, as well as material composition (phases), microstructure, deformation, imposed electrical potential, and other factors. There are many examples where self-healing films have performed for the lifetime of a component in both aqueous and gaseous environments. In other cases, these protective films can fail (break down), resulting in substantially reduced lifetimes (including catastrophic failure) at great economic and energy costs. Causes of failure that lead to inadequate lifetimes include the following:

- the environment is more extreme than realized (although this can, in practice, sometimes be beneficial);
- uncontrolled impurities or incorrect materials selection for the environment (i.e., not realizing the material and, in particular, its self-healing film or engineered barrier are not stable or are too reactive in the chosen system);
- mechanical factors, such as strain or erosion contributing to film degradation; and
- lack of rigorous approaches to predicting chemically controlled materials lifetimes.

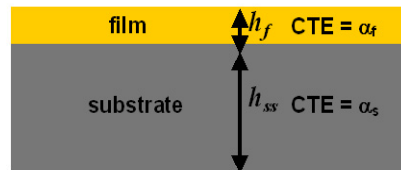
Indeed, all these factors ultimately arise from the lack of the mechanistic understanding of the ramification of thermodynamic and kinetic processes under reactive environments.

A protective film must be stable across a range of environments. For example, environments can become more extreme through localization effects that occur in crevices, pits, or cracks that sometimes form as part of the corrosion processes. Even though the film on a material may be stable at the outset of a component's life, the conditions can evolve into one that is too extreme for the stability of the protective film, which is dependent on both the type and concentration of chemical species in the environment. Thus, there is a compelling need for the development of a new generation of surface layers that are extremely robust under aggressive conditions. These new protective layers cannot be realized unless a fundamental knowledge of reaction dynamics and film stability in such environments is obtained. The underlying atomic-scale interfacial processes involve fundamental physical concepts, such as equilibrium and nonequilibrium thermodynamics and reaction kinetics, but are often coupled in ways that are not currently understood. This knowledge gap is a key challenge for developing new protective films that will provide long-lived stability to materials in extreme conditions.

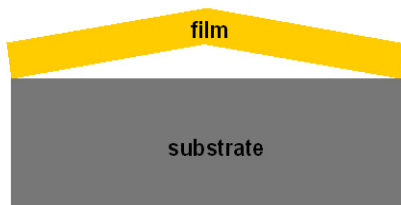
Protective Surface Layers in Reactive Environments



(Courtesy, K. L. More, ORNL)



$$\sigma_f = \int_{T_f}^{T_i} \frac{(E_f / (1 - \nu_f)) \cdot (\alpha_f - \alpha_s)}{(1 + (h_f / h_s)) \cdot (E_f / E_s) \cdot ([1 - \nu_s] / [1 - \nu_f])} dT$$



A surface layer of Al_2O_3 (alumina) grown at 1150°C on a Ni-Pt-Al alloy is illustrated in the accompanying image (shown in cross section in a scanning transmission electron microscope). Alumina is one of the best protective surface oxides for very high-temperature, reactive environments. It is thermodynamically stable in oxygen-containing environments down to vanishingly small levels of O_2 (10^{-25} ppm), resists volatilization in the presence of environmental species like water vapor, and has good permeation resistance to environmental oxygen and other reactive species. Therefore, many alloys targeted for very high-temperature service rely on aluminum to form protective alumina or are protected by coatings that form such. However, to be truly protective, alumina (or any other protective film) must be sound (no through-thickness porosity or cracks) and remain adherent in the presence of stresses formed during layer growth or thermal cycling (i.e., the interfacial adhesive energy between the layer and substrate must be high). Typically, measured stresses from the cooling to ambient temperature (thermal stresses) are much greater (order of GPa) than those from growth.

The thermal stress in the film (σ_f) from cooling from a temperature T_i to T_f can be calculated from the difference in respective coefficients of thermal expansion, α , between the film (subscript f) and the substrate (subscript s), and the respective Young Moduli (E), Poisson's ratios (ν), and thicknesses (h), as shown by the equation. For alumina on a Ni-Pt-Al alloy (and many other metallic substrates), $\alpha_f < \alpha_s$, and the oxide is under compression on cooling. Therefore, a weak oxide-metal interface and/or extreme thermal stress will result in decohesion by a buckling mechanism, as shown in the lower schematic.

Breakdown of initially stable films is another area where fundamental insight into atomic- and molecular-level processes is critically needed. Two prominent breakdown processes in aqueous environments are pitting and stress corrosion cracking (see sidebar, Localized Breakdown of Protective Barrier Films). Related phenomena exist in gaseous environments, such as preferential grain boundary oxidation. However, the most prominent breakdown route for high-temperature films is related to cracking or decohesion of protective layers. This breakdown arises from accumulation of strain energy from growth stresses as well as strains that develop from thermal cycling due to thermal expansion mismatch between surface products and the substrate on which they are grown or deposited [1] (see sidebar, Protective Surface Layers in Reactive Environments).

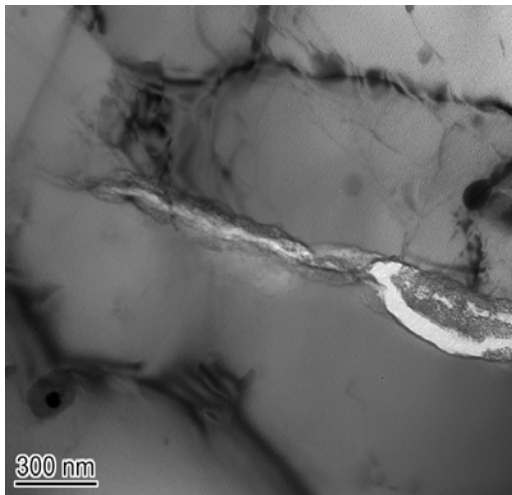
The kinetics of surface film growth is (usually) rapid initially but then slows to a steady-state regime. During the steady state, not only does the growth rate become constant, the level of elastic internal stress also approaches a constant value. Processes that take place during the initial stage are often under nonequilibrium conditions but can dictate the steady-state film structure and phase constitution. Indeed, in the case of reaction with oxygen-bearing species, oxygen adsorption and oxide formation on an alloy surface, for example, are functions of numerous variables, including surface orientation, chemistry, and defect structure; the principal oxidizing species (e.g., for oxygen, O₂, CO₂, or H₂O) and its partial pressure; alloy composition and nano- and microstructure; oxide stabilities; and transport properties of both the alloy and the surface product.

An example of alloy chemistry on high-temperature alloy oxidation behavior is indicated in Figure 6, which shows gravimetric plots of unmodified and modified Ni₃Al undergoing periodic thermal cycling between the reaction temperature of 1150°C and 100°C. It is seen that the binary Ni₃Al exhibits a relatively rapid initial mass gain that is followed by mass loss caused by oxide decohesion from the metallic substrate (spallation) due to the imposed thermal strain. Addition of 5 at. % platinum to the Ni₃Al alloy promotes the formation of an adherent, exclusive protective Al₂O₃ surface layer that shows mass gain (i.e., no spallation) throughout the same exposure. Moreover, further addition of 1 at.% hafnium to the Ni₃Al(Pt) causes a substantial reduction in the growth kinetics of the strongly adherent Al₂O₃ layer. The first few thermal cycles (graph on right in Figure 6) shows that the hafnium-containing alloy initially oxidizes more rapidly than the Ni₃Al alloy containing only platinum addition but eventually leads to a significantly slower-growing Al₂O₃ layer. It is highly noteworthy that not only did the hafnium addition lead to a significant decrease in Al₂O₃ growth, but it also caused the time dependence of the rate to decrease from $\sim t^{0.5}$ (i.e., parabolic) to $\sim t^{0.3}$ (i.e., sub-parabolic). The reason(s) for such a significant change has been qualitatively ascribed to changes in the influence of oxide structure on transport behavior [2]; however, an accurate, quantitative mechanistic description has not yet been forthcoming. This is just one illustration of how underlying mechanistic knowledge is needed to achieve the goal of obtaining a stable surface that is resistant to extreme chemical environments through control of composition, structure, and interfacial energetics.

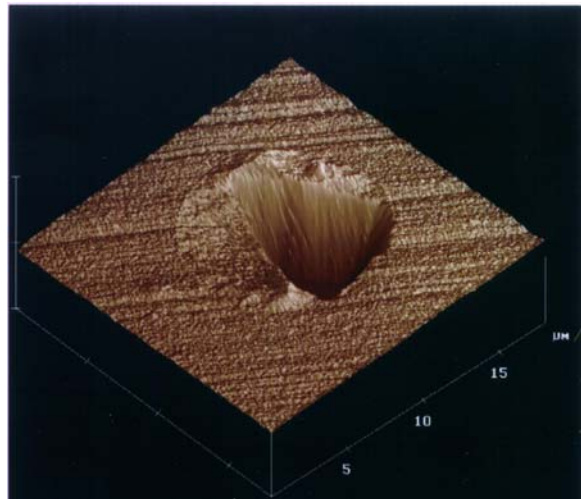
Localized Breakdown of Protective Barrier Films

Breakdown in otherwise stable barrier films can result in accelerated corrosion. Two examples of such breakdown often seen in aqueous environments are pitting and stress corrosion cracking (SCC). Once initiated, the local conditions within a pit or crack can rapidly become very aggressive, and, in fact, propagation of these pitting or cracking events often does not occur without the extreme conditions caused by localization (chemical for pitting, chemical and mechanical for stress corrosion cracking).

Two examples of breakdown are shown below. The first is a bright-field transmission electron micrograph (TEM) of a SCC crack tip propagating in austenitic stainless steel exposed to high-temperature water. The second is a pit produced in stainless steel that was observed in situ in an electrochemical atomic force microscope. In both cases, a breakdown in the protective oxide film results in rapid cracking or pitting due to extremes in chemical and/or mechanical driving forces in the local environments and thus can cause component failure rather suddenly. In some materials, the generation or presence of hydrogen produces cracks much like those associated with SCC, with their propagation rate often exceeding that of the latter by many orders of magnitude.



TEM of SCC crack in stainless steel exposed to high-temperature water



In situ atomic force microscopy (AFM) of a pit in stainless steel in NaCl solution

Sources: Left, courtesy of S. M. Bruemmer and L. E. Thomas, Pacific Northwest National Laboratory, unpublished. Right, R. E. Williford, C. F. Windisch, Jr., and R. H. Jones, *Mater. Sci. Eng. A*, **A288** 54, 2000.

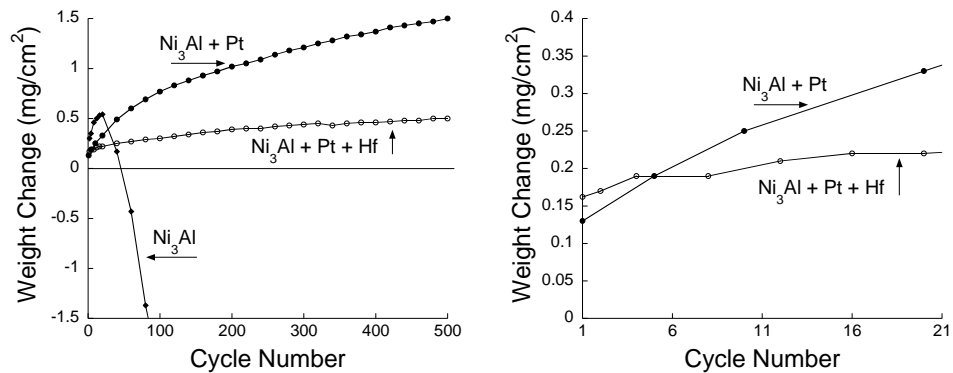


Figure 6. Behavior of binary Ni_3Al and Ni_3Al with noble and reactive metal additions during thermal cycling between 100°C (15 min) and 1150°C (60 min) in air. Initial weight changes during the first 20 cycles are highlighted to the right. Source: B. Gleeson, W. Wang, Hayashi, and D. Sordelet, "Effects of Platinum on the Interdiffusion and Oxidation Behavior of Ni-Al-Based Alloy," *Mater. Sci. Forum* **461–462**, 213 (2004).

An excellent example of the constructive use of chemical reactivity normally associated with corrosion is the use of oxidation to passivate silicon and other materials for semiconductor applications (e.g., see Ref. [3]). Another is the production of porous materials by anodic oxidation [4]. These examples of controlled oxidation synthesis [5] rely on the same principles of reaction energetics and dynamics that govern the reactivity at solid-fluid interfaces and the ability to form stable surface layers. Therefore, gaining atomic-level knowledge of how to control reaction paths and kinetics under extreme conditions has enormous potential to lead to new materials and materials processing routes that will enable the development of materials with greatly improved resistance to surface degradation and other desired properties.

Basic Science Challenges and Opportunities

Extreme reactivity most often is associated with materials degradation arising from chemical reactions occurring at interfaces. As discussed previously, establishing stable surface conditions that resist adverse reactions is the normal way to mitigate this degradation. The discovery of the principles underlying dynamics and pathways of chemical reactions in extreme environments present exciting opportunities not only for the discovery of routes to attain these stable surface configurations but also for synthesis of heretofore inaccessible materials. While materials degradation arising from chemical processes (e.g., corrosion) has been studied for many years, today's rapidly developing capabilities in observing, predicting, and controlling these processes at the nanoscale hold enormous promise to provide significant breakthroughs needed for developing materials that meet requirements for future energy technologies. To achieve necessary breakthroughs that will provide new classes of materials for future energy applications, the following key fundamental questions must be addressed.

- How do reaction pathways/mechanisms, products, interfacial and intra-layer transport, and rate-limiting steps change when materials are subjected to either static or dynamic extremes in chemical or electrochemical environments?

- How are processes that are typically controlled by morphology, structure, and defects affected by extreme chemical activities?
- What new phenomena emerge under extremes in chemical reactivity and can these be exploited in a beneficial manner, such as for novel synthesis?
- Can processes that occur at chemical extremes be modeled computationally to predict lifetimes or new and existing materials?

As outlined previously, the range of chemical extremes that are possible in energy systems is very broad—including exposure of materials to supercritical water, ionic liquids, molten metals, and sulfur-bearing gases—and is often complicated further by extremes in temperature, pressure, electrical field, or radiation (see Resource Document, *Technology and Applied R&D Needs for Materials under Extreme Environments*, Appendix A). In all cases, however, the fundamental issues of materials degradation involve the interface between a material and its environment. Hence, the concept of an ideal interface, or protective surface layers, under extreme conditions emerges. It actually presents multiple challenges of developing a basic understanding of phase boundary reactions and stability using state-of-the-art tools, including modeling and simulation, under dynamic, extreme conditions. In each case, considerations of energetics and reaction pathways form the foundational science that underpins development of revolutionary new materials that can resist degradation in extreme environments or can be synthesized by controlling the reactivity under these conditions.

Atomistic and molecular understanding of oxide growth and breakdown in aggressive aqueous solutions. An atomistic and molecular understanding of chemical and electrochemical processes at fluid-solid interfaces is required to unravel the complex and interrelated effects of interfacial processes on the properties and behavior of materials in highly reactive fluids. An important example is understanding the electrochemical processes controlling ionic-to-electronic-current conversion. These processes are associated with both high-impedance interfaces and high-field (e.g., 10^7 volts/cm) conduction of ions across an oxide film and associated breakdown mechanisms, particularly at high temperatures ($\geq 200^\circ\text{C}$) (Figure 7). There is also a need to understand the chemical and mechanical stability of these films and charge transport across them. These are very challenging issues to address and can be enormously difficult when these interfaces are under additional extreme conditions. For example, under the influence of radiation, the role of displacement damage on the physical and electronic characteristics of the protective oxide film can affect the integrity, chemistry, or physical properties of the film.

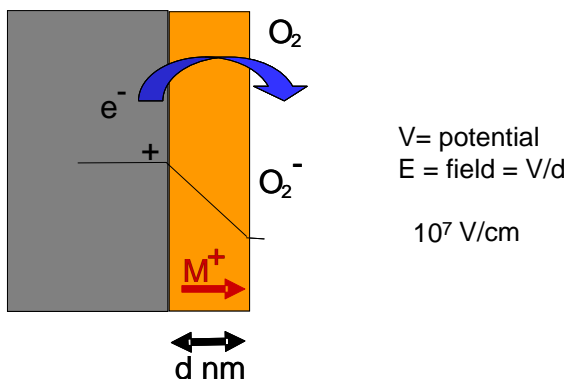


Figure 7. Schematic of the high-field ion conduction across growing oxide film experienced under electrochemical conditions. Cabrera-Mott electrons tunnel across oxide to dissociate oxygen and produce fields that enable this high-field conduction. Courtesy of H. S. Isaacs, Brookhaven National Laboratory.

Growth, adhesion, and stability of surface products formed in high-temperature gaseous environments. As in aqueous systems, surface films (products of interfacial chemical reactions) formed in gaseous environments play an important role in controlling the environmental reactions and protecting the underlying material. However, because these systems are typically at much higher temperatures, subsurface solid-state processes are active and, with microstructure, thermodynamics, and stress, play an important role in mediating overall reactivity of the material with the environment and/or setting the physical and chemical stability of the product layer. Most problems of scientific and practical interest involve multiple components as well as multiple reaction pathways. For example, conditions that can be both oxidizing and sulfidizing to alloy components are found in fossil energy systems. The sulfidation rates of most of the major metallic constituents in conventional high-temperature alloys are generally 10^4 – 10^6 times higher than their oxidation rates, depending on temperature (i.e., the activation energies are different). As a consequence, avoidance of sulfidation is an important constraint in materials selection and process control. The occurrence of sulfidation under oxidizing-sulfidizing conditions depends critically on the gas composition and, in some cases, the extent of equilibria. Understanding the factors leading to sulfide formation under such conditions is important to understanding and hopefully avoiding accelerated failures in extreme service. Consideration of the thermodynamic aspects of oxidation-sulfidation reactions provides a foundation for understanding how the environmental conditions can influence possible reaction pathways under complex conditions [6].

In many cases, minor changes in composition and/or environment can lead to substantially different material responses. Accordingly, a key scientific challenge is to gain an understanding of the energetics and kinetics associated with the atomic-level structure and processes at all relevant interfaces (internal and external to the solid) to develop mechanistic descriptions that are qualitatively and quantitatively accurate. With knowledge of material transport and reactant speciation, defect and chemistry changes leading to stable “non-reacting” layers can be identified.

It has long been recognized that stress plays an important role in the formation and stability of protective layers in high-temperature systems. Because these layers often have a significantly different coefficient of thermal expansion than the substrate on which they form, adhesion of the high-temperature surface product must be adequate to withstand the high thermal stress on cooling from the reaction temperature (see sidebar, Protective Surface Layers in Reactive Environments). Consequently, the atomic/molecular-level understanding of interfacial adhesion of a surface layer to the substrate and how this is affected by the reaction energetics and dynamics, structure, and material composition are critically important.

Fundamental reaction dynamics and materials synthesis at extremes. Extreme conditions challenge fundamental chemical concepts such as bonding and periodicity. Therefore, chemical reactions strongly coupled to extreme pressure, temperature, or electromagnetic fields may lead to completely new materials behaviors. For example, superionic phases of water are predicted theoretically to exist at combined high pressure and temperature [7, 8]. In these phases, atomic hydrogen is only weakly chemically bound to oxygen, giving rise to

extremely high hydrogen mobility, while oxygen remains fixed in the crystal lattice (Figure 8). A principal scientific challenge is to develop experimental and theoretical methods to gain insight to reactivity in such unusual and complex reactive systems. In turn, this will provide the means to explore, and ultimately define, approaches that lead to new structures with novel physical and chemical properties. This knowledge will generate new paradigms in chemical reaction dynamics.

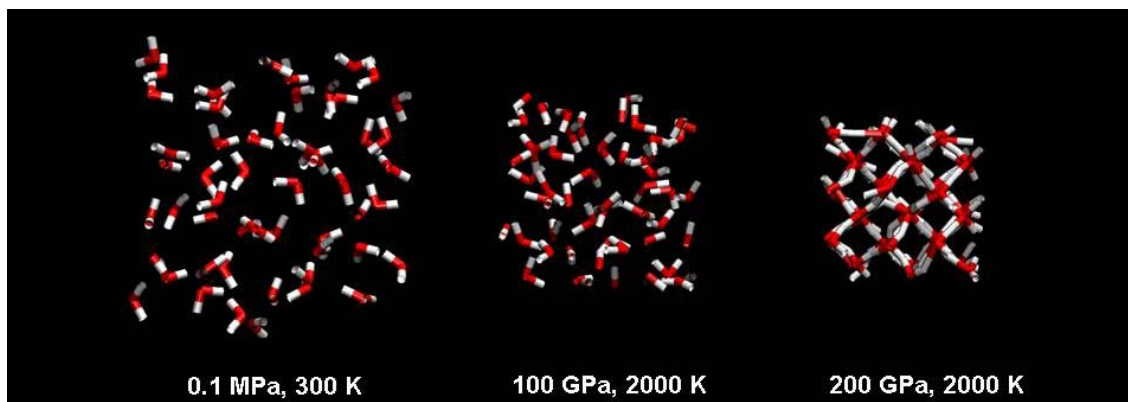


Figure 8. Water can be extremely reactive, especially under extreme pressures and temperatures. The above shows molecular dynamics simulations of H₂O at ambient conditions (1 bar, 300 K), 100 GPa and 2000 K, and 200 GPa and 2000 K, highly reactive, non-molecular, and superionic forms that are not understood. Source: N. Goldman, L. E. Fried, I-F. W. Kuo, and C. J. Mundy, “Bonding in the Superionic Phase of Water,” *Phys. Rev. Letters* **94**, 217801 (2005).

Enabling advances in characterization and modeling. To gain the fundamental knowledge required to understand and control chemical processes occurring at materials interfaces under extreme interfaces will require advances in analytical and computational tools. Novel methods are needed to measure electrochemical properties in high-temperature, low-density aqueous environments. Traditional electrochemical measurements normally span 25 to 90°C at ambient pressure where the experimental media is a well-conducting liquid solution. Higher temperatures represent a number of fundamental (e.g., low media conductivity, high reactivity, high pressures) and practical (seals, reference electrodes, etc.) challenges in accurately characterizing the behavior of materials in an electrochemical environment [9, 10]. Knowledge about exchange current densities and the anodic and cathodic transfer coefficients for even the most fundamental electrochemical reactions in high-temperature environments is sparse. New methods for controlling the mass transport processes to allow accurate measurement of electrochemical kinetics and corrosion processes over a wide range of temperatures are needed. Recent progress in this area has been made: for example, a high-temperature electrochemical system for measuring electrochemical reaction rates in high-temperature dilute electrolyte solutions at temperatures up to 400°C and pressures up to 26 MPa using sweep voltammetry and electrochemical impedance spectroscopy has recently been described [11]. However, extension of these approaches to even more extreme conditions, such as those associated with advanced power generation facilities, is highly important. Furthermore, new techniques are needed to conduct electrokinetic studies to understand surface chemistry at solid oxide-water interfaces. It will be particularly challenging to extend such measurements to temperatures above 300°C, but the resultant

capability would present a great opportunity to discover new interfacial chemical and electrochemical properties of aqueous solutions at high temperatures.

Analytical techniques that complement traditional electrochemical approaches are needed to provide new capabilities to monitor film growth and breakdown and identify surface and solution species, including spatial localization effects. An overarching challenge is the development of new characterization tools that allow the in situ, dynamic, and quantitative examination of surface and buried interfaces with high chemical and spatial resolution. For example, in situ interrogation of buried interfaces and surface layers under reaction conditions to monitor the development of structure, defects, chemistry, and stress will be critical in developing a full understanding of the factors that govern interfacial adhesion. Similar approaches can be applied to the study of growth stress, which arises from the strain caused by accommodation of the reaction product [12]. Advances in techniques such as x-ray and neutron scattering, electron microscopy, and scanning probe microscopy offer great potential for the generation of new atomic-level knowledge about chemical reactivity at the interface of materials and extreme environments. X-ray techniques can be very powerful in the examination of passive film formation, modification, and dissolution and to characterize solutions in localized corrosion cells [13, 14]. Recent advances in photon scattering need to be applied and paired with accurate theoretical calculations. New “multidimensional” capabilities that simultaneously combine two or more analytical tools would enable examination of the material surface and the direct examination of transition states and reaction kinetics. For example, such capabilities could permit femtosecond imaging of chemical reactions on material interfaces while simultaneously conducting three-dimensional tomographic studies of the interface.

The insight provided by these advanced characterization tools will be particularly valuable when paired with computational tools. Indeed, progress in theory and modeling will be essential in understanding surface and boundary layer structures and dynamics. Progress in effectively modeling processes that couple over multiple length scales should be a rich area for accurately predicting these reaction processes in extreme, multi-reactant, multi-component systems. A further challenge is the quantification of the extent and departures from linearity of the energetics and dynamics dictating surface-reaction selection and product formation and, ultimately, stability. As an example, Figure 9 shows a simulation of a (110) TiO_2 (rutile) surface in a 2m SnCl_2 solution. Ab initio density functional theory (DFT) was used to model the bulk crystal and interfacial solution structure and energetics, and to provide interaction potentials for incorporation into large-scale classical molecular dynamics (MD) simulations of aqueous solutions in contact with the rutile (110) surface [15]. The agreement between the simulations and 3-D x-ray imaging of ion sorption sites and the water structure at this interface demonstrates the power of these new techniques to greatly extend our modeling and understanding of effects of extreme environments on surface stability and dynamics.

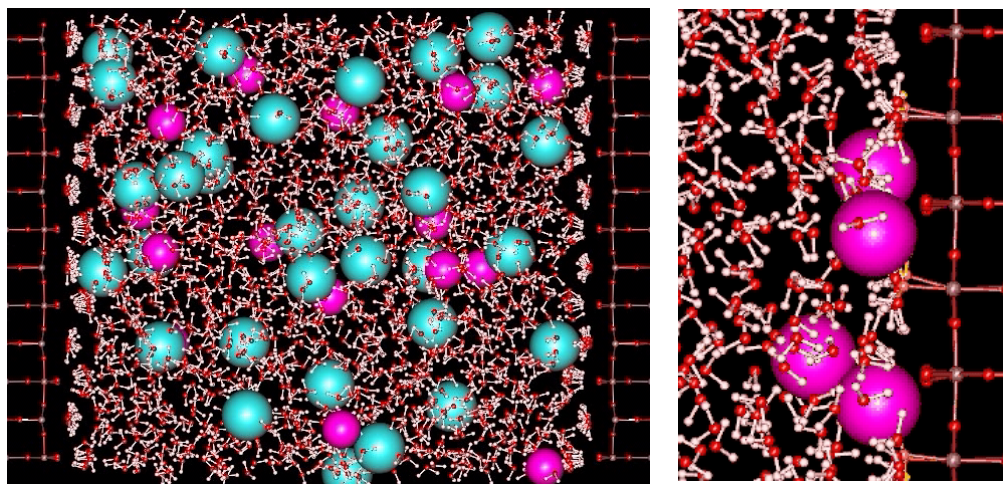


Figure 9. Ab initio density functional theory is used to model the bulk crystal and interfacial solution structure and energetics and to provide interaction potentials for incorporation into large scale. Classical MD simulations of aqueous solutions in contact with the rutile (110) surface. Left: 2m SrCl₂ solution in contact with uncharged rutile 110 surfaces; Right: SrCl₂ solution at negatively charged rutile 110 surface. Color code for atoms: Sr²⁺, Cl⁻, O²⁻, Ti⁴⁺, (white, yellow) – H⁺. Source: M. Predota, Z. Zhang, P. Fenter, D. J. Wesolowski, and P. T. Cummings, “Electric double layer at the rutile (110) surface. 2. adsorption of ions from molecular dynamics and x-ray experiments,” *J. Phys. Chem B.*, **108**, 12061 (2004).

Development of revolutionary new materials for advanced energy technologies. The achievement of a level of understanding that would enable materials to form and maintain ideally stable, protective surfaces under extreme environments would have great implications for material design and future energy technologies. This is because obtaining basic knowledge of energetics and reaction dynamics under extreme chemical conditions is a key part of the science needed to formulate conditions for ideal surface layers. This knowledge would, in itself, have far-ranging impact with respect to discovery of new forms of chemical behavior, unique synthesis approaches, and materials with superior properties (e.g., ultrahardness, high corrosion resistance, high strength) and extreme temperature (>1700°C) stability. For example, platinum and iridium nitrides recently created at high pressures and temperatures have shown unusual material properties such as high incompressibility, refractory character, and potential chemical resistance [16, 17], providing a glimpse into the types of new materials that may be achievable in the future.

New paradigms in chemical dynamics emerging from studies under extreme conditions will be

- the interplay of long- and short-range interactions in governing the energy landscape and associated kinetics in systems exhibiting multiple reaction pathways,
- the extent to which surface, subsurface, and/or bulk reaction pathways can be predicted and ultimately controlled, and
- the necessity for developing nontraditional approaches to reaction pathway determinations in extreme conditions to accurately describe the kinetics of phase selection and stability.

Conclusion

Extreme chemical environments provide the ultimate scientific challenge and opportunity to understand and control materials reactivity, phase boundary and bulk stability, and synthesis. Without fundamental understanding of the limitations presented, the development of materials for advanced energy systems for next-generation applications will not be possible. Fundamental knowledge of the type needed to address the challenge and associated opportunities for developing materials with superb resistance to extreme environments and/or prescribing new synthesis routes to compositions and structures with extraordinary properties will only be attained by developing new experimental and theoretical techniques that can probe energetics and kinetics at the atomic and molecular scale, on and below surfaces, and statically and dynamically—and relate this information to larger-scale properties and behaviors. Two priority research directions, in particular, will provide the impetus to achieve these ambitious goals. One is related to the study of the underlying physical and chemical processes that control surface stability of materials in aggressive environments so as to impart ideal resistance to reactivity. The other is to develop the scientific insights into the mechanisms and control of reaction dynamics under extreme conditions so as to tailor proactively materials reactivity and synthesize new and novel structures and compositions with unusual and extraordinary properties.

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THERMOMECHANICAL EXTREMES

Current Status

The behavior of materials under thermomechanical extremes of high pressure and stress, strain and strain rate, and high and low temperature is at the heart of many energy problems of crucial importance to the nation. New materials that can withstand higher temperatures and stresses without failure are required for the next generation of efficient turbines and heat exchangers for more efficient jet engines, for steam and nuclear electrical power plants, and for future fusion power applications. Similarly, strong, lightweight materials are needed to reduce energy consumption in future transportation systems. We currently do not understand the full range of chemical and physical processes that cause materials to fail at the atomic and molecular levels. To meet future energy technology requirements, a new paradigm for the design of new materials that can withstand thermomechanical extremes is needed. The only way to achieve this goal is to gain a fundamental understanding of materials under static, quasi-static, and dynamic thermomechanical extremes, as described below. Armed with this information, new materials can be designed for meet future energy technologies. Further, it will be possible to employ these extreme conditions to synthesize revolutionary new materials.

Synthesizing new materials with properties specifically tailored to withstand thermomechanical extremes begins with understanding the physical nature of the processes involved, including the properties of the atoms and molecules extending from the nanoscale to the collective behavior at the macroscale. Uncovering the chemical rules of atomic bonding and the physics of collective interaction has historically been facilitated by subjecting materials to varying chemical composition, temperature, and pressure, followed by observation and analysis of the resulting changes in the material structure and properties. Indeed, the use of chemical substitution as an analogue to pressure has been successfully applied to the synthesis of higher temperature superconductors. New capabilities in analytical tools are opening up new avenues to observe these changes in situ. Similarly, advances in computational tools allow these processes to be modeled and simulated. In addition, we have new capabilities to study materials at ever more extreme conditions.

Static thermomechanical extremes. Of all physical parameters, pressure has one of the largest ranges in the universe, spanning over 64 orders of magnitude (Figure 10). In fact, most of the materials in the universe are under conditions that are far different from those we experience here on Earth. Compression induces changes in bonding properties, giving rise to altogether new compounds and causing otherwise inert atoms or molecules to combine. This is illustrated in Figure 11 by the transformation of gaseous molecules (left) to weakly bound molecules in the low-temperature, higher-pressure solid (middle), to strongly bound and extremely energetic extended solids at very high pressure (right). When combined with changes in temperature, altogether new forms of matter may be produced. For example, it has recently become possible to use laboratory techniques to compress materials to the point where the interatomic spacings are reduced by up to a factor of two and densities increased by over an order of magnitude. At these densities, the changes in the electronic structure

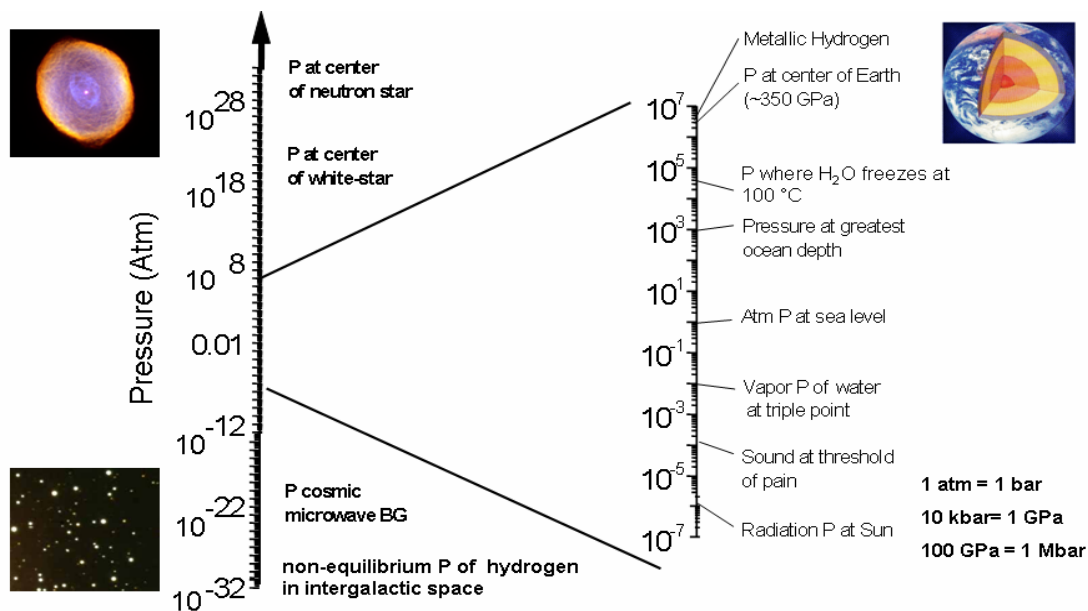


Figure 10. Range of pressures in the visible universe. Source: N. W. Ashcroft, “Condensed Matter at Higher Densities,” in *High Pressure Phenomena*, Proceedings of the International School of Physics Course CXLVII, eds. R. J. Hemley et al., IOS Press, Amsterdam, Oxford, Tokyo, and Washington, 2002.

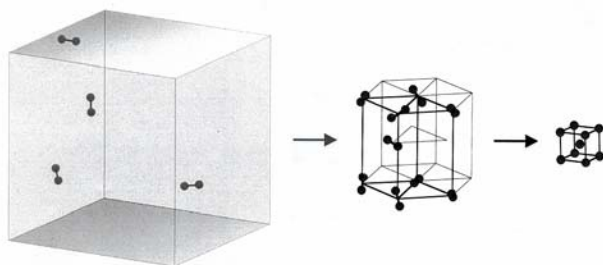


Figure 11. Effect of pressure on atoms and molecules showing conversion from (left) essentially independent molecules of a gas freezing to (center) a weakly bound molecular crystal at modest pressure and low temperature and (right) the ultimate destruction of the molecules as the atoms bind strongly to each other at high compressions.

begin to influence our very notions of chemical interaction and atomic bonding. For example electrons that are essentially localized about nuclei or ions become delocalized, changing materials that are insulators—or even gases—into metals, a transition that can introduce altogether new physical phenomena under extreme conditions [1]. Extreme pressures have also been applied to transform oxygen and sulfur not merely into metals but into superconductors at low temperatures. Materials that are metallic under

normal conditions can be dramatically altered and behave as entirely different elements under extreme conditions. The fundamental bases of these transitions must be understood, and this knowledge will open exciting opportunities to use extreme thermomechanical conditions to design new classes of materials.

Quasi-static thermomechanical extremes. Failure of materials in most energy applications involves defect generation and motion, phase transformations, and crack propagation under quasi-static (or slowly varying) and dynamic thermomechanical conditions. In this regard, relative thermomechanical extremes exist for any material subjected to mechanical and thermal loading, in addition to the absolute thermomechanical extremes described above. One such extreme is the “theoretical strength” of a material, which is the stress needed to shear atomic planes of an ideal crystal across each other. Unfortunately, most real materials

contain defects called dislocations, which cause them to deform plastically at shear stresses that are typically two orders of magnitude lower than this theoretically attainable strength. While this leaves considerable room for improvement, new scientific breakthroughs in our understanding of confinement effects on dislocation behavior are needed to bridge the gap between what is theoretically possible and the behavior of real materials. Another intrinsic limit of a material is associated with melting. Most real materials, with one prominent exception discussed below, become extremely soft and cannot operate at much above half their melting temperatures. Breakthroughs in scientific understanding are needed both to develop new materials and increase the temperature capability of existing materials. Fortunately, because of recent developments in nanoscale materials synthesis and characterization techniques and new computational capabilities, the scientific community is poised as never before to tackle these difficult problems.

Dynamic thermomechanical extremes. The complement of static or quasi-static thermochemical extremes is dynamic loading, which includes shock compression. Pressures reached on dynamic compression can reach to the terapascal (TPa or 10 Mbar) range. The dynamic processes of shock compression are so fast that the loading is adiabatic, and as a result, the temperature also rises and typical durations range from picosecond to millisecond time scales, with temperatures reaching $>10^4$ K, depending on the compression. Dynamic compression provides detailed information on the deformation of materials under extreme conditions and on time-dependent phenomena such as detonation, kinetic, and non-equilibrium processes. This approach accesses different regimes of pressure, temperature, and strain rate compared with conventional static techniques. At these extreme conditions, fundamental changes in the atomic bonding, structure, physical properties, and chemistry of materials present new opportunities for understanding routes for synthesis of new materials. As such, dynamic compression is crucial for numerous energy problems by providing information on the failure of materials, matter under extreme environments associated with fusion and fission, and the creation of new states of matter that are unique to extreme dynamic compression.

Basic Science Challenges and Opportunities

Understanding and predicting the effects of thermomechanical extremes on material behavior requires knowledge of interactions at the atomic, molecular, and microstructural levels, so that we can control them and design revolutionary new materials for future energy applications. These materials can have profound and diverse implications for future energy technologies, including hydrogen, solar, fossil, electrical transport and storage, fission, and fusion. An excellent example is provided by the behavior of hydrogen and hydrogen-containing materials. Materials can be greatly weakened as hydrogen is introduced into their structures under extreme conditions. However, we know little about the high pressure/temperature chemistry of hydrogen itself or how hydrogen interacts with materials that would provide insight as to how to prevent this embrittlement or to develop new resistant materials for a hydrogen economy.

The availability of materials with high strength at elevated temperatures is critical to the further development of power generation systems with improved efficiency and lower emissions. High-temperature processes for power generation are far more efficient, as

dictated by fundamental thermodynamics; however, structural materials in these applications fail far below their theoretical strength limit due to the presence of defects. Improved understanding of how to approach this theoretical strength would result in extraordinary breakthroughs in materials, which would have enormous impact on future energy technologies. For example, these materials could contribute to lighter weight vehicles and result in significant energy savings. Further, designing materials with novel chemical bonding behavior could result materials that are stronger, as well as lighter. Predicting the strength or hardness of materials, particularly in the presence of defects or second phases, remains a significant scientific challenge. Improved understanding is needed of the many interrelated chemical and physical factors that dictate the trade-offs between various thermomechanical characteristics, such as strength versus ductility and toughness. This knowledge has enormous potential for revealing and exploiting unusual mechanical properties for nanostructured materials, including both alloy and ceramic systems.

Increasing our fundamental understanding of materials over the broadest range of thermomechanical extreme conditions is thus essential for enhancing materials performance and for the design and synthesis of new materials to address the broad range of future energy applications. New experimental tools, ranging in scale from bench-top laboratory instruments to major national user facilities, are needed to measure the resulting physical and mechanical effects of materials under extreme thermomechanical conditions quantitatively. Together with new analysis tools, new capabilities in modeling, simulation, and theory for materials under extreme conditions are required. The ability to synthesize, characterize, and computationally study materials, all at similar length and time scales, sets the stage for profound improvements in our current knowledge base and will have enormous impact for future energy technologies and other important applications such as national security. Novel synthesis techniques, ranging from nanoscale tailoring of materials to large-scale growth of defect-free single-crystal structures, are needed to design materials with specific functionalities and improved thermomechanical properties. This research will also require greatly improved experimental techniques to generate a broader range of thermomechanical extremes with a larger variety of sample types. New methods will be required to probe the motion of atoms and molecules directly—both dynamically and quantitatively—under these conditions. Such studies will require new combinations of in situ characterization techniques, such as x-ray and neutron diffraction, scattering, and imaging, high spatial resolution and ultrafast spectroscopies. Experimental investigations using static-to-dynamic high pressure/temperature methods need to be coupled with high-performance computational simulations at the same length and time scales. Traditionally, these experiments have followed three fundamental approaches: static, quasi-static, and dynamic compression. The challenges, opportunities, and needs for materials studies under static, quasi-static, and dynamic extreme thermomechanical environments are outlined below.

Static thermomechanical extremes. In static compression experiments, the pressure may be sustained indefinitely at a controlled level in an apparatus, and the temperature varied independently. In a diamond anvil cell, for example, pressures above 300 GPa can be reached while varying temperatures from the extremely low millikelvin range to those in excess of the surface of the Sun (>6,000 K). Under these conditions, elements and compounds take on unexpectedly complex structures, including both crystalline, nanostructured, and very dense

glassy forms. For example, static high pressure/temperature experiments have generated novel forms of matter, including the three-dimensional network structure of polymeric high-energy-density nitrogen [2] and superhard structures of CO₂ [3]. The materials formed under pressure can contain a great deal of stored energy, a “high-energy-density” property with important implications for energy storage. The polymeric form of nitrogen was predicted to store three times the energy of conventional explosives [4]. This profound transformation was confirmed experimentally [5], and the predicted structure to a atomic framework not unlike diamond was confirmed.

These static compression experiments require characterization in situ under these extreme pressure and temperature conditions. New and emerging analytical capabilities, including synchrotron x-ray and infrared sources, neutron beams, and optical spectroscopies, will enable detailed insight into the atomic structures of materials, as well as the dynamics and transport properties of materials at thermomechanical extremes. These types of experiments can reveal remarkable phenomena in densified molecular systems, new superhard materials, and gases transformed into superconductors. These types of experiments hold promise for breakthroughs in our understanding of matter as well as for making new classes of useful materials, indeed opening a new era of research on materials under extreme pressure conditions.

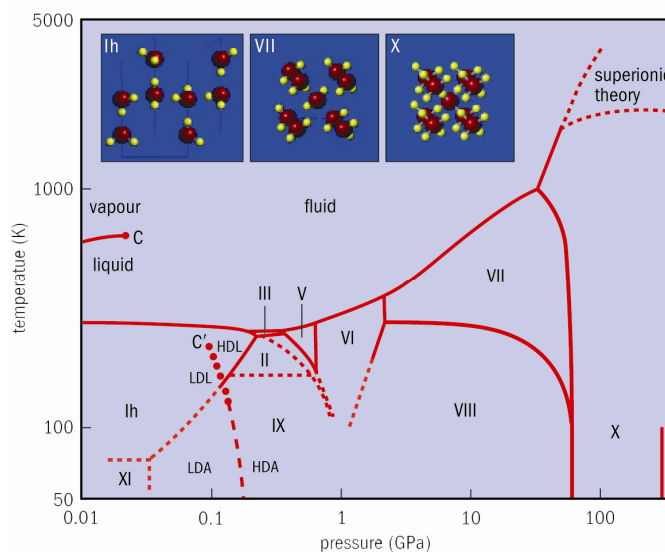
Understanding the modifications of water at high pressure and temperature (see sidebar, Water at the Extremes) has far-reaching implications for aqueous chemistry, geological water/rock interaction, and structural biology. A remarkable transition between two forms of liquid water has been found; such amorphous-amorphous transformations represent a new class of transitions in condensed materials now called polyamorphism. These types of transitions could be harnessed for applications in thermal cycling of materials, storage of heat, preservation of materials, and creation of other new phases. However, the fundamental basis of these transitions and the extent to which they can be understood using conventional thermodynamic and kinetic theory is not known. Moreover, there is a rich chemistry of water at high pressures and temperatures that is both a problem and an opportunity. While water is very corrosive under extreme conditions, weakening and degrading materials, it can also react to form new materials. For example, hydrocarbons can be synthesized from oxides using water under extreme pressure [6]. At more modest thermomechanical extremes, water reacts with hydrocarbon gases to form energy-rich clathrates, a potential energy resource.

The origin of these intriguing behaviors is not yet understood, yet this knowledge has enormous potential to lead to the discovery of new physical principles involving bonding, coordination, and phase transitions under extremes in pressure. In situ measurements, including integrated analytical studies using calorimetry, x-ray, and neutron scattering, are crucial for probing the fundamental bonding changes that take place. This knowledge is also required for designing routes to stabilize novel materials after release of the extreme pressures. Some materials can be recovered from high-pressure conditions—perhaps the most well-known example is the high pressure/temperature synthesis of diamond—but we do not understand how to recover other materials with intriguing properties formed under these extreme conditions. In some cases, composition can be used as a proxy for pressure to

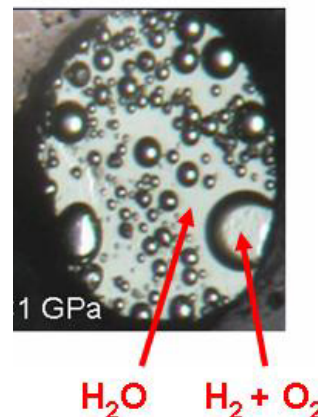
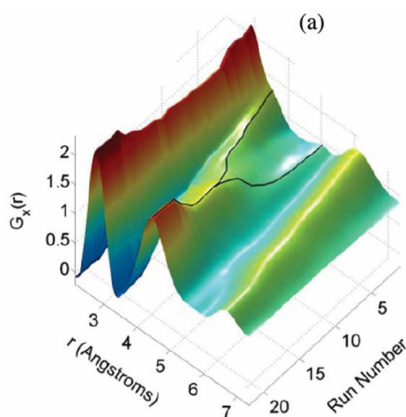
Water at the Extremes

We are all familiar with the changes water undergoes as a function of temperature, from a solid at low temperatures, through liquid water, and then steam at high temperatures. Pressure can also be used to change the state of a material, as shown below. In fact, a wealth of new phenomena under pressure have been uncovered that are not understood. As a solid, water ice can form many packing motifs under applied pressure that result in at least 15 crystalline modifications, in addition to a variety of hydrogen-bonded network glass structures. For example, recent studies have reported evidence for a transition between two forms of liquid water, synthesis of an unusual high-energy-density $\text{H}_2\text{-O}_2$ compound using combined pressure- and x-ray-induced dissociation of ice and formation of superionic form of “hot” ice at megabar pressures and temperatures of several thousand Kelvin. Understanding these and other phenomena is critical to developing new materials using extreme environments.

A phase diagram shows the stable states in which a system can exist as a function of pressure and temperature (and in principle other variables including composition). The P-T diagram of H_2O shows numerous stable as well as metastable transitions in this system. The unusual melting curve of ordinary ice (ice Ih), with its negative melting slope, is shown. Ice X is a non-molecular, ionic form; all others shown are structures based on H_2O molecules. The proposed transition between low-density and high-density liquids (LDL and HDL) follows that of the low-density amorphous and high-density amorphous (LDA and HDA) forms. Source: R. J. Hemley et al., “A pressing matter,” *Phys. World* **19**, 26–30 (2006).



Left: The determination of structures of amorphous materials under extreme conditions is essential for understanding their properties. Left: Neutron diffraction of very-high-density amorphous ice showing a continuous modification of the network structure followed by an abrupt change of the local ordering as a function of pressure. Source: C. A. Tulk et al., “Adding a length scale to the polyamorphic ice debate,” *Phys. Rev. Lett.* **97**, 115503 (2006). Right: Photographs of a diamond anvil cell sample showing H_2 and O_2 bubbles formed on decompression of the new compound formed from x-ray irradiation of ice VII. Source: W. L. Mao et al., “X-ray induced dissociation of H_2O and formation of an $\text{O}_2\text{-H}_2$ alloy at high pressure,” *Science* **314**, 636–638 (2006).



produce a chemical pressure, which along with temperature can stabilize them under ambient conditions. It was an appreciation of the concept of chemical pressure in cuprates that led to the discovery of the first 90 K superconductor [7]. Some 23 elements, including pure oxygen, have been converted to superconductors under pressure. In fact, the highest temperature conductivity on record (165 K) is that of a cuprate under pressure [8]. The mechanism of forming these superconductors is not understood, and there is potential for generating still higher temperature superconductivity under pressure extremes (Figure 12).

Theory can play a critical role in predicting novel properties of materials exposed to extreme pressures. For example, it is predicted that metallic hydrogen will never crystallize at the lowest possible temperatures and can exhibit both superconductivity and superfluidity over a broad range of temperatures [9]. Close interaction between theory and experiment is needed to explore the existence and recoverability of such novel materials. New computational and experimental capabilities are needed to predict, synthesize, and characterize the full potential of exciting new materials with novel properties that can be accessed using extreme pressures.

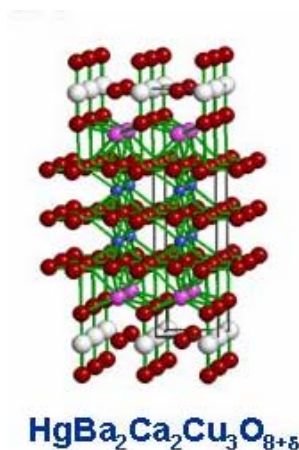


Figure 12. Crystal structure of the highest T_c material (165 K at 30 GPa). There is a great potential for converting other elements alone and in combination to novel superconductors under pressure. See K. A. Lokshin et al., “Enhancement of T_c in $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\sigma}$ by fluorination,” *Phys. Rev. B* **63**, 064511 (2001).

Grand challenges for energy research on materials under static extreme thermomechanical conditions include the following:

- High-pressure experiments have led to materials with extraordinary mechanical and chemical properties. What dictates the limits of material hardness and chemical inertness? Can still harder and tougher materials be created? Can more inert materials be achieved that would withstand high-temperature, high-corrosion environments?
- Electronic states change dramatically when atoms are close together. Can the movement of electrons be predict and controlled to form bonds under pressure? Are there totally new kinds of bonds in these regimes? Will the materials formed under these conditions have unique chemical (reactivity) and physical (electronic, magnetic, and superconducting) properties?
- Static extreme pressures can introduce unusual disorder in materials with novel properties, including high-density oxide glasses and ultratough metallic glasses and high-density amorphous oxides. How can disorder be selectively introduced into materials over various length scales as thermomechanical conditions are varied? Can variations in atomic disorder introduced by extreme pressures be tailored to produce desired functionalities? Can a true thermodynamic framework for transitions from one non-equilibrium disordered state to another be formulated?

- The search for new sustainable fuels, propellants, and energy storage materials requires achieving higher energy densities to be stored and appropriately released in materials. Can still higher-energy-density materials under pressure be created and can these materials be recovered to ambient conditions?

Quasi-static thermomechanical extremes. Quasi-static thermomechanical extremes are those associated with deformation and plasticity, and failure of materials is important to a broad range of energy applications, including production, use (e.g., transportation), and storage. Experimentally, these extremes are imposed and are studied at facilities ranging from small-scale benchtop laboratories to large facilities. The ability to produce and probe materials at small length scales has recently undergone tremendous advances, allowing researchers to isolate and examine deformation and fracture processes individually for the first time. By reducing the volume of material probed, we are fast approaching a time when the “unit events” responsible for material behavior can be separately investigated. This ability, coupled with recent increases in the resolution with which material response can be measured, puts us in the best position in decades to make huge leaps in our fundamental understanding of deformation and failure. Examining these fundamental processes is critical for the understanding of existing structural materials, for developing materials that undergo thermomechanical stresses at small length scales, and for developing new materials that have “extreme” responses—new hard materials, highly elastic materials, and materials that remain strong under high-temperature conditions.

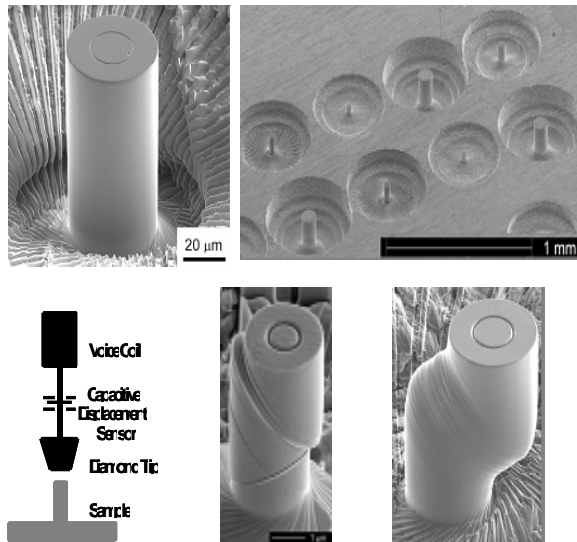
There are several advantages of performing small-scale mechanical tests: the experimental length scales better match the simulation length scales, it is easier to obtain extreme environments in small volumes, certain novel materials whose properties need to be characterized are available only in extremely small quantities, and in multiphase materials, it allows the characterization of individual constituents at the microscale and nanoscale. In large volumes, the mechanical behavior is the result of an ensemble of dislocations moving and multiplying over macroscopic distances. By decreasing the sample volume, it will be possible to interrogate single dislocations and separate the nucleation event from dislocation motion and multiplication. At the significantly improved load and displacement resolutions that are foreseen in the future, it will become possible, for example, to distinguish between homogeneous and heterogeneous nucleation of single dislocations. This will allow direct comparisons with theory, which is currently not possible.

The emergence of microelectromechanical systems (MEMS) technologies and availability of microscale and nanoscale processing techniques for making and shaping micron- and nano-sized specimens have empowered experimentalists with an unprecedented ability to probe the mechanical response of increasingly smaller volumes of materials (see sidebar, *Elucidating the Origins of Materials Strength*). These advances have been combined with increasingly finer techniques for manipulation, loading, and strain measurement, and for examining the fundamental processes in situ—observing the response of the material to the stress state. Techniques such as photolithography, vapor deposition, reactive ion etching, lithography/electroplating/molding (LIGA), and electroplating are available in MEMS foundries and can be used to fabricate micro test specimens as well as micro devices.

Elucidating the Origins of Materials Strength

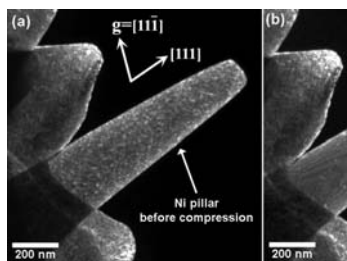
The traditional method for measuring the strength of materials has been to utilize macroscale, multi-grain specimens gripped in a fixture in which the samples can be pulled, pushed, heated, cooled, twisted, or vibrated to measure their mechanical properties. Though this works well for measuring the macroscopic behavior of the material, the combination of multiple grains, multiple interfaces, dislocations, particles, and other defects in a typical sample preclude the use of these tests for understanding the fundamental origins of material strength.

Recent developments in small-scale sample preparation such as focused ion beam (FIB) milling and new generations of high-resolution micromanipulators have allowed new approaches to testing mechanical properties at a much more fundamental level. One such technique utilizes FIB milling to fabricate micro-pillars ranging from hundreds of nanometers to several tens of micrometers in diameter (see figure at right). Compression tests of these pillars in a modified nanoindenter can provide fundamental understanding of dislocation confinement effects in metals and shear bands in metallic glasses as never possible before.



Micro-pillars fabricated by FIB milling for subsequent compression in a modified nanoindentation system. Sources: Uchic, Dimiduk, Florando, and Nix, “Sample dimensions influence strength and crystal plasticity,” *Science* **305**, 986–989 (August 13, 2004). Dimiduk, Uchic, and Parthasarathy, “Size-affected single-slip behavior of pure nickel microcrystals,” *Acta Mater.* **53**, 4065–4077 (2005). Dimiduk, Woodward, LeSar, and Uchic, “Scale-free intermittent flow in crystal plasticity,” *Science* **312**, 1188–1190 (2006).

An exciting extension of this micro-pillar research is the ability to perform these tests on even smaller nanoscale samples, in situ in the transmission electron microscope (TEM). This allows defects within the nano-pillars to be directly observed during deformation. New developments in sample preparation and sample holders for the microscopes are being combined with advanced imaging technology to capture the generation and motion of defects in real time (see figure below).



In situ compression test of a nickel nano-pillar showing the evolution of the microstructure and the stress-strain behaviour from the test. In isolated pillars, such as those shown, the strength is more than five times that of bulk nickel. Image courtesy of Z. W. Shan, S. A. Syed, O. L. Warren, and A. M. Minor (LBNL and Hysitron).

These emerging analysis methods are in their infancy and will dramatically improve our understanding of the underlying mechanisms of deformation and fracture, especially as alternatives to FIB milling are developed that will allow the preparation of small-scale specimens without the confounding effects of FIB damage. The ability to perform elevated-temperature mechanical and tensile tests in submicron specimens, especially with highly resolved load and displacement sensing in situ, is another opportunity for future research. Using techniques such as these, unusual (and unpredicted) size effects may be uncovered which challenge current theories of mechanical behavior.

Traditional machining processes are not applicable, but specialty electro discharge machining, laser machining, chemical mechanical polishing, and focused ion beam milling may be used to create microspecimens from bulk materials. Underlying substrates and frame geometries facilitate handling and nanoindenters, and piezo stages facilitate loading.

In addition to dislocations, the role of material interfaces is critical. Many such interfaces can exist, such as grain boundaries separating differently oriented crystallites and phase boundaries between different crystal structures (possibly with different compositions). These can serve as sources or sinks for other defects, obstacles for dislocation motion, or convenient fracture surfaces if they are sufficiently weak. The role of interfaces becomes increasingly important at the nanoscale. Understanding the chemistry, thermodynamics, and dynamical behavior of interfaces, including their motion under shear stress and temperature, as well as the interaction of interfaces with dislocations, alloying elements, and other interfaces, is critical for controlling material behavior. These properties are more easily studied than ever, from a wide variety of techniques. High-resolution microscopy provides detailed information on the atomic structure of interfaces, interfacial steps, and structure of materials near the interfaces. In situ microscopy allows for observation of stress-driven motion of materials. 3D atom probe experiments studies allow for spatial characterization of chemical compositions through a system at small length scales, identifying precipitates at interfaces and dislocations. The ability to machine nanoscale samples from specific locations in a material allows the isolation of specific interfaces for testing. Small-angle scattering (particularly neutrons) allows for nondestructive probes of size distributions of precipitate phases. Simulations provide key information, ranging from first-principles studies of interface structures and energies, to molecular dynamics simulations of interface motion and dislocation-grain boundary interactions, to phase-field modeling of precipitate morphology and growth.

High-temperature extremes are important for applications, and currently used materials have reached a bottleneck. Nickel-based superalloys retain their strength close to their melting temperature due to the presence of coherent secondary alloy phases that are present at very high volume fractions and the absence of strength-degrading grain boundaries. For many other structural materials, the practical operating temperatures are well below melting. How can such materials be strengthened at high temperatures? Aluminum alloys are illustrative of some of the interesting scientific challenges to be overcome because, although they have γ - γ' phases analogous to those in nickel-based alloys, the γ' phases form at very-low-volume fractions under equilibrium conditions. As a result there are no “high-temperature” aluminum alloys that can operate above half the melting temperature.

A critical question is whether metastable secondary phases can be formed at high enough volume fractions to strengthen such materials? Can first-principles calculations help guide the development of alloy compositions that would produce favorable precipitation of phases? How can the morphology of such phases be controlled? Recent evidence suggests that it may be possible to replicate the microstructures of nickel-based superalloys in other alloy systems, such as in cobalt-based alloys [10]. Which other similar systems might be discovered in the future with significantly higher melting temperatures? Certain oxide-dispersion-strengthened alloys with nanoscale precipitates are known to have extreme

stability at very high fractions of the melting point. The underlying mechanism governing their stability remains unclear, but first-principles calculations suggest that complex point defect structures may be responsible. These complexes dramatically slow down diffusion of defect elements, and dramatically improve high-temperature behavior. If we understand the fundamental principles of what makes these nanoscale precipitates so stable, it may be possible to apply the same principles to other alloy systems and produce these precipitates using a less cumbersome process than mechanical alloying. Never before has there been such an availability of methods to directly examine processes affecting thermomechanical response.

In situ techniques allow direct study of the material under extreme conditions and range from benchtop instruments that allow real-time microscopy of materials under stress to large-scale user facilities for rapid characterization of small amounts of materials during conditions of extreme pressure or temperature. Computational modeling at different length scales provide a description of materials and processes in materials that cannot be probed directly by experiment but provide predictions that may be experimentally verifiable. These range from electronic-structure-based techniques that describe, for example, changes in bonding that occur under pressure to atomistic calculations of melting of materials at high pressures and temperatures to continuum-level modeling of microstructural evolution and deformation of materials. These descriptions have recently become possible by dramatic improvements in algorithms and models, in experiments that probe specific processes in materials, and by the accessibility of large-scale computing resources. In situ, real-time experimental techniques combined with advanced theory, modeling, and simulations are required to address the following questions.

- *How do defects form and move under complex stress states?* How is this modified by temperature and by other pre-existing defects? The defect structure of a material is typically non-equilibrium and reflects the history of the material. The deformation of materials is controlled by the formation and movement of the defects, which may be driven either by external stress or temperature. The ability to probe small volumes or examine motion in situ will dramatically affect our understanding of these processes, and ultimately allow for a better control of material behavior.
- *How do local stress states affect material stability?* Stress-induced phases often occur and in some cases can dramatically alter material behavior. This is more difficult to study than phases that appear under hydrostatic pressure, as it is difficult to statically hold a material under significant shear stress. Therefore, transformed states tend to occur near stress-concentrating defects, such as crack tips and dislocations. How do such transformations affect the material response? How can such transformations be studied in small volumes? How does increasing the surface-area-to-volume ratio (by going to the nanoscale) affect the way in which stress affects material stability?
- *How do phase boundaries affect the thermomechanical response?* It is now well established that materials containing multiple phases may have significantly different behaviors from the isolated phases. The origins of such behavior are many-fold and material specific but often tie into the microscopic properties of the interface itself. Controlling growth, boundary sliding or boundary failure, are essential to improving materials for extreme conditions. An important unanswered question relates to the role of microstructural refinement in lamellar structures on mechanical behavior. The holy grail is

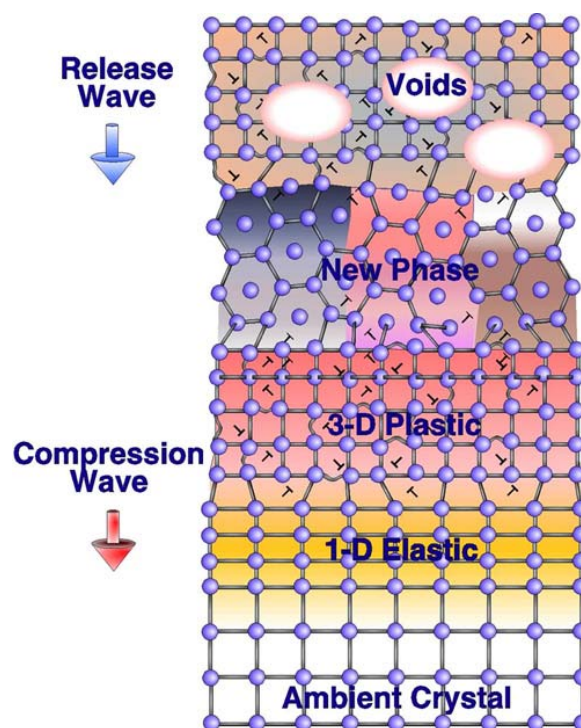
to enhance both strength and ductility/toughness of structural materials. There are tantalizing indications that decreasing the lamellar spacing is one way to accomplish this goal. However, the evidence is sparse, and we understand very little of the underlying physical mechanisms. Similarly, we do not understand what it is about certain nanoscale phases (but not others) that allows them to exhibit extreme stability at very high fractions of the melting point. Small amounts of alloy additions can alter interface chemistry and, in turn, the deformation and fracture behavior of materials in dramatic ways, both positively and negatively. Often, the discovery of such effects is currently empirical, rather than by design. Advances are needed in the fundamental understanding of how solute atoms modify interface properties.

- *How can metastable phases be formed and utilized?* Materials that affect thermomechanical response, or have extreme thermomechanical limits (such as the hardness of diamond), may be *metastable*; that is, thermodynamically they favor other structures and/or compositions. How can such materials be formed and utilized under ambient conditions? Can these materials be used in conjunction with other materials to improve their properties? The equilibrium phase diagrams of many potentially useful alloy systems limit the volume fractions of the phases that can co-exist with each other. Understanding how to promote the formation of metastable phases will have a dramatic impact on enhancing the thermomechanical response of otherwise very attractive materials.
- *How do minor solute additions affect material response?* Small amounts of alloy additions (1–2%) can dramatically change materials behavior, in either positive or negative ways. Often, the discovery of such effects is currently empirical, rather than by design. Minor additions often segregate to grain boundaries and can either weaken or strengthen the cohesion of the material. They may also alter the motion of interfaces or dislocations, affecting the strength of the material, or its creep resistance. Solute atoms at interfaces may modify growth processes, leading to different microstructures that affect the material behavior. Enhanced diffusion at grain boundaries can result in precipitation of new phases. Understanding these changes can yield new pathways to the synthesis of vastly improved materials.

Dynamic thermomechanical extremes. Dynamic thermomechanical extreme studies address problems at higher pressures, higher temperatures, and a broad range of strain rates. As such, studies of materials under dynamic thermomechanical extremes complement those of static and quasistatic approaches. The initial response of a material to dynamic compression creates stress in one direction, leading to what is known as a strong shear (see sidebar, Materials Response to Dynamic Compression). If the shock wave propagating through the material exceeds a critical value of strain, this shear stress leads to the creation of dislocations in the material that allow it to deform plastically [11]. Exactly how the lattice responds to the uniaxial shock compression as a function of time is still not fully understood, and experimental investigations probing the lattice level are sparse and limited. The rate of relaxation to hydrostatic conditions is determined by the nucleation rates and the mobilities of dislocations, which in turn depend upon the microstructure (grain boundaries and other imperfections). The plastic behavior of shocked solids is controlled by defect mechanisms that follow a complicated time-dependent history, with very high dislocation densities present at some times and significant recombination processes active over the entire

Materials Response to Dynamic Compression

Consider a notional crystalline solid, as illustrated here. In the case of a planar drive, the initial response is a uniaxial compression that is elastic; that is, once the disturbance is removed, the lattice will relax back to its original configuration. However, under high-stress conditions, atoms in the lattice will respond irreversibly. The local nucleation and kinetics of defects structures lead to plastic relaxation, known as the one-dimensional (1D) to three-dimensional (3D) transition. Subsequently, the material may also undergo structural transformations (including melting), exemplified here as a change from a cubic single crystal to a hexagonal polycrystal. Upon release of pressure, the modified microstructure influences the nucleation and growth of phases, voids, cracks, and failures, leading to dramatic and important consequences to most macroscopically observable behavior such as the material's thermodynamic state (pressure, temperature, density) and mechanical properties (strength, fracture toughness). The nature of nucleation and mobility of defects, phase nucleation and growth, and void nucleation and growth under these highly dynamic stress conditions is poorly understood.



process [12]. Lastly, under certain conditions, the combination of anisotropic plasticity and thermal softening because of the heating caused by plastic deformation creates zones of material instabilities. When this behavior occurs in a material, in general the material fails very rapidly. The theoretical and simulation tools needed to represent this behavior adequately are currently lacking. Understanding the morphology, nucleation rates, mobilities, and relaxation timescales in situ and in real time is a requisite for developing a predictive capability of the evolution of plasticity over extreme dynamic thermomechanical conditions.

Observation of spatial and temporal changes in materials at the very small length and time scales (i.e., nanometers and picoseconds) is crucial for understanding how materials deform. While observations of a material's response to a single thermomechanical stimulus at these length and time scales were unfathomable just a decade ago, new technologies, scientific approaches, and experimental facilities—currently available and on the horizon—ring these goals within reach for the first time. These facilities include the National Ignition Facility (NIF), the upgraded Z-pinch facility, the Linac Coherent Light Source (LCLS), and others, which will be able to create novel states of matter under extreme thermomechanical conditions and diagnose these states with unprecedented accuracy and resolution. These devices offer special opportunities to study the time evolution and interplay of the thermal and mechanical response of materials to extreme environments. Coupling dynamic drivers

with advanced scattering probes using x-rays, neutrons, and electrons at other national user facilities will also provide especially promising opportunities.

The broad pressure-temperature regimes explored by dynamic compression in principle allows direct measurements of the balance between mechanical properties, thermal effects, and chemical dynamics and kinetics. Recent experiments provide a way to separate the role of pressure and temperature on material strength and deformation. Additionally, the ability to control the rise time of the loading pulse provides a unique opportunity to examine the time evolution of inelastic deformation for different loading times. By varying pressure, temperature, and rise time in a controlled manner, dislocation motion and generation can now be probed for the first time. The interplay between compression and deformation can be used to explore the coupling between pressure-induced phase changes and material deformation.

As in the cases for static and quasi-static extremes, there are major gaps between theory and experiment for dynamic thermomechanical extremes. Under dynamic compression, solids generally exhibit a rich spectrum of phases, some of which are metastable and may differ from those produced under static compression. Like water, carbon displays a wide range of structural states under pressure that are both stable and metastable. These include cubic, hexagonal, nanocrystalline, and amorphous diamond, all observed on shock compression [13, 14]. The transformation from one phase to another is comprised of at least three physical phenomena that constrain the transformation kinetics: access to new, metastable phases due to pathway kinetics, nucleation of the new phase, and subsequent growth to fill the volume. The relaxation time observed in atomistic simulations is on the order of picoseconds for the nanoscale sample sizes utilized in large-scale molecular dynamics simulations (Figure 13). These timescales are often several orders of magnitude faster than the linear relaxation times determined from gas gun experiments, possibly because of the small system sizes or the high strain rates in these simulations. In situ, real-time studies are critical to understand the differences between the simulations and experiments.

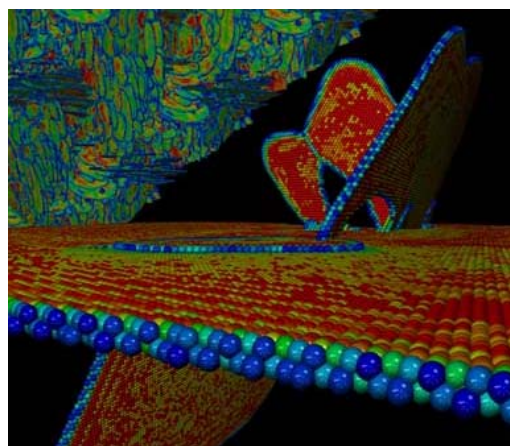


Figure 13. Molecular dynamics simulation of the 1D→3D transformation of plastic flow in shocked single-crystal copper. Source: E. M. Bringa et. al., “Shock deformation of fcc metals on sub-nanosecond time scales,” *Nature Materials* 5, 805 (2006).

Dynamic wave loading is accompanied by considerable defect production during both the compression and unloading portions of the process. Defects and other microstructure (grain boundaries, second-phase regions) can act as nucleation sites for the formation of voids that begin on nanoscales and subsequently grow and coalesce under tension, resulting in bulk material failure. The incipient damage has been predicted to occur in as fast as tens of picoseconds. The experimental observation of bulk damage varies according to the drive conditions but typically represents longer timescales, from a few tens of nanoseconds to a

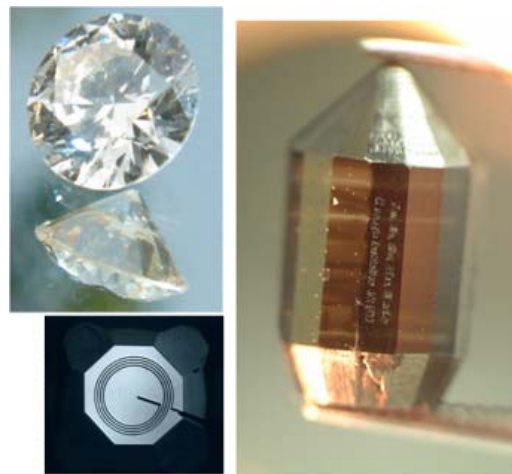
fraction of a microsecond. The entire process is termed spall. Much of the current understanding of damage produced by dynamic loading is derived from recovery experiments [15]. The nucleation, early void growth, and final void linkage regimes that are critical to predict this process from a fundamental basis are not yet understood.

Two basic approaches for investigating such dynamical behavior under extreme conditions have been pursued: study samples recovered from dynamic compression and real-time, in situ bulk-property measurements. The first approach uses microstructural investigations to probe the sample but not under the described extreme conditions. In the second approach, real-time measurements of the bulk response are recorded with fast diagnostics. While these approaches have proven to be valuable and are largely responsible for our current understanding, they provide only limited insights about critical processes originating in the atomic and picosecond regimes. Altogether new approaches are needed to answer the following questions for the first time:

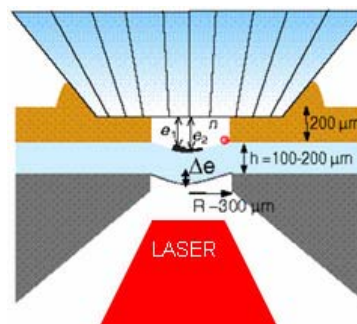
- *How do atoms move during transformations?* Traditionally, the study of the dynamic response of materials to compression has been from a continuum point of view—treating a solid like a fluid and ignoring the existence of atoms. Understanding how solids deform plastically and ultimately fail requires information on how the atoms move. We need to be able to watch atoms move during the course of pressure- and temperature-induced transformations.
- *What controls different deformation mechanisms of materials? How are defects created and how do they move? What is the atomic basis of damage and other failure processes? How is the microstructure modified under high dynamic compression?* This will require the ability to probe, understand, and predict atomic motions and the dynamics of larger domains such as dislocations, voids, and grain boundaries under extreme conditions.
- *Does melting and resolidification always occur as predicted by the equilibrium phase diagram (i.e., what kind of metastable states form)?* A pressure-temperature phase diagram (e.g., as shown in the sidebar on water) defines the limits of stability of a material as a function of pressure, temperature, and composition. However, when transformations occur very quickly, temperature and pressure may not be the relevant variables. For some transitions that occur during decompression, the rate of entropy production may be more relevant. The phases that occur may be completely different, or the pressure and temperature where the transformations take place may be altogether different. The kinetics may be such that the combination of pressure, temperature, and composition can produce material well outside its normal “stability” range, as occurs for diamond produced by chemical vapor deposition *below* atmospheric pressure.
- *Are there phases that are unique to dynamic high-pressure processing? How do molten and solid phases and the kinetics of the transitions affect the final state? Does a transition even reach completion during the short timescales involved in the dynamic thermomechanical process?* Direct probes of materials during transformations and reactions, along with the development of appropriate theory, are needed to understand these phenomena and to guide the search for new materials.
- *What is the nature of materials at very high temperatures (i.e., $\sim 10^4$ K or the electron-volt range) and high pressures when they are strongly shocked?* Can these conditions form new materials with unique functionalities? Under these conditions, both the valence electrons and the core electrons are redistributed in the material. Understanding materials in these challenging regimes, which border between condensed matter and plasma physics, requires new capabilities in theory, experimental apparatus, and characterization.

New Generation of Materials for Extreme Conditions

Single-crystal diamonds exemplify a material which was originally only found at extremely high *pressures and temperatures* but can now be synthesized at ordinary pressures by manipulation of chemical bonding in a hydrogen-rich methane plasma by chemical vapor deposit (CVD). Diamond is a material of extremes properties that stands out among all materials. It has the highest known hardness, very low friction and adhesion, unmatched thermal conductivity, ultrahigh melting temperature, extremely low thermal dispersion, radiation hardness, high-magnetic-field compatibility, biocompatibility, chemical inertness, and unique electronic behavior ranging from a wide-gap insulator and high electron mobility in its pristine form to semiconductor or superconductor. These properties of diamond can be exploited for structural, functional, electronic, and optical materials applications, and at the same time, diamond can endure the harshest extreme environments. Experimentally, diamonds have been used for both static and dynamic compression while enabling in situ observations of myriad phenomena. Single-crystal diamonds produced with increasing size and quality by CVD could form the basis of a new instrumentation for studying materials under extreme pressures, temperatures, chemical environments, and applied fields, including plasmas generated by ever larger microwave and radio frequency sources.



New generation of diamond technology. Top left: Single crystal CVD anvils. Top right: 10 carat CVC diamond. Source: S. S. Ho et al., “Prospects for large single crystal CVD diamonds,” *Industrial Diamond Review* **66**, 28–32 (2006). Lower left: Electrical circuits imbedded inside the diamonds to use as “smart anvils” for electrical and magnetic measurements under thermomechanical extremes. Source: Yogesh K. Vohra and Samuel T. Weir, “Designer Diamond Anvils in *High Pressure Research: Recent Results and Future Opportunities*,” pp. 87–105 in Proceedings of the International School of Physics—Course CXLVII, eds. R. J. Hemley et al., Amsterdam, Oxford, Tokyo, and Washington, IOS press, 2002.



Schematic of combined static and dynamic compression experiments using a diamond anvil and laser to drive a shock wave into the sample through a diamond window. Advancements in diamond and laser technologies will allow generation of pressures well into the TPa range with these techniques. Source: P. Loubeyre et al., “Coupling static and dynamic compressions: first measurement in dense hydrogen,” *High Press. Res.* **24**, 25–31 (2004).

Conclusion

New materials that can perform reliably under thermomechanical extremes are critical for next-generation fossil, fission, fusion, and other technologies. Understanding how materials fail under these conditions is the key to revolutionary breakthroughs. Understanding how atoms and electrons move can provide insight into defect production and eventual evolution into microstructures (grain boundaries, etc.). This information can also provide insight into how new bonds can be designed to form under these conditions, giving rise to remarkable new materials with novel properties. The response of materials to extreme thermomechanical conditions encompasses a broad range of processes and properties such as structural phase transformations, including melting and solidification, elastic and plastic deformation, fracture and failure, and the creation novel materials, including possibly new states of matter. Recent developments in experimental and computational methods promise to transform our limited understanding of the origins of these extremely rich physical and chemical behaviors. Further, this knowledge will provide new capabilities to predict responses and properties of materials under such conditions over multiple length and time scales from the atom to the macroscopic and from femtoseconds to centuries.

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ELECTROMAGNETIC EXTREMES

Current Status

Electricity accounts for about 40% of our primary energy, with a projected 50% increase in demand by 2030. These demands will swell further, perhaps to 70% or more, over the next 50 years [1] as solar, wind, advanced nuclear, and other technologies mature and displace carbon-based fuels. Much of today's electric technology was developed in the middle of the last century when the demand for power was lower, reliability and power quality were less important, and standards of esthetics and safety were less stringent. Meeting the future demands for electricity in the next 50 years at significantly higher standards of reliability, quality, esthetics, and safety requires technologies based on new materials capable of operating at extreme electric and magnetic fields. These new materials include insulators that withstand extreme electric fields, permanent magnet materials that produce dramatically higher magnetic fields for generators and motors, and conductors and superconductors for coils that carry higher current at lower voltage for generators, motors, and transformers. Such materials would enable a much higher capacity electrical infrastructure in a much smaller package, operating with a higher standard of reliability and quality. Discovery and understanding of these new materials require pushing the limits of extreme electric and magnetic fields to reveal and control new correlated electron behavior. The performance of these new insulating, conducting, and magnetic materials depends on controlling the behavior of the atomic and nanoscale defects that permeate their structures. The emerging capabilities of nanoscience to design, synthesize, characterize, and model atomic and nanoscale defects and structures in real materials enables broad new horizons for high-performance materials that can dramatically enhance the capacity and reduce the footprint of the electric power system.

Our ability to meet the burgeoning electricity demands of the next 50 years is ultimately tied to our ability to harness electric and magnetic fields at their extremes. The performance of electric power generators depends on the strength of permanent magnets spinning inside coils to induce the electrical voltages and currents that power our homes, businesses, and industries. Transforming electricity to high voltage for long-distance transmission and converting it to mechanical motion for end use depend on the maximum magnetic field that can be produced by conducting and superconducting coils in transformers and motors. Maintaining the voltage differences across copper coils in generators and motors and, additionally, across long-distance high-voltage transmission lines depends on insulation that can withstand large electric fields and field gradients without failing. Moreover, electric fields are increased as the size of motors, generators, and transformers that make up the electrical infrastructure are decreased, and as electronic components in integrated circuits are reduced in size while maintaining the same operating voltages. Further, finding new insulators that can withstand higher electric fields is a primary requirement for creating smaller, lighter, and less expensive electrical and electronic components.

The capacity and performance gaps blocking development of future electric technologies can be bridged only by fundamental breakthroughs in materials. This requires discovering, developing, and utilizing new permanent magnet materials that produce higher magnetic

fields, new insulation materials capable of withstanding higher electric fields, and new high-strength conducting and superconducting materials capable of carrying higher electric currents at lower voltages. Dramatic advances in understanding, synthesizing, and designing materials at the atomic and nano-length scales hold enormous promise for new generations of magnets, insulators, and conductors that can satisfy our rapidly growing demand for electricity delivered in a smaller space and with higher reliability and quality. Breakthroughs in our fundamental understanding of materials operating in extreme electric and magnetic fields—and of materials failure under these extremes—are needed to enable reshaping traditional approaches to generating, distributing, and using electricity to meet our rapidly expanding power needs in the 21st century.

Extreme electric fields. Controlling electric fields is basic to every aspect of the electric power and electronics industries. Confining electricity from the high-current wires of the power system and to the nanoscale pathways of semiconductor electronics requires insulators that can withstand extreme electric fields in a wide range of environmental conditions. A key property of an insulating material is its dielectric breakdown strength (Figure 14), which is the maximum electric field strength a material can withstand without losing its insulating properties. Designing new insulators with much higher dielectric breakdown strength is a primary need for increasing the capacity and reducing the footprint of the electrical power infrastructure.

The efficiency of long-distance transmission of electrical power is increased by transforming power to higher voltages and lower current to reduce resistive losses in the lines. The highest voltage now used in the United States is 765 kV, limited primarily by the breakdown strength of the large ceramic insulators that isolate overhead lines from their surroundings. Motors and generators operate at much lower voltages, but the windings of their copper-wound coils are separated from each other and from the coil support by only a few hundredths of a millimeter. Even moderate voltage differences over such small distances induce large electric fields, at the limit of the dielectric breakdown strength of the insulation separating the coil windings. Integrated circuits shrink electrical pathways to nanoscale dimensions, requiring isolation of a few volts over a few nanometers in the gate circuits of transistors. Because the dimensions are tiny, the electric fields required to operate these devices are enormous. The electric fields in gate dielectrics of next-generation semiconductor electronics are the largest

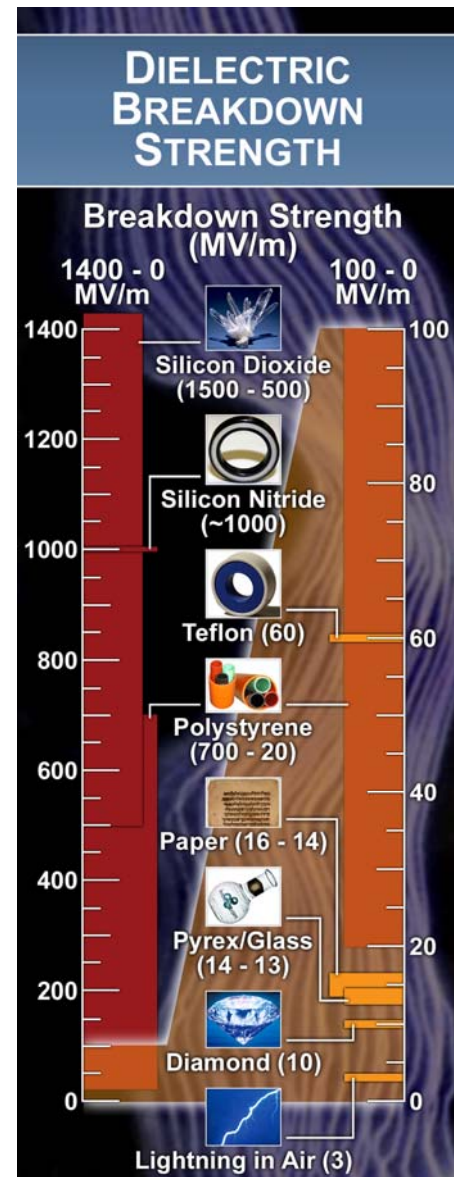


Figure 14. Dielectric breakdown strength of various materials. Scale between 0 and 100 MV/m.

in electric and electronic technology; finding insulators that can withstand these high electric fields is a major challenge for next-generation electronics. Silicon dioxide (SiO₂), the current standard, is already operating at the limit of its capability. The challenge for next-generation electric power and electronics is to raise the dielectric breakdown strength of insulators to enable motors, generators, and transmission lines to operate at higher voltages and higher efficiencies, and for nanoscale electronics to continue their remarkable march to smaller sizes, higher speeds, and lower cost.

Despite their importance, the mechanisms of dielectric breakdown remain largely hidden in the subtlety of atomic and nanoscale defect structures. Breakdown of insulation occurs in three stages [2, 3]. In the *first stage*, sometimes called ageing, high electric fields acting continuously on a dielectric force migrate to penetrate from the surface to the interior of the insulator. A perfect insulator would simply resist this charge migration, but the structures of real insulators are permeated by random atomic and nanoscale defects that enable charge penetration. These defects may pre-exist the electric field or may be created slowly over time by the continuous action of the electric field. The defects gradually trap charges that arrive through conduction or tunneling across the insulating regions surrounding them. As long as the charged defects remain well separated, their captive charges cannot jump from one defect to the next, and the overall insulating character of the dielectric is maintained. However, over timescales as long as months or years, the charged defects in a given region become dense enough that electrons can jump from one defect to another via a continuous percolation path. Although the charge accumulation at defects is a slow process, the discharge of current across the insulator once a percolation path is established is sudden and violent. This is the *second stage* of breakdown.

Once initiated, the catastrophic breakdown event occurs very quickly, with the local breakdown spot expanding longitudinally to bridge the entire thickness of the insulator and laterally to enlarge the breakdown area. The lateral expansion of the breakdown front is remarkably fast, of the order 10⁶–10⁸ cm/sec, and the longitudinal expansion is even faster [4]. The fast propagation of charge across the insulator triggers the *third stage* of breakdown, electrical heating along the conduction path that is capable of raising the local temperature of the dielectric above its melting point, up to 1650°C and beyond. Thermal and electrical damage arising from the discharge current often destroy the insulator along the discharge path, replacing it with a conduction path that short circuits the insulation.

Our understanding of dielectric breakdown is limited by our ability to see the atomic and nanoscale defects that trap charges during the first or ageing phase. These defects are beyond the resolution of the current generation of x-ray scattering and imaging probes but are within reach of emerging focused beam x-ray techniques. Because they are randomly placed, these defects cannot be characterized by traditional Bragg scattering that examines only the periodic structure of the insulator. New approaches exploring the diffuse x-ray and neutron scattering between Bragg peaks, however, can characterize these randomly placed nanoscale defects [5]. Small-angle x-ray and neutron scattering using high-intensity sources at user facilities is another promising approach to measuring the evolution of these defects quantitatively. The new generation of Transmission Electron Aberration-Corrected Microscopes (TEAM) now under development will be capable not only of imaging the

defects but also of measuring in situ the changes in their atomic and electronic structure as they accumulate charge under the influence of an applied electric field. These kinds of time-resolved in situ characterization with atomic and nanoscale resolution are essential to developing a quantitative understanding of dielectric breakdown.

In addition to new measurements, new theoretical understanding of high-electric-field conduction in solid insulation systems is critical to controlling breakdown phenomena [6]. The multi-scale nature of breakdown, from slow charging of isolated, randomly placed atomic defects to the sudden discharge of electrons along a macroscopic percolation path, is beyond the reach of standard simulation methods. The catastrophic second stage of breakdown, with its very fast discharge of current and heat, requires combining atomic, electronic, and thermal degrees of freedom in a common theoretical framework. Recent advances in computational quantum mechanics have shown the potential for providing tools with which to understand high-field conduction at the atomic and molecular level, while transient nonlinear finite-element analysis can enable high-field modeling at greater length scales [7, 8].

Extreme magnetic fields. Magnetic fields are at the very heart of the electrical power system, from the spinning permanent magnets in generators that create electric power to the transformers that raise and lower voltage levels for long-distance transmission to the motors that convert electrical currents to mechanical motion. Electric motors are pervasive throughout our economy, converting electricity to motion for applications such as compressors for refrigerators and air conditioners, fans that distribute heat in houses and commercial buildings, robotic assembly lines in industry, electric trains for urban mass transportation, and perhaps soon plug-in hybrids for personal transportation. Industrial motors alone use an estimated 25% of all electricity generated in the United States [9].

A prime limitation of our electrical infrastructure is the strength of the magnetic field that can be created in permanent magnets and electromagnetic coils. Increasing these magnetic fields by a factor of ten enables increasing the power output of generators and motors by the same factor without increasing size; alternatively, it would enable reducing the size (and construction cost) by a factor of ten for the same power output. Such breakthroughs are needed if we are to meet the projected large increases in electricity demand in the confined spaces of our cities and suburbs.

Today's most powerful permanent magnet is $\text{Nd}_2\text{Fe}_{14}\text{B}$, with a field of 1.6 T. However, there is no fundamental reason why permanent magnets with magnetic fields at least an order of magnitude larger cannot be developed. Superconducting trapped field magnets achieve fields of 17 T, produced by a distribution of nanoscale superconducting current loops trapped at structural defects in the host material [10]. High-temperature superconducting trapped field magnets maintain their fields provided they are kept below their operating temperature, typically 30–77 K. Steady magnetic fields produced by electric currents in hybrid coils of superconducting and normal wire produce fields of 45 T, and pulsed magnets produce fields of hundreds of Tesla for a few microseconds to milliseconds. The highest pulsed field magnets are designed to explosively self-destruct as they produce fields of microsecond duration—fields of up to 1000 T have been achieved. None of these fields, however, are

close to an intrinsic limit of magnetic field. The fields in neutron stars, for example, are in the 1- to 100-MT range, a million or more times larger than the steady fields we can now produce on earth.

Generating magnetic fields. The major factor limiting extreme magnetic field production in coils is the mechanical strength of materials needed to confine the energy of the magnetic field. The energy density and the required strength grow with the square of the field, a severe limitation which needs to be considered when making even small improvements in the maximum field. The preferred conductor for state-of-the-art hybrid magnets is a copper-silver composite with a yield strength of over 800 MPa, and a conductivity 75% of the International Annealed Copper Standard (IACS), enough to contain the present maximum steady-state field of 45 T. Pulsed magnets with fields of 100 T use copper-niobium conductors with strengths higher than 1000 MPa and conductivity better than 70% IACS. In both cases, the strengthening components in these conductors are copper or niobium fibers with diameter smaller than 50 nanometers. The challenge of accessing significantly higher fields will be creating new composites, with much higher strength while maintaining adequate conductivity. For example, carbon nanotubes, one of the strongest materials known, have a tensile strength of 63 GPa or more, approximately 30 times that of the best copper-niobium composite ever made [11]. It may be possible to take advantage of other nanophase materials to meet these challenges.

For production of lower fields appropriate for use in motors, generators, and transformers, the major limiting factor is not material strength but ability to carry high currents with low resistive losses. Superconductors are one of the most promising materials for producing the higher magnetic fields needed for next-generation electric power generation, distribution, and use. Superconductors carry high current at low voltage with resistive losses a factor of 100 lower than conventional copper at the frequency of the power grid. Because superconducting losses are so low, much lower voltages can be used for efficient long-distance transmission, reducing the need for insulation with higher dielectric breakdown strength. In motors and generators, the higher current capability of superconductors translates into double or triple the power output for the same size and weight, and the low resistivity of the superconducting windings eliminates half the losses.

The challenge for superconducting materials is raising the current-carrying capability by a factor of 10 or more in the 0.5- to 10-T magnetic fields needed for generators, motors, and transformers. For high-temperature superconductors, the effect of magnetic field is drastic: a field of 1 T lowers the current-carrying ability of state-of-the-art superconducting wire by a factor of 10. Raising the current-carrying capability requires introducing nanoscale defects, called pinning sites, into the local structure of the superconductor in order to trap magnetic vortices. Each of these vortices consists of a normal core containing a magnetic field surrounded by a circulating supercurrent. The size of the vortex core is only a few nanometers in high-temperature superconductors, requiring defects of approximately the same size to trap them. The scientific challenge is to identify the defects that most strongly pin the vortices and deliberately incorporate them into the superconducting host.

The tools of nanoscience offer exciting new research directions for creating the tailored defects that will raise the current-carrying ability of superconductors by an order of magnitude. We are now learning to control the internal self-assembly of nanostructures embedded in bulk materials by harnessing techniques such as spinodal decomposition and nanophase separation. These innovative approaches draw inspiration from both traditional materials synthesis and bottom-up self-assembly. They are capable of creating extended networks of arbitrarily small islands of distinct composition or structure in an otherwise perfect host. The islands comprising the network communicate and organize themselves via the strain fields they generate in the surrounding host material. To be effective pinning sites, such islands must have controllable morphologies and network structures, objectives that are now coming within reach as we understand the principles of self-assembly. Beyond fabrication, we need to be able to observe these internal networks in the presence of the vortices they are meant to trap, to explore and increase their trapping effectiveness. This requires advanced techniques of electron microscopy such as Lorentz imaging with spherical and chromatic aberration correction, and innovative approaches to magneto-optical imaging and scanning tunneling microscopy.

New states of matter in extreme magnetic fields. The failure of materials—insulators, magnets, conductors, and superconductors—is the primary factor limiting electric power technology. The search for new materials that push the envelope of functionality in extreme electric and magnetic fields is key to creating next-generation electric technology that will substantially increase the capacity and decrease the footprint of our electric infrastructure.

One of the most fruitful areas to search for new materials with enhanced properties is at extreme magnetic fields. Extreme fields especially affect the outer-shell valence electrons that control insulating, magnetic, conducting, and superconducting behavior through their strong correlations. Magnetic fields affect these electrons by raising and lowering their spin energies, exerting torques on their orbital and spin magnetic moments, and driving metal-insulator transitions. Figure 15 shows the richness of correlated electron behavior in extreme magnetic fields in URu₂Si₂. A wealth of correlated electron-phase transitions cluster around a quantum critical point at 35 T [12]. The complexity of these new conducting and magnetic phases induced by magnetic fields rivals that of new bonding and structural phases induced by high pressure (see Panel 3, Thermomechanical Extremes). These new phases in extreme magnetic fields expose the fundamental electron correlations governing insulating, magnetic, conducting, and superconducting phenomena. Discovering and understanding correlated electron behavior at

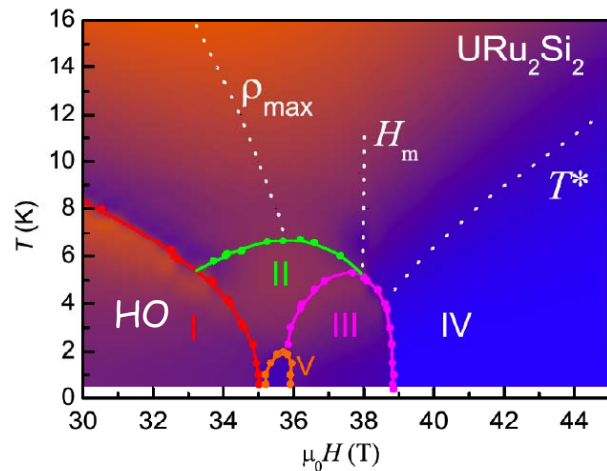


Figure 15. Magnetic phase diagram of URu₂Si₂ showing the richness of correlated electron states induced by extreme magnetic fields. The quantum critical point at 35 T is the anchor for a variety of phase transitions to local, metallic, and magnetic states. Source: Yinmin Wang, Mingwei Chen, Fenghua Zhou, and En Ma, “High tensile ductility in a nanostructured metal,” *Nature* **419**, 912 (2002).

extreme fields where fundamental interactions can be separated and studied provides the inspiration and guidance for synthesizing similar materials at zero or low magnetic fields.

Extreme magnetic fields are required to access and explore the diversity of correlated electron states in insulators, magnets, conductors, and superconductors, well above the limit of the steady fields we can now produce. Dramatically higher magnetic fields are needed if we are to discover and understand the fundamental principles governing correlated electron behavior and apply them to the synthesis of new materials with enhanced properties. To probe the correlated electron phases in the normal state of the high-temperature superconductor $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$, for example, requires magnetic fields in excess of 500 T, the estimated critical field to quench its superconductivity. In the absence of such fields, the phenomena governing the strongly correlated normal state of high-temperature superconductors remain hidden. The value of probing materials at extreme fields is indicated by the recent discovery of quantum oscillations in the resistivity of the high-temperature superconductors. This discovery promises to reveal fundamental details of their highly correlated electronic structures, the key feature contributing to their unusual normal and superconducting states [13].

A dramatic example of the electronic diversity in an element is plutonium, which forms the heavy fermion superconductor PuCoGa_5 with an unexpectedly high superconducting transition temperature of 18.5 K, ten times the value of the next highest heavy fermion transition temperature [14]. Similar behavior is expected in the compounds and alloys of other 4f and 5f elements such as cerium, praseodymium, and uranium, but many compounds of these multivalent materials remain unexplored. The controlling feature of the competing states in plutonium is its highly correlated 5f electron behavior. As in URu_2Si_2 , a wealth of revealing phases and phase transitions can be expected in high fields for plutonium and its compounds, though we are just beginning to explore them systematically. Extreme magnetic fields are key to separating the competing phases and valence states of plutonium and its compounds. The selectivity of high magnetic fields in isolating the competing phases of plutonium and uranium in these extreme environments is a powerful tool for understanding their complex behavior.

Basic Science Challenges and Opportunities

Understanding the fundamentals of the performance of materials under extreme conditions will enable the creation of new materials that can meet future power needs, replacing the empirical “cut and try” approach that has been the mainstay of materials discovery for the last century. The materials of the future, with complex and interacting crystal, electronic and magnetic structures, require a guided approach informed by a basic understanding of the principles governing their behavior. Understanding the atomic and nanoscale phenomena that underlie the performance of materials allows their design from first principles to target specific performance objectives. Dielectric breakdown, strong permanent magnets, high-strength conductors for solenoid and coil magnets, and high-current superconductors all are governed by atomic or nanoscale defects and structure that traditionally have been just out of reach of our best spatial and time resolution characterization tools. Nanoscience is allowing us to synthesize materials with tailored architectures that are designed for specific behaviors. A new generation of characterization tools enables direct observation of the tiny defects that

accumulate charge and eventually trigger dielectric breakdown, the distribution of elementary dipoles and their bonding structure in permanent magnets, the nanoscale structure of composite materials that can simultaneously deliver high strength and good conductivity, and the complex defect structures that trap vortices and raise critical currents of superconductors. These new characterization tools include scanning probe microscopies that resolve structural and charge inhomogeneities with atomic resolution, intense sources of x-rays, and neutrons at user facilities that enable diffraction and imaging of nanoscale objects and ultrafast and ultrabright coherent x-ray sources that can resolve femtosecond events in single molecules. These new characterization tools push the envelope for resolving ultrasmall and ultrafast phenomena and open broad new horizons for observing and understanding the defect structures and dynamics that govern the behavior of materials in extreme electric and magnetic fields.

The experimental challenge of observing atomic and nanoscale defect dynamics is balanced by an equally important theoretical challenge: understanding how the nanoscale behavior of defects evolves to affect the large-scale behavior of macroscopic materials. The challenge of following the evolution of defect behavior across the length scales is a central issue in materials physics, affecting areas as diverse as plastic deformation of solids, the current-carrying ability of superconductors, the polarization switching of magnets, and the dynamic susceptibility of glasses. Materials under extreme electric and magnetic fields are a prime example of this macroscopic emergence and provide not only motivation for capturing the multiscale behavior in a single framework but also fertile ground for proposing and testing innovative approaches to multiscale modeling. Advances in multiscale modeling are needed to understand the failure modes and control the performance of materials in extreme electric and magnetic fields.

Atomic-level understanding of dielectric breakdown. The challenge of raising the limits of dielectric breakdown divides naturally into three directions following the three stages of breakdown, and in all three stages an atomic-level understanding of these processes is lacking. In the first or ageing stage, in situ experiments are needed to characterize the nature of the defects that accumulate charge and to observe the accumulation process as it occurs. Instrumentation for creating high electric fields of 1000 MV/m or more is required to accelerate the normally slow defect creation and charge accumulation processes so these processes can be thoroughly characterized. The second stage of breakdown, when the charges trapped at defects are spaced closely enough to create a percolation path and ultrafast discharge across the dielectric, requires a second kind of in situ experiment capable of characterizing events that occur at the femtosecond timescale. Observing this catastrophic event is critical for understanding breakdown. The conditions that trigger the electrical discharge need to be understood, such as the spacing of charged defects and the local electric fields surrounding them, before a means of preventing them can be formulated. This key information remains well hidden with present measurement technology; the new ultrafast and ultrabright sources such as the Linac Coherent Light Source (LCLS) are needed to probe these time and length scales. The final stage of breakdown, where thermal or electrical damage from the initial discharge creates more conduction paths and more damage, also requires in situ observation. If the thermal and electrical energy from the initial discharge can

be contained by locally high heat capacity or local nanostructures that act as capacitors, the breakdown might be prevented from propagating beyond the charged defects that initiated it.

If the atomic-level processes of dielectric breakdown were understood, it may be possible to predict dielectric breakdown in materials. Conventional wisdom holds that dielectric breakdown is the inevitable result of slow defect formation and charge accumulation in the dielectric material forced by the presence of an electric field. The question is not if but when dielectric breakdown will occur. Lifetimes of 40 years are desirable, as that matches the lifetime of other components in the electrical power system. Predicting this long lifetime, however, on the basis of short tests on the order of a few months is a practical challenge with high impact on the reliability and cost of the electrical infrastructure. A fundamental understanding of the formation of defects and charge accumulation in the incubative first stage of breakdown, and the conditions that trigger the catastrophic discharge across defect sites in the second stage, would enable the development of computational models for predicting dielectric lifetimes at decades-long lifetimes with greater certainty. The prediction of the lifetime to dielectric breakdown is a major challenge for the electric power industry and would be invaluable for maintaining secure and reliable electric infrastructure.

Realizing higher magnetic fields. The highest known field for a permanent magnet (1.6 T in Nd₂Fe₁₄B discussed above) is far from any fundamental materials limits. Nevertheless, despite the passage of more than two decades since its discovery, no higher-field permanent magnet has been found. This bottleneck in permanent magnet materials reflects the shortcomings of the traditional paradigm of materials discovery by serendipity. The enormous number of complex structures and compositions of potential permanent magnet materials makes it virtually impossible to discover them in the laboratory by the traditional route of trial-and-error synthesis. To identify high-field permanent magnets and other next-generation complex materials, we must create a new paradigm for materials discovery. Density functional theory implemented on multi-hundred or multi-thousand node computer clusters is capable of describing the electronic and magnetic structure of complex crystalline, magnetic, and molecular materials that were well beyond the reach of simulation a decade ago. These techniques inspire a new paradigm for materials discovery by prediction. They can be used to numerically simulate whole classes of materials examining many compositions and structures and predicting key properties such as the magnetic phase diagrams and magnetic field strength of the magnetic phases. On the basis of these simulations, those few promising materials from among thousands of candidates can be selected for actual synthesis in the laboratory. Such predictive surveys would streamline the discovery process, eliminating an enormous number of unpromising materials before any synthesis effort is committed. For especially challenging materials such as permanent magnets, where discovery is overwhelmed by sheer numbers of candidates, materials by prediction would stimulate breakthroughs that could never occur by serendipity. This approach would qualitatively change the way we discover next-generation materials for energy and security technologies.

The highest magnetic fields are produced not by permanent magnets but by electromagnets. The maximum field that can be produced in electromagnets is limited by the very practical constraint of the strength of materials needed to confine the field. The energy in a 1-T

magnetic field can be contained by materials with very low strengths of ~ 0.4 MPa, while a 50-T field requires ~ 1 GPa, near the strength limit of known conducting materials. While today's magnets are composites of copper-niobium or copper-silver, with tensile strengths slightly larger than 1 GPa, revolutionary new materials for producing high-field magnets may be possible using materials that incorporate nanoscale materials. Nanoscience has the potential to greatly expand the base of composite materials that can be designed for next-generation magnets. For example, nanoscale integration of dissimilar materials may produce functionalities that are normally mutually exclusive, like carbon-fiber-reinforced plastics that are both tough and flexible. As discussed above, carbon nanotubes have tensile strengths that are ten times that of carbon fibers and far stronger than the conventional materials used for magnet construction. If the fundamental principles governing nanoscale self-assembly of composites can be understood, then new composites could be designed with atomic or molecular integration using, for example, layer-by-layer growth techniques or self-assembly of polymer backbones with functional side chains. Such synthesis techniques open the door to novel nanoscale composites for high-strength resistive magnet conductors where, for example, the strength is provided by one material, such as carbon nanotubes or other fibers, and the conductivity by another material, such as copper or its alloys. Even pure copper itself, properly articulated with appropriate nanostructures, might provide the required combination of strength and conductivity [15].

Superconductors offer a highly attractive approach to higher magnetic fields because they carry high current at very low or zero voltage. Conventional superconductors made of niobium alloys and compounds

remain superconducting only up to about 23 T, and their mechanical strength is too weak to confine higher fields. New generations of high-temperature, high-magnetic-field superconductors are needed to make extreme magnetic fields more widely available. The present generation of high-temperature superconductors based on $\text{YBa}_2\text{Cu}_3\text{O}_7$ may be capable of producing extreme magnetic fields, as indicated by the recent achievement of nearly 27 T, a record field for a superconducting magnet [16]. Estimates of the strength of the $\text{YBa}_2\text{Cu}_3\text{O}_7$ composites (Figure 16), created expressly to achieve a critical combination of strength and superconducting performance, suggest that 50 T may be achievable in an all-superconducting magnet. This would nearly double the currently available superconducting magnetic field and trigger an explosion of research on the behavior of

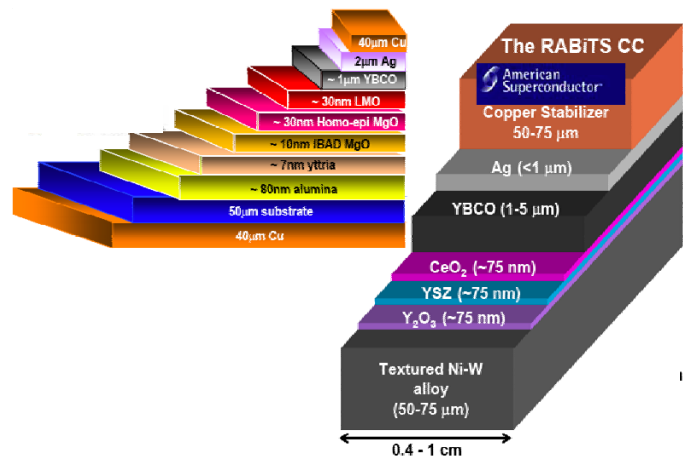


Figure 16. The architecture of coated conductors, flat wire based on the high-temperature superconductor YBCO. The development of superconducting generators, motors, and transformers with dramatically increased performance and reduced footprint requires raising the current-carrying ability of these superconductors in fields up to 10 T by an order magnitude. Source: X. M. Xiong et al., “High throughput processing of long-length IBAD MgO and epi-buffer templates at SuperPower,” *IEEE Transactions on Applied Superconductivity* **17**(2), 3375–3378 (June 2007).

materials in extreme magnetic environments. But even 50 T is small compared with the fields needed to induce new magnetic phenomena. A field of 500 T is required to quench superconductivity and expose the unconventional normal state in the present generation of high-temperature superconductors. The same field is needed to reduce the size of an electron orbit to 1-nanometer, needed to explore electron confinement effects in nanostructured conducting materials. To achieve such fields requires entirely new superconducting materials with operating temperatures a factor four higher and current-carrying ability a factor ten or more higher than existing materials now achieve. The lack of these new superconducting materials is a major gap blocking progress in understanding materials under extreme magnetic environments. Bridging this gap requires creative approaches to the discovery of new superconducting materials.

Controlling materials properties and synthesis with electric and magnetic fields. Extreme electric and magnetic fields offer a unique opportunity to control the synthesis and properties of new materials. The effect of electric and magnetic fields is well known in electrically and magnetically ordered materials, where application of a field changes the polarization state and can be used for storing information or executing digital logic. In electro-optic materials the effect of electric fields can be dramatic, switching between transparency and opacity through rotation of polarization of light. Beyond orienting electric dipole moments, electric fields can also transfer charge to the near-surface region of a material. This effect, known as electric field doping, can have dramatic effect on materials behavior, but its influence has hardly been explored.

The range of states that can be accessed by electric field doping is notably large, including antiferromagnetic insulators, paramagnetic metals, semiconductors, and superconductors (Figure 17).

Accessing these diverse states, however, requires application of extreme electric fields, at the limit of those now available. The scientific challenge for exploring the control of materials properties by electric field doping is increasing the electric fields that can be applied to the surfaces of materials by an order of magnitude. This requires raising the breakdown strength of dielectrics by a similar factor, a goal that may be pursued by the same in situ

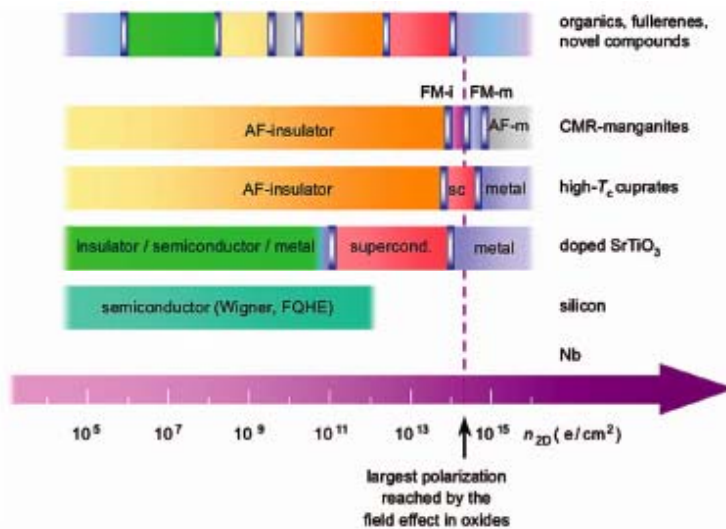


Figure 17. The range of magnetic and electronic states accessible in complex oxide materials by electric field doping. Source: R. Vasic et al., “Probing multiferrocity and spin-spin interactions via angular dependent dielectric measurements on Y-doped HoMnO₃ in high magnetic fields,” *J. Appl. Phys.* **101**, 09M102 (2007).

characterization experiments and computational modeling of dielectric breakdown phenomena needed for raising the performance and efficiency of the power system and designing high dielectric gate oxides for next-generation electronics.

Understanding the response of materials to extreme electric fields will open up the potential of using these extreme fields to control their behavior. Electric fields impart significant electrostatic energy to electrons and ions through the Coulomb interaction and orient atoms and molecules through torque on their electric dipoles. The ability to shift energy levels in materials with electric fields is the basis of electron tunneling that reveals the energy gaps and electronic structure of metals and semiconductors and gave birth to the explosion of scanning tunneling microscopies that map local electronic structure with atomic resolution. Electric fields that control energy levels and charge densities can be adapted to create smart materials by injecting or extracting electrons to drive metal-insulator transitions, adjust the band gaps of semiconductors, or induce superconductivity [17]. Electric fields find increasing utility in switching dipole moments of ferroelectrics and inducing length changes in piezoelectrics. The recent emergence of multiferroics (materials with simultaneous electric and magnetic order where magnetism can be controlled with an electric field and vice versa) will dramatically extend the reach of smart materials for sensing and controlling the operation of the electric power system [18].

Because magnetic fields affect only magnetic dipole moments and not charges, they cannot add electrons directly to materials. By the same token, magnetic fields are not screened by surface charges and thus penetrate through the bulk of materials, in contrast to electric fields that are often screened within one or a few lattice constants of the surface. Magnetic fields have their greatest effect where several closely spaced states compete for the lowest energy, as near phase transitions or in 4f and 5f electron materials with multiple valence states. The effect of magnetic field on the bulk phase diagrams of such materials is dramatic, as shown in Figure 15, displaying the many electronic phases near the quantum critical point of the 5f electron material URu₂Si₂ at 35 T. Similar effects occur in the 4f electron material cerium, where a phase transition with a dramatic volume collapse arises from competition between Ce³⁺ and Ce⁴⁺ valence states [19]. A magnetic field of 55 T drives the volume collapse to zero temperature, as shown in Figure 18, where one expects a quantum critical point and additional new correlated electron phases as in URu₂Si₂. This part of the cerium phase diagram remains unexplored, due to the lack of steady magnetic fields in the required range.

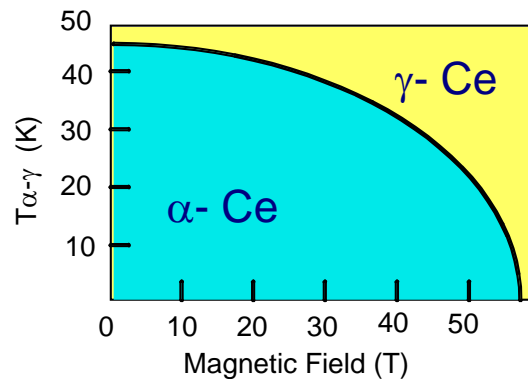


Figure 18. A dramatic 17% volume collapse occurs at the α - γ phase transition in cerium. A magnetic field of 55 T drives the transition to zero temperature, where a quantum critical point and novel correlated electron phases are likely to be found. Higher steady magnetic fields are needed to explore this behavior. Source: F. Drymiotis et al., “Suppression of the γ - α structural phase transition in Ce_{0.8}La_{0.1}Th_{0.1} by large magnetic fields,” *J. Phys.: Condens. Matter* **17**, L77 (2005).

Steel research provides another example of magnetic fields dramatically affecting phase diagrams. As shown in the sidebar entitled Extreme Magnetic and Electric Fields as a New Synthesis Paradigm, a magnetic field of 30 T considerably shifts some of the key phase boundaries in the Fe-C phase diagram by over 100°C and over 30% for the eutectoid chemistry carbon concentration. Such dramatic shifts in phase boundaries offer unprecedented opportunities to control the synthesis of materials to produce specific properties.

In all of these examples of magnetic fields controlling materials properties, the key ingredient is magnetic field strength. Steady fields at and beyond the limit of today's availability, 45 T, are critically needed to control the properties of materials. We are just scratching the surface of this emerging field. Much higher electric and magnetic fields are needed to manipulate electronic phase transitions in itinerant, heavy fermion, and local moment compounds. There is a wealth of new behavior and of new properties that can be reached only in high electric and magnetic fields.

Conclusion

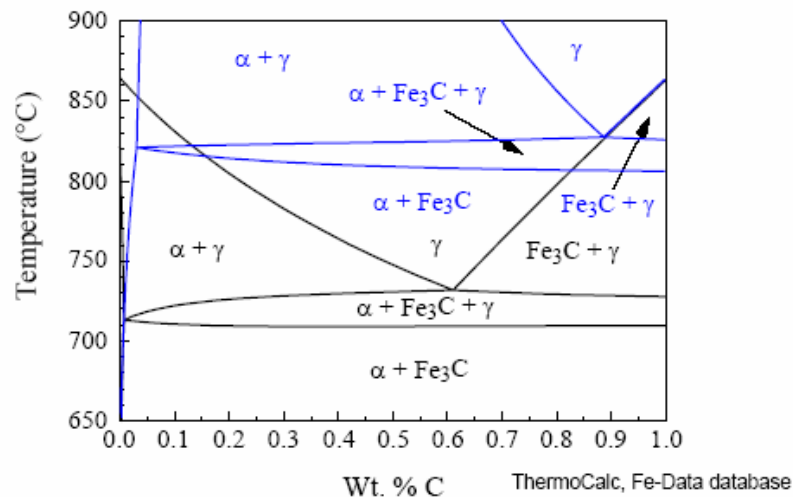
The capacity and performance gaps blocking development of electric technologies can be bridged only by fundamental breakthroughs in materials science. The subsequent breakthroughs that would result in the next generation of advanced materials that would enable a much-higher-capacity, more-energy-efficient electrical infrastructure in a much smaller package, operating with a higher standard of reliability and quality.

The performance of insulators, permanent magnets, conductors, and superconductors is limited by atomic and nanoscale structure and defects that govern dielectric breakdown, anchor the elementary dipoles in permanent magnets, and trap flux-bearing vortices in superconductors to prevent their motion and increase their current-carrying ability. The emerging characterization tools of nanoscience—scanning probe microscopies, scattering of electrons, neutrons, and x-rays from high-intensity sources at user facilities with nanoscale spatial resolution and femtosecond time resolution, allow unprecedented, quantitative observation of the structure and dynamics of the atomic and nanoscale defects that control dielectric breakdown, permanent magnet field strength, and the current-carrying ability of superconductors. Comprehensive in situ studies of the defects and structures of these materials under operating conditions are needed to observe their behavior at the moment of failure—catastrophic dielectric breakdown in insulators or massive de-pinning of vortices in superconductors. These comprehensive, dynamic, in situ studies will enable new quantitative theoretical descriptions of dielectric breakdown in insulators and of vortex depinning and critical current in superconductors that capture the multiscale features that make them so difficult to understand and to control. Such in situ observations with nanoscale space resolution and femtosecond time resolution hold the promise of transforming the empirical “cut-and-try” approach to dielectric breakdown in insulators and vortex pinning and critical current in superconductors into a strategic, science-based research enterprise.

Extreme Magnetic and Electric Fields as a New Synthesis Paradigm

Extreme electric and magnetic fields add new dimensions to conventional equilibrium phase diagrams, revealing a rich diversity of new phases and physical phenomena. Using these fields as additional parameters in materials synthesis holds exciting potential to yield new materials with tailored functionality. For example, the magnetic free energies compare well with many energies of interaction such as energies of mixing, ordering, and formation as well as energies associated with structural defects, such as stacking faults, twins, short-range order, end vacancies, diffusional barriers, and elastic constants. Novel microstructures and transformation sequences, unachievable through other means, become feasible via these revolutionary processing approaches. This combination of extreme environments affects phase stability, phase solubilities, phase solubilities, diffusion barriers, defect structures dislocation cores, magneto- and electro-plasticity, phonons, and magnons. Nucleation and growth rates, transformation kinetics, and microstructure product phases are impacted during solidification and solid-state phase transformations. Contributing factors include differences in magnetic moment between parent and product phases, magnetocrystalline anisotropy, shape magnetic anisotropy, induce magnetic anisotropy, and magnetostriction effects. Similarly, electric fields can affect phase transformation kinetics and phase stability by accelerating the dissolution of unstable phases or retarding the formation of precipitates by impacting vacancy mobilities and concentrations. These extreme environments provide a disruptive technology for making significant major scientific and technological advances in developing the next generation of novel structural and functional material for broad energy applications.

An example of the major phase equilibria shifts achieved with a high-magnetic-field environment is shown here where a 30-T magnetic field has shifted transformation temperatures on the order of 100 K and increased the solute solubility of Fe-C alloys. Similarly, a dramatic increase (on the order of 30%) for nickel solubility in both the α and γ phases has been demonstrated for an Fe-15Ni alloy. Of major significance is the fact that these metastable conditions were maintained at ambient conditions after the field was removed. These results clearly show that high field processing represents a completely new unexplored synthesis methodology for fabricating materials with designed functionality.



Prediction of the phase diagram for a steel for both the no-magnetic field conventional equilibrium (black lines) and 30-T magnetically enhanced equilibrium (blue lines) conditions. Source: "Exploring ultrahigh magnetic field processing of materials for developing customized microstructures and enhanced performance," G. M. Ludtka, R. A. Jaramillo, R. A. Kisner, G. Mackiewicz-Ludtka, and J. B. Wilgen, ORNL Tech. Memo, ORNL/TM-2005/79, March 2005 (<http://www.ornl.gov/~webworks/cppr/y2006/rpt/123141.pdf>).

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PRIORITY RESEARCH DIRECTIONS

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DESIGN OF MATERIALS WITH REVOLUTIONARY TOLERANCE TO EXTREME PHOTON AND PARTICLE FLUXES

Abstract

Materials subjected to extreme photon and particle beams fail at fluxes an order of magnitude below their intrinsic limits. Although failure occurs at the macroscopic scale, the root causes are to be found at the atomic scale and nanoscale where structural defects are created and evolve. A major, coordinated effort is needed to elucidate the mechanisms of defect creation and evolution using innovative characterization tools coupled with creative approaches to multiscale modeling that can expose the cause-and-effect relationship between nanoscale defects and macroscopic performance. Such a coordinated experimental and theoretical effort will provide a comprehensive new knowledge base for understanding materials behavior from atomic to meter length scales and femtosecond to millennia timescales. The order-of-magnitude advances in materials performance and lifetime enabled by this knowledge base will dramatically expand the horizon and effectiveness of new technologies essential to our future energy and security needs.

Background and Motivation

Extreme particle and photon fluxes are central to many energy and security applications including photovoltaic systems, solar collectors, lasers and optical systems, nuclear fission/fusion reactors, long-lived radiation waste forms, and nuclear stockpile materials. The drive for higher efficiencies enabled by higher operating temperatures and higher radiation environments pushes well beyond the limits of current materials. New materials with superior properties need to be designed and developed on an accelerated time frame if the energy and security challenges are to be met. The needed advances will be achieved only through dramatically expanded knowledge of the fundamental processes of defect creation at the atomic scale and of the subsequent migration, interaction, and assembly of these atomic defects into larger clusters that ultimately control macroscopic behavior. A primary challenge involves the enormous time and length scales over which the creation and evolution of defects must be understood, ranging from atomic dimensions to meters and from femtoseconds to even millennia in the case of nuclear waste storage. Revolutionary advances in experimental methods, characterization tools, computational power and computer-based simulation approaches are needed to characterize and describe the evolution of damage from its creation to its final form, and to predict the macroscale degradation of materials properties arising from atomic and nanoscale defect events. This comprehensive new knowledge base of damage evolution mechanisms spanning atomic to macroscopic dimensions will enable strategies to resist, control, or mitigate performance degradation and extend the lifetime of materials. These strategies include not only novel microstructures that are defect resistant but also dynamic responses that self-repair damage as it occurs.

Research Directions

The degradation of performance and failure of materials under energetic particle and photon fluxes is the major limitation for many energy and security technologies. For example, although failures of optical and structural materials appear to be qualitatively different in character and functionality at the macroscopic level, they share a common origin in atomic defect creation and evolution at the nanoscale level. The systematic investigation of the

creation, migration, interaction, and large-scale organization of these atomic defects, regardless of type, is the essence of this research direction. This overarching theme falls naturally into three tasks:

- Understanding the fundamental origins of the performance limits of materials under high-flux environments
- Understanding material response over the full range of time and length scales, from defect creation by atomic ionization or displacement in attoseconds or femtoseconds, to defect migration and assembly into large clusters over microseconds, to macroscopic degradation of performance and eventual failure over years or millennia
- Developing defect-free, defect-tolerant, or self-repairing materials for application in high-flux environments

To meet the material requirements of next-generation energy and security systems and to create materials that can survive in energetic particle and flux environments require meeting several key scientific challenges.

The *first challenge* is establishing a priori knowledge of the absolute physical limits of materials behavior in extreme energetic flux environments. In some cases, such as high-power optics, the physical structure of the material and the irradiation field are sufficiently well known to calculate the ideal limits, showing that a five- to ten-fold performance improvement is theoretically possible. However, the route to reaching these limits is not yet known. In the cases of more complex materials, such as plasma-facing components and structural materials in fusion/fission devices, the scientific key task that remains is determining the ultimate limits themselves. These performance limits are rooted in many complex fundamental materials properties and their interaction with radiation. Our current understanding of the interplay between these properties and the macroscopic performance of these materials is sparse and largely empirically based.

Once the limits of materials behavior are understood, the *second challenge* is to understand experimentally and theoretically the damage evolution mechanisms that lead to materials degradation and failure. Experimental approaches to observing these mechanisms are often thwarted by the enormous range of length scales, nanometers to meters, and timescales, attoseconds or femtoseconds to years and even millennia, that apply to defect creation and damage evolution (see sidebar in Panel 1 report, From Nanoscale Defects to Macroscopic Property Changes). The high-intensity sources of x-rays, neutrons, and electrons that are beginning to come online extend the range of time and length scales that can be probed experimentally. Innovative next-generation instrumentation to apply the scattering and imaging capability of these sources to characterize the damage and failure modes of energetic particle and photon fluxes must be developed. Key enabling characterization techniques include in situ, time-resolved transmission electron microscopy, imaging by x-rays focused to 1-nm spot sizes, analysis of diffuse scattering between the Bragg peaks of neutrons and x-rays to observe the evolution of complex defect structures, and use of phase information in the scattering from coherent x-ray sources. Development of a new generation of characterization tools making full use of the intensity, coherence, and short pulse time structure of the coming scattering sources is essential to understanding the damage and failure modes of materials subjected to energetic particle and photon fluxes.

Although emerging experimental tools promise the resolution and sensitivity needed to characterize the response of materials to energetic particle and photon beams, they are not yet coupled directly to a source of energetic beams. Characterization tools such as time-resolved electron microscopy and sources of energetic beams such as megawatt lasers or heavy-ion accelerators are each large machines requiring special installation and operational attention. Co-location will allow the kind of in situ experiments needed to observe the damage and failure modes triggered by extreme irradiation environments.

The orders of magnitude in time and length scales that characterize defect creation and damage evolution present a challenge not only to experimentation but also to modeling and simulation. The challenge of partitioning information according to the relevant time or length scale and sharing information among the scales is pervasive in materials modeling, and it is especially daunting for simulating particle and photon damage evolution. Although defects are created at the atomic scale, they migrate, interact, and self-assemble across the time and length scales to ultimately determine the macroscopic performance and failure of materials. A single heavy-ion event creates a displacement cascade of many defects in a few femtoseconds, but its subsequent dynamic evolution continues over nanoseconds and microseconds, and the clusters of defects grow to micrometer dimensions. With continued ion bombardment, the defect structures of multiple cascades interact, and the aging effects impact millimeter to meter dimensions and persist over decades and even millennia. Spanning these time and length and time scales with modeling is a critically important but technically daunting task that remains beyond our reach. The challenge is exacerbated by mixed irradiation environments that include ionizing events that strip electrons from atoms and displacive events that permanently knock atoms from their lattice sites. This is particularly important during the time and space intervals immediately surrounding the initial damage event, when the nascent damage remains linked to the initiation event. The interaction of ionization and displacive damage produces complex defect structures that can migrate and relax in a wealth of intricate and still unexplored ways. Developing effective multiscale modeling approaches that capture defect creation and damage evolution in its full complexity and spanning decades of time and length scales is a fundamental challenge for understanding the behavior of materials in energetic particle and photon fluxes.

An important factor for understanding energetic particle and photon damage to materials is multiple extreme environments. In real applications, energetic particle and photon beams occur in conjunction with other conditions that dramatically affect materials response, such as high temperature, high pressure, highly corrosive chemistry, or high electromagnetic fields. In nuclear reactors, for example, stress corrosion cracking of metal components is accelerated in the presence of neutron irradiation. Coupling sources of energetic photon and particle beams with apparatus for applying high pressure, temperature, and electromagnetic fields is essential to understanding the damage and failure modes of materials under extreme environments.

The *third challenge* is to synthesize new materials and modify existing materials to make them immune to exposure to high-flux environments. A natural approach to increase performance and extend lifetime is to employ materials that begin their operational life free

of defects or detect initiation sites. This approach is particularly relevant to materials such as SiO_2 that have simple compositions and uniform lattice structures and are used extensively in high-power optics and semiconductor devices. The presence of pre-existing or induced damage initiation sites, the nature of which are often unknown, is a primary cause of materials performing far below their intrinsic limits. These initiation sites must be identified before strategies for negating or repairing them can be developed. A second approach is to design materials with microstructures and compositions that direct and mitigate the evolution of damage due to radiation fields. The pre-existing material microstructure strongly influences the response to particle irradiation and can play a central role here. Identifying initial microstructural features that annihilate the initial defect damage or block the damage evolution path offer qualitatively new routes to prolong material lifetime and enhance performance in the presence of radiation fields. This approach will include the development of materials capable of dynamic self-healing. A simple example is exploiting a high-temperature ambient environment to anneal radiation damage. Much more advanced and effective techniques can be developed that exploit that energy of the particle or photon flux itself to repair damage. Often damage arises from local heating at an initial damage site that drives the local temperature above the melting point. Microstructures can be designed that slow the local cooling rate so that the perfect lattice structure is restored on refreezing. Challenges for this approach are preventing saturation or loss of these key microstructural features during the lifetime of the component and avoiding undesirable side effects they may produce. A third approach, and one that is as yet unexplored, is to use a second energetic beam to repair the damage of the first. For example, a low-energy particle or light beam may be employed to smooth the surface of a damaged component without removing it.

Scientific Questions and Opportunities

The research directions outlined above represent significant scientific opportunities that will have far-reaching impact on materials science. The first major impact is a synoptic multi-length-scale and multi-timescale understanding of defect physics. This will include a detailed understanding of the short-time evolution of individual cascades and damage events, as well as the cumulative effects of repeated damage events. The latter is presently poorly understood in comparison with individual cascades. A second impact is an understanding of sub-threshold particle irradiation. Long exposure to weak radiation fields, too low in energy to produce conventional displacement cascades, still produces significant damage that can ultimately lead to degraded performance and failure. The mechanisms of this sub-threshold damage remain mysterious, though fatigue is thought to play a role. A third impact of understanding defect physics over multiple time and length scales will be advanced development of multiscale simulation approaches that are of prime importance across all fields of science including physics, chemistry, biology, and engineering. Defect creation and damage evolution caused by energetic particle and photon fluxes are a leading motivation and fertile testing ground for breakthroughs in this field.

Potential Impact

The ability to design materials capable of surviving extreme photon and particle fluxes will enable a broad range of technologies such as advanced nuclear fission and fusion, photovoltaics and solar collectors, radiation-tolerant sensors and electronics, and lasers and optical systems. The performance degradation and failure of materials in energetic particle

and photon environments is a major limitation for all of these technologies. Most optical materials fail at photon fluxes that are a factor 10 below their intrinsic limits; for structural materials, the limiting performance in particle fluxes may be even higher. Understanding and achieving these limits of materials performance dramatically expand the range of applications and efficiencies that these technologies can achieve. The control of macroscopic performance by atomic and nanoscale defects is an enormously powerful “lever arm” for materials science. Experience has shown that manipulating macroscopic properties will not produce the order-of-magnitude advances in materials performance needed to enable new and innovative energy and security technologies. The secrets of higher performance and longer lifetime are hidden instead in atomic and nanoscale defect creation and damage evolution. The high-resolution in situ experimental tools and multiscale theoretical models that are now coming within reach will unlock these secrets and create broad new horizons for materials performance. The new generations of high-performance, long-lifetime materials enabled by this fundamental knowledge will drive breakthroughs in energy and security technologies for decades and will have enormous impact on a broad range of other technologies as well.

NONEQUILIBRIUM SYNTHESIS AND PROCESSING WITH ENERGETIC PARTICLE AND PHOTON BEAMS

Abstract

A new generation of energetic particle and photon sources delivers energy and momentum to materials with unprecedented control at nanometer spatial precision and femtosecond temporal duration. The highly nonequilibrium states of matter induced by these focused energetic fluxes enable entirely new synthesis strategies for creating novel materials with enhanced properties that are not accessible by conventional near-equilibrium techniques. To capitalize on this opportunity to create novel materials from nonequilibrium states of matter requires coordinated theory, simulation, characterization, and fabrication to reveal, understand, and control the fundamental processes by which particle and photon beams control the properties of materials.

Background and Motivation

New materials with significantly enhanced structural, electronic, magnetic, optoelectronic, and other properties are required to meet our future energy and security needs. Synthesis of such new materials requires adopting revolutionary approaches to materials synthesis and processing. One approach with considerable potential is harnessing extreme particle and photon fluxes to manipulate atomic and molecular structures in the bulk of materials and on their surfaces in order to produce new structures, chemistries, and topographies that are thermodynamically or kinetically inaccessible by conventional synthesis and processing routes.

Adding energetic fluxes to the mix of synthesis tools will open up unexplored regions of materials science. For example, the high average and peak powers achievable in high-repetition-rate, ultrashort light pulses can drive materials into nonlinear, highly excited states, where novel chemical and structural transformations are induced. Similarly, particle beams with a wide range of energies and focal-spot properties deliver momentum or massive electronic excitation on nanometer spatial scales. Realizing these new capabilities requires understanding how energetic particles and photons control the properties of materials on the atomic and molecular scales, learning how to manipulate this control, and predicting how the atomic- and molecular-scale changes govern the emergent macroscopic behavior of material. These challenges can be met through synergistic coupling between advanced computational methods and experiments using advanced particle and photon beams for material synthesis and modification and as diagnostic tools. Such synergy is a new and exciting possibility as the temporal and spatial spaces probed by computational and experimental methods begin to converge. Without a coordinated effort, the full potential of synthesis of novel phases and structures by energetic particle and photon fluxes will not be realized. The technological impact of synthesis from nonequilibrium states is wide ranging and includes photovoltaics, extreme radiation-hardened materials, new sensor platforms, durable thin-film coatings, polymeric light-emitting diodes, advanced organic optoelectronic devices and sensor architectures, and materials with the ability to self-repair.

Research Directions

The research directions for control and synthesis of materials with novel properties through application of energetic particle and photon beams are defined by two broad thrusts:

- understanding how energetic particle and photon beams interact with matter and learning how to control and manipulate these interactions to create targeted phases and structures and
- using energetic particles and photons to synthesize materials with unique microstructures, microchemistries, topologies, and morphologies that possess properties inaccessible by conventional near-equilibrium synthesis and processing routes.

Synthesizing new materials with enhanced properties from the nonequilibrium states induced by energetic particle and photon beams creates a host of fascinating scientific challenges. We must be able to manipulate atoms and molecules predictably with energetic particle and photon beams so that the desired material structure, chemistry, or property is achieved. This requires a fundamental

understanding of how energy is transferred between different states of matter, how the modified states evolve with time and with further irradiation, how material is ejected from and redeposited on a surface, and how these modifications ultimately control macroscopic properties. Figure 19 shows the breadth of the processes that need to be understood. We must develop probes of materials behavior at attosecond, picosecond, and microsecond timescales and, for radioactive material, for years or even millennia, and

at lengths from nanometers to meters. This is a daunting challenge that until recently was approachable only in modeling and simulation. Recent advances in analytical tools have changed the landscape such that, for the first time, we have the ability to “see” the motion of electrons within atoms, of atoms within molecules, of atom clusters or defects within solids, and of molecules on surfaces. For example, novel short-pulse lasers provide the opportunity to probe plasmas, such as those that exist in the extreme environments of nuclear fusion or those that are used to generate novel carbon nanostructures in high-temperature reactive plasmas. Time-resolved transmission electron microscopy enables direct visualization of phase transformations, melting, and solidification as they occur—the essential processes of materials synthesis and modification that until now have lain hidden beyond our observational reach. X-ray facilities are enabling time-resolved “movies” of high-pressure shock-induced phase transformations and strain evolution in highly deformed materials. The

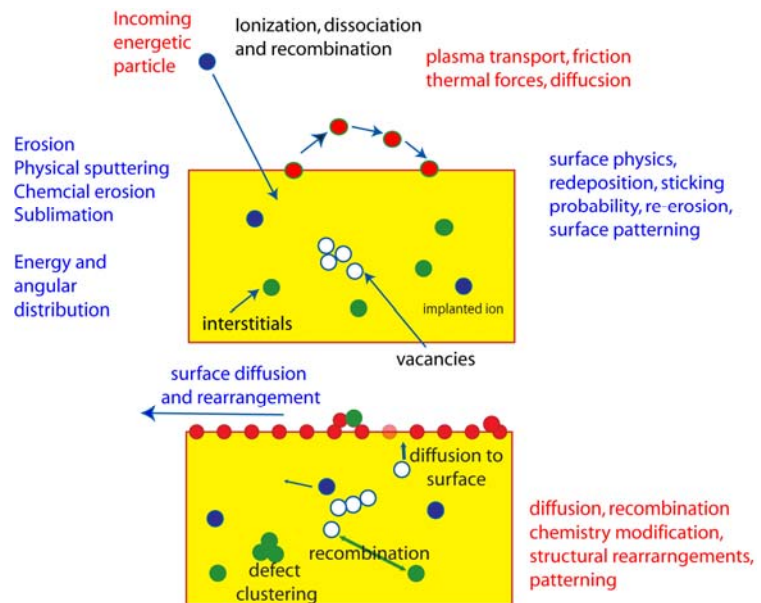


Figure 19. Important processes in particle interactions with solids.

insight gained from these experiments is revising and extending our view of materials formation as unanticipated reactions and processes are discovered.

There are major challenges in developing these experimental techniques. Collecting, analyzing, storing, and manipulating the massive data sets generated by experiments with nanoscale and femtosecond resolution go well beyond conventional practice. Significant advances are needed in conceptual models of complex multicomponent systems that can describe the behavior of these new exotic states and capture the transitions and transformations of nonequilibrium dynamics. Novel experimental facilities are needed to integrate energetic particle and photon fluxes with diagnostic tools and with other extreme environments. For example, high-temperature furnaces must be combined with energetic fluxes to explore the effect of temperature on modification processes.

An additional challenge is to advance computer modeling and simulation to interpret time-resolved experiments and to assess and guide new strategies for making new materials. In this regard a significant challenge is to develop multiple-length and multiple-timescale simulations that can model the evolution of the energetic flux-induced changes over the time and length scales needed to follow the evolution of nano- and macro-scaled structures. The challenge is formidable as the timescale can vary from attoseconds for electron dynamics, to femtoseconds for atom and molecule motion over interatomic distances, to seconds for diffusion of defects, to years and even millennia for macroscale properties. The relevant length scales span many orders of magnitude, ranging from subnanometer to centimeter or meter dimensions.

Major advances are needed to accelerate computational methods, such as molecular dynamics and kinetic Monte Carlo, to extend the time and length scales that they can accommodate. Capturing multiple time and length scales in simulations is a grand challenge across all of science, and it is nowhere more challenging or important than in nonequilibrium defect formation and evolution. Traditional hierarchical approaches that consider each length scale sequentially and innovative concurrent approaches that treat all the length scales simultaneously must be pursued. Coupling defect behavior to macroscale properties requires adding the effects of electronic stopping, thermal transport, stresses, and surface effects. These must be introduced in a realistic but computationally tractable manner. Multiscale models must be extended to the realm of property prediction of multicomponent systems that contain defects and other microstructural features. The validity of simulations at larger length scales and timescales depends on the accuracy and quality of inputs taken from shorter length scales and timescales. Therefore, experimental validation at the microscopic scale is required to predict material properties confidently at the engineering scale, where the design and simulation of a system or device are often performed and where synergistic or emergent effects may be manifest.

The final challenge is to utilize this new knowledge to manipulate and control atoms on the subnanometer distance scale and the subfemtosecond timescale by application of energetic particle and photon fluxes. The ability to drive systems into regimes that are, for thermodynamic or kinetic reasons, otherwise difficult to access affords new possibilities for creating materials with unique functionality and topography. For example, conventional

“laser peening” applies an intense laser pulse to a surface, causing surface layer ablation and subsequent material compression and hardening in the near-surface volume. Developing the potential of this technique may involve tailored pulses of photons in the terahertz frequency spectrum matched to a vibrational mode of the material. Exciting a single surface vibrational mode enhances the surface stress and creates higher hardness and has the potential to produce a material with improved wear resistance and possibly better corrosion resistance.

There are many other opportunities to exploit nonequilibrium conditions to produce new synthesis and modification routes that are beyond the reach of traditional near-equilibrium synthesis techniques. These include the use of lasers in a gas environment to produce materials such as “black silicon,” with its uniquely high photon absorption over most of the optical spectrum and its appealing properties as an optoelectronic or photovoltaic device (see Panel 1 Report, Energetic Flux Extremes). Ultrahigh-energy heavy ions can be used to remove the magnetic anisotropy due to stresses in thin films, to uniquely shape nano-sized magnetic nanoparticles, and to create nanoscale templates on which novel materials can be grown. This is an emerging area with tremendous potential to create materials that will solve key technological problems, but significant progress is hindered by current methodology that is empirically based. A paradigm shift to scientific design of targeted synthesis outcomes using nonequilibrium states induced by energetic particle and photon fluxes will open broad new horizons for novel materials for energy and security technologies.

Scientific Questions and Opportunities

The potential scientific impact of synthesis of novel materials with enhanced properties using energetic particle and photon fluxes ranges from fundamental condensed matter science to applied materials physics. An important spin-off is a more comprehensive understanding of the dynamics of the response of materials to energetic particles and photons, from initial excitation and defect creation to ultimate relaxation and thermalization in new microstructures with macroscopically different properties. The knowledge base of nonequilibrium dynamics developed for this new synthesis approach will be invaluable for understanding the degradation and failure of materials in a wide range of practical applications, from megawatt lasers to nuclear reactors. A primary scientific impact will be the rich variety of new materials that these nonequilibrium synthesis techniques using particle and photon beams will produce. An example of conventional nonequilibrium processing is rapid quenching to “freeze in” a high-temperature phase for use at a lower temperature, where it is not thermodynamically stable. Replacing the high-temperature treatment with irradiation by a sequence of tailored terahertz photon pulses would dramatically extend the range of nonequilibrium states that could be induced. The coherent terahertz pulse could selectively excite specific vibrational modes that drive off certain surface atoms, reposition atoms to promote chemical reactions to make new compounds, or impose nanostructures by selectively altering targeted nanoscale sections of the sample with focused beams. These outcomes cannot be achieved using temperature as the controlling variable as it is in conventional quench processing.

Potential Impact

The tailored nanoscale and microscale structures enabled by nonequilibrium synthesis and processing using energetic particle and photon fluxes promise exciting new in situ diagnostic

and repair capabilities for materials operating under extreme environments. For example, terahertz photon beams tailored to excite vibrational modes in solids could repair defects such as atomic displacements or dislocations, defects that are conventionally treated by generic heat treatments that affect all microstructures and often have undesirable side effects. With terahertz frequencies, repairs can be made as quickly as defects are created, preventing the agglomeration of defects into larger structures that require more energy to modify. Particle beams can repair defects as well, by delivering energy to reconfigure point defect clusters and second-phase precipitates that cause radiation hardening in reactor environments. These defects and the radiation hardening they cause will be a major source of materials degradation and failure in the extreme environment of next-generation nuclear reactors.

Extreme fluxes of particles and photons offer extraordinary opportunities for the rational design of materials with the unique topologies and morphologies and the novel properties required by many energy technologies, for example,

- highly absorbent and robust surfaces for photovoltaics,
- uniform-sized nanoparticles for catalysts required for fuel cells and other chemical energy conversion processes,
- precise templates for assembling nanocomposite structures,
- highly corrosion-resistant surfaces in boiler, membranes, and combustion chambers, and
- wear-resistant moving parts.

Nonequilibrium synthesis and processing with particle and photon beams have the potential to impart all of these properties. Such tailored surfaces and nanostructured properties will have an enormous impact on materials for future energy technologies and for many other application of importance to the security and economy of this nation.

TOWARD IDEAL SURFACE STABILITY

Abstract

Energy systems envisioned for the future will require novel materials able to withstand chemical extremes such as strong acids, molten salts, highly reactive gases, and supercritical fluids. To meet this challenge, materials that are virtually inert in these environments must be developed. This goal can only be achieved by obtaining an atomic- and molecular-level understanding of the physical and chemical processes that occur at material interfaces and the related subsurface processes. This fundamental knowledge will lead to the creation of materials with surfaces that have remarkable chemical and physical stability. Protecting materials from extremes of chemical reactivity will dramatically enhance the efficiency and robustness of future energy technologies.

Background and Motivation

Protection of component surfaces against chemical environments that degrade or erode the material is crucial in many energy generation, storage, and transfer technologies. Examples include heat transfer surfaces in aggressive fluids (e.g., pressurized water, ultrasupercritical steam, sulfur-bearing gases), membranes and materials in the sulfur-iodine cycle for high-temperature hydrogen production, and turbine blades and vanes under advanced combustion conditions. The ideal protection is provided by a surface layer that bonds strongly to the component material substrate yet is itself inert to the chemical reactions of corrosive gaseous or liquid environments. The challenge of realizing such a protective surface obviously scales with the severity of the environment. Its protectiveness depends fundamentally on atomic-scale defects, impurities, chemical reactions, and internal stresses that occur at the exposed surface, within the surface layer, and at the buried interface of the layer with the substrate. These processes involve not only fundamental physical behavior, such as equilibrium and nonequilibrium thermodynamics and reaction kinetics, but they are often coupled in ways and to extents that are currently poorly understood. Probing these atomic-scale defects, chemical reactions, and stresses with insightful experiments, theories, and simulations offers exciting opportunities for creating next-generation materials that will display extraordinary resistance in aggressive environments via idealized surface protective layers.

The development of imperfections within the substrate significantly limits the protectiveness of surface films under extreme conditions. Such imperfections cause the film to break down either in the environment in which it was created or during subsequent changes in temperature or pressure as a result of local chemical reactions or internal stress. If the causes of breakdown can be prevented, the rates of attack on the underlying substrate will decrease with time, leaving a stable surface that protects the substrate.

The thicknesses required for fully protective films vary from nanometers to micrometers depending on the temperature and the substrate composition. The phenomena that control the growth of the films depend on processes taking place at the buried film-metal and exposed film-environment interfaces. These interfaces have a dominant effect on the defect structure of the film, which in turn influences the rate of film growth and the stresses developed during that growth.

The ultimate goal of this priority research direction (PRD) is to achieve a fundamental understanding of atomic-level processes at exposed fluid-solid and buried solid-solid interfaces that will lead to the control of these processes to achieve ideal surface stability. This goal will be accomplished only through obtaining a fundamental mechanistic understanding of reaction kinetics under often severe chemical and electrochemical gradients and the interplay of stress-mediated changes and defects in these systems. Emerging techniques for in situ interrogation of interfaces at atomic-length and moderate timescales and recent advances in computational modeling offer compelling new opportunities for elucidating the roles of interface and defect structures and of materials chemistry in the degradation and protection of material surfaces exposed to extreme chemical environments.

Research Directions

The instability of a surface in an extreme chemical environment represents a phase-boundary reaction that spans significantly large temporal- and spatial-scale ranges. These phase boundaries can be between a solid and a liquid (e.g., water) or a solid and a gas (e.g., oxygen). Regardless of the type of phase boundary, the form and reaction rate of a resulting phase-boundary product are critically dependent on intrinsic and extrinsic variables, including temperature, total pressure, nature and abundance of reacting species, structural and chemical factors, and interfacial phenomena. This PRD addresses the development of a broad understanding of phase-boundary reaction processes to achieve stable, nonreacting surfaces (surface products) in extreme environments, meaning the reaction products are thermodynamically stable, the rate of reaction-product formation is sufficiently low to be well within a given design specification, and no other product transformations or side reactions take place.

Achieving this goal of surface stability in extreme chemical environments will require heretofore unrealized levels of effective material design and reaction control. Such capabilities can only be obtained through the close coupling of experimental and computational approaches to achieve predictive capabilities for interfacial phenomena at the environment-product and product-substrate boundaries. Because the processes requiring control are truly dynamic and interrelated, the experimental efforts will require the advancement of high-resolution techniques to allow in situ interrogation of reaction-product interfaces for fully elucidating structural, chemical, and defect developments. Concurrently, advanced computational approaches will be needed to determine the energetics and dynamics controlling interfacial processes. For example, little is known about the effects of stress on product layer growth/composition. However, the ability to perform in situ analyses with advanced light and neutron sources and other advanced characterization tools holds considerable promise for substantial progress in this research area.

More generally, there is a lack of understanding of how structure and processes at the nanoscale manifest themselves in terms of ultimate surface stability in reactive environments. This knowledge gap can be closed with the emerging capabilities of structural and chemical imaging with near atomic resolution. These capabilities are especially exciting when extended to probe in situ dynamics and the buried interfaces that often control the establishment and stability of protective surface layers.

Causes for the breakdown of protective surface layers may be related to heterogeneities present at the initial (i.e., unreacted) substrate surface; the film growth mechanism; and the formation of defects, often voids, within the film or at the film/substrate interface. Impurities present throughout the system may also play an important role at various stages of film growth. Under sufficiently high temperatures, internal stresses can be relaxed by material deformation, producing different types of defects in the microstructure of the surface film and/or the film-substrate interface that evolve as a result of this relaxation. Stress-induced microstructural changes can in turn affect processes such as transport rates through the film, further stress relaxation, and/or the nucleation of new phases or layers, all of which may further induce stresses, perhaps in different ways. It is important to understand how these processes are coupled, particularly when the extreme environments result in conditions far from equilibrium, and, subsequently, how to model these processes so vastly improved surface layers can be designed.

Part of the challenge in gaining mechanistic knowledge regarding surface stability in reactive extremes lies in the competing needs to (1) measure multiple parameters dynamically at multiple sites, including variation of composition, transport rates, and stresses within and across a growing film as a function of its thickness; (2) characterize the role of nanoscale defects throughout the film-substrate system; and (3) correlate the defects with breakdown locations and mechanisms to determine the causes of loss of chemical and mechanical stability. Complementary theoretical developments and modeling are required to allow predictive capabilities for long-term stability and material discovery.

Scientific Questions and Opportunities

Initial stages leading to stable surface film formation. Fundamental understanding of surface layer and substrate stability and dynamics is needed, particularly with respect to the critically important (and underexplored) initial stages of oxidation and the effects of extreme environments. Specifically, basic information is needed about the following.

- To what extent can surface and associated subsurface reactions be predicted and ultimately controlled?
- How do surface segregation and surface structure affect the room-temperature native oxide layer on an alloy surface, and how does this layer affect further product nucleation and growth at high temperatures?
- To what extent will understanding atomic-scale properties/phenomena, such as nearest-neighbor interactions, site selectivity, and structure and orientation of the alloy substrate, contribute to controlling the structure of the surface layer and its subsequent evolution?
- Can steady-state growth kinetics be influenced in a controllable manner by the product formed in the very early stages of oxidation?
- How do multiple oxidants, simultaneously present, impact protective surface nucleation and growth?

Addressing these questions will significantly contribute to the understanding and eventual control of steady-state surface layer development and lead to an array of advanced protective films for a variety of extreme chemical environments. Answers will require state-

of-the-art, time-resolved characterizations of reaction kinetics and surface compositions and structures in the reactive environments.

Causes of breakdown of surface films. An ideal protective surface must have mechanical, physical, and chemical stability. Unfortunately, little is understood about the relationships between physical and chemical characteristics of protective surface films (particularly at the atomic level) with respect to breakdown processes. In the case of liquid-solid interactions, thin oxide films grown under high field conditions (resulting from the fundamental electrochemical instability of a metal in an aqueous environment) are generally very stable and breakdown is inferred to be the result of heterogeneities present at the metallic surface. For protective layers formed and operating at high temperatures, breakdown can be from loss of a critical surface concentration needed to maintain a film of correct composition and stoichiometry (by depletion from the substrate) and/or from cracking/spallation of the product due to stress that occurs during thermal cycling (typically cooling) from the difference in the coefficients of thermal expansion between the surface layer and substrate (often on the order of a few GPa for oxides on metals). Other proposed causes of breakdown for low- and high-temperature films relate to growth mechanisms of the surface product and formation of pores at the film-substrate interface. However, as mentioned previously, the basic relationship between film breakdown under extremes of electrical potential, chemical gradients, or stress and the (often coupled) atomic-level processes controlling it are not known in most cases. This critical information can only be gained by delineating the roles of nanoscale defects, stress, and subsurface chemical depletion in determining the causes of breakdown. Emerging capabilities in analytical tools, such as structural and chemical imaging and electrochemical and mechanical characterization, can provide insight into these important processes. For example, for pitting in extreme aqueous solutions, rapid methods of interrogating the metal surface are required to determine the presence of heterogeneities at a size level on the order of 100 nm and the low frequency of pit formation, on the order of 1 Hz cm⁻². If the critical sites for breakdown are much below 100 nm, probes with high spatial resolution and the ability to scan a large surface area within the short time frame will be required.

Reactions at the boundary between a product and a liquid. Comprehensive understanding of the film-formation boundary (i.e., the liquid/metal interface) is a critical area for fundamental research as it determines the extent of continued dissolution of the metal in the concentrated solution of dissolution product. Surprisingly little is known about the reaction pathways for metal dissolution or the influence of water activity at the liquid/metal interface. For example, different pathways may be taken to form either the dissolved solvated products or the protective oxide layer may reside with lower valence metal species [e.g., Fe(I) as the metal loses electrons to form the oxide Fe(III)₂O₃ or dissolved Fe(II)]. The amount of free water (water molecules not involved in the hydration of the ions in the concentrated solution of dissolved metal) available in the concentrated solution may be critical but is currently understood. Resolving these uncertainties and critically differentiating between these paths would be a major breakthrough in our understanding and provide an unprecedented level of sophistication in controlling material reactivity.

Another possible limiting condition for films formed at the interface with liquids is the solubility of the film itself. Interestingly, the solubility of such films is generally far lower than that of bulk materials of similar composition. Further, distinct differences in the structures of the films and their bulk counterparts exist. Advances in modeling may provide greatly needed breakthroughs required to predict the types of phases that may form, taking into account the energy differences present at the surface and the different structure of water at the interface. This critical information would yield valuable insights into achieving surface stability.

The reactions and stability of a material in the extreme environment of a hydrothermal solution at temperatures above 300°C are not well understood. At high temperatures, the dielectric constant of water is significantly lower than at room temperature, which markedly reduces the solvation behavior of dissolved ions. The kinetics of reactions nevertheless continues to increase and, thus, appropriately stable materials for use in supercritical water are a major problem. As noted previously, an atomic-level understanding of the competitive nature of oxide-layer formation under extreme conditions, the solubility of oxide layers, the solvated structure of ions in solution, and the mechanics of the electrochemistry taking place under supercritical conditions is needed to achieve ultimate surface stability. Because of the supercritical nature of the environment, acquiring this knowledge will be even more challenging with respect to advanced in situ characterization. It will also require development of high-temperature electrochemical techniques suitable for probing electrochemical kinetics and corrosion processes over a wide range of temperatures and pressures.

Reactions at buried interfaces. Reactions at the boundary between a protective surface layer and the solid from which it derived are key to establishing and maintaining stability in extreme reactive environments, particularly those involving high-temperature gases. At present, only high-resolution scanning transmission electron microscopy (STEM) can provide the needed information on the structure and chemistry of buried interfaces at an atomic level. This technique can be useful for studying surface reactions, such as the initial stage of reaction-product nucleation and growth, with limited introduction of relevant environmental conditions. However, STEM cannot be used in situ for buried interfaces, and it is limited to such an extremely small sampling size that the broader behavior of the reacting system may not be accurately captured. Furthermore, the nature of the analysis normally limits examination to strong interfaces that are usually free of extended defects. At present, only a few facilities are available to investigate the roughness or even chemistry of buried interfaces; however, all of them require a relatively thin surface film, in the tens of nanometer range, and the film surface, as well as the interface, must be smooth within about the same range. A significant yet achievable challenge is to use modern synchrotron or neutron radiation sources in ways that enable in situ investigations of buried interfaces. The goal is to have the capability to study an interface for its chemistry, structure, and/or stress developments while it is growing in a dynamic environment. High spatial resolution is desired because local variations are known to occur in many reacting systems. The timescale for initial stage developments is in the subsecond range but on the order of minutes for the approach to steady-state conditions. Similar studies will be needed to provide information on the dynamics of constituent segregation and stress development and their relations to microstructure evolution, the initiation and growth of different types of defects, and the effect

of chemical and structure changes on material transport or film growth rates. While such techniques have not been explored in any detail for these types of studies, examples include x-ray reflectivity for interrogating the buried interfaces and small-angle scattering for monitoring porosity formation. A combination of techniques that would allow monitoring of interfacial and film characteristics simultaneously is highly desirable. Such direct knowledge of the relationships between interface processes and the nature of the surface layer would yield critical mechanistic information heretofore unavailable. This research can also be expected to yield knowledge of many other phenomena not yet known, and this information will undoubtedly provide new insights for the next generation of scientists working to develop new materials with low surface reactivity or surfaces that are nearly nonreactive.

Effects of reactant speciation and multiple reactants on product stability. Increasing extreme and diverse environments are being envisioned for future energy generation and utilization processes, and different types of reactants may be present and cause surface degradation. For example, oxidation of an alloy can occur under atomic oxygen, air, oxygen, water vapor, or CO/CO₂ mixtures, but reaction-product stabilities and associated growth rates can vary significantly under different types of oxidants for reasons that are seldom clear. In some cases, subsurface carburization of an alloy may occur in oxidizing, carbon-containing atmospheres (e.g., CO₂), and the presence of water vapor may confer poorer film adherence, but these observed effects do not appear in every system. Further, oxides formed in an environment containing sulfur can present differences in permeation resistance to mobile species. The fundamental reasons an effect is observed under one condition but not another or why speciation affects film formation are presently unknown. Addressing these issues is critical to understanding and ultimately predicting surface reactions and stable reaction paths and products in more extreme environments. Advances in real-time, high-resolution chemical imaging would provide the type of information needed to unravel the relationships between speciation and surface stability in complex, extreme environments.

Potential Impact

Fundamental research focused on understanding the underlying atomic-scale processes at fluid-solid and solid-solid interfaces could form the basis for a heretofore unrealized approach to the design of materials that exhibit remarkable stability in highly reactive environments. This research would supersede current scientific knowledge and efforts that are severely limited by simplified treatments of reaction kinetics under chemical and electrochemical gradients. This research would also reveal the interplay of stress-mediated changes and defects in these systems, because of previously intractable analytical and experimental problems. Advances in this area would allow for more rigorous prediction capabilities. In particular, the anticipated advances in modeling, simulation, and experimental techniques should yield new ways to tackle multiple reactants and multiphase stability problems. In this regard, development of the theoretical and experimental tools needed to achieve this level of understanding will, in and of itself, have scientific impacts in many areas related to environmental reactions and the dynamics at free surfaces and buried interfaces.

Stability and compatibility of materials in high-temperature gaseous and aqueous environments currently limits performance in many systems of importance to the

development of next-generation energy systems. Examples include metallic interconnect materials in solid oxide and proton exchange membrane fuel cells, vessels in gas reformers and thermochemical systems for hydrogen production, fusion blankets, nuclear waste containers, and fossil fuel plants. The rates of improvements in materials compatibility in both aqueous and gaseous environments (particularly under aggressive conditions) have been slow, with incremental advances often relying on extrapolation of current experience and knowledge to more extreme environments and extended time scales. However, a confluence of new and novel computational and experimental tools is emerging, and fundamental advances toward materials with greatly reduced reactivity and enhanced predictability can be envisioned. Progress toward this goal of materials with ideal, nonreactive surfaces will have a substantial positive impact on a wide range of Department of Energy missions, especially future energy and security technologies.

FUNDAMENTAL REACTION DYNAMICS AT EXTREMES

Abstract

Chemical reactions at extreme conditions are both a challenge to be overcome and an opportunity for the future. The investigation of the rich science underlying interactions within solids and at solid-solid and solid-fluid interfaces under extremes set by temperature, pressure, electrical/magnetic fields, and/or chemical potentials challenges our core understanding of reaction energetics and dynamics, as well as our ability to probe and model such. Yet, these challenges also present an extraordinary opportunity in that basic knowledge of materials behaviors under extreme reactivity conditions also provides the means to create new transformational structures and compositions that yield remarkable functionalities such as ultrahigh strength, hardness, chemical inertness, conductivity, and energy storage capacity. Advances in high spatial and time-resolved analytical techniques combined with new computational methodologies, including theory, modeling, and simulation, offer unprecedented potential to acquire knowledge of multiphase chemistry at extremes.

Background and Motivation

Chemical reactions at extreme conditions of chemical potential, temperature, stress, or electromagnetic field lead to completely new behaviors that are not understood and severely limit the lifetime of materials. These lifetime limits often prevent the use of higher temperatures/pressures or complex reactive environments that enable more efficient energy production and use. At the same time, chemical processes that occur at extremes can be fundamentally different from those at ambient conditions. These differences can potentially be exploited to create a new generation of materials with improved corrosion resistance, hardness, strength, or other properties.

Materials science today critically lacks fundamental understanding of the mechanisms and driving forces governing the control of reactions occurring with materials, particularly in high-concentration, complex, multireactant, and multicomponent systems. Achieving such an understanding would provide essential guidance for controlling the structural assemblage of atoms or molecules and for developing promising synthetic routes for designing new materials for meeting future energy needs. Many commercial and advanced developmental materials are in fact thermodynamically unstable, which means that different structures having the same composition can result by changing the synthesis or processing conditions or by destabilizing the material due to changes in internal state (e.g., composition, residual strain) or external stimulus (e.g., temperature, magnetic field, environmental conditions). “Structure” in the present context includes pattern formation and morphological and surface stabilities and can involve different length scales, spatial arrangements, and system dimensionality. The multiple possible routes in structural evolution or selection processes are herein generically referred to as *reaction pathways*, which is a major theme of this research direction. Central to this PRD is the need to significantly improve our understanding and the predictability of material reactivity at increasing levels of complexity that stem from strong coupling to imposed external conditions. This PRD is thus concerned with advancing our knowledge of fundamental reaction dynamics and pathways associated with the full range of extreme conditions important to next-generation energy science and technology.

Elucidating the physics and chemistry associated with reaction pathways under extreme conditions is a complex problem that underpins many areas of materials science. Conventional rules for chemical reactions near ambient conditions cannot be directly applied to extreme pressures, fields, and temperatures because of the new complexities of chemical bonding and strong coupling among environmental variables that come into play. While a number of simple, “classical” systems have been studied and the pathways, energy landscapes, and thermodynamic driving forces for phase stability and phase changes have been fairly well determined, in real applications materials encounter systems of much greater complexity with more subtle competing interactions. At the same time, there are new and enhanced experimental tools than can be applied to understanding the challenging issues encountered in these highly complex and sophisticated systems. Although tremendous progress has been made in computational materials science, analysis of extensive data from complex material systems and interactions over large length and time scales remains a huge challenge. The range of systems and phenomena is immense. The underlying science may be familiar, but it can be hidden by phenomena emerging from complexity.

To elucidate fundamental principles of reaction dynamics within the conceptual framework of chemical evolution in nonequibrated systems, a comprehensive, multidisciplinary research effort is envisioned. This effort will lay the foundation for significant advances in materials science that will contribute to a broad range of DOE missions related to U.S. energy security via improved materials performance through innovative materials design, synthesis, and processing.

Research Directions

The overarching goals of this PRD are related to obtaining a detailed understanding of the atomic and molecular mechanisms responsible for the reactivity and synthesis of materials under the full range of extreme conditions and the ability to predict the structure of formed phases. These goals are highly relevant to all areas of materials crucial to the development of future energy technology needs, including ceramic, polymer, and metal and alloy materials science.

One of the desired outcomes of this PRD is the establishment of guiding principles for new paradigms for both extreme chemical reactivity as well as chemical reaction dynamics in extreme environments. Time-resolved experiments with atomic-scale surface resolution that challenge current capabilities will be required to probe stable and transition states. An integrated basic research effort is needed to understand how to create multiphase, multiscale models founded on first principles. Thus, theory and experiment need to be coordinated closely to attain the in-depth knowledge required. More specifically, experiments that integrate imposed extreme environments with advanced probes (x-rays, neutrons, electrons, protons, new pump-probe techniques, advanced imaging techniques) and theory/modeling are needed to capture the complexity of dynamical processes of chemical reactions under extreme conditions. In situ studies to identify reaction intermediates under well-characterized conditions combined with accurate theory are required to understand the complex and interrelated chemical and physical phenomena and to optimize experimental conditions.

Approaches that closely couple simulations and experiments are also required because many experimental regimes have not been fully explored (e.g., chemical reactivity in very high electrical fields), simulation results need careful validation. The use of established simulation methods such as traditional molecular dynamics (e.g., using interatomic interaction potentials appropriate to ambient conditions) needs to be carefully examined for applications to these complex systems. In addition, experimental results on complex phenomena under extreme conditions can be difficult to interpret, and simulations are needed to elucidate the chemical mechanisms underlying experimental results.

Progress in modeling can be made through the development of algorithms to treat interatomic interactions accurately coupled over multiple length and time scales. The technical challenge is to couple multiple modeling paradigms such as molecular dynamics, kinetic Monte Carlo, and hydrodynamic flow in altogether new computational approaches.

In the area of computational theory, new density functional studies are needed to examine complex heterogeneous systems and reveal energetically favorable structures. Embedding techniques and hybrid methods can capture dynamics and allow the study of extended systems. Finally, statistical mechanical methods can calculate the free energies of phases and cluster variation method calculations predict phase equilibria in multicomponent materials.

Future challenges include resolving inhomogeneous phase reactions at progressively finer spatial and temporal resolution. An ultimate goal is femtosecond imaging of chemical reactions on material interfaces with atomic-scale spatial resolution. This effort can be complemented with three-dimensional tomographic studies of chemically reacting solids at extreme pressure, temperature, or applied fields.

Scientific Questions and Opportunities

As described above, the key to mitigating chemical damage to materials or creating new materials is to develop a fundamental atomic- and molecular-scale understanding of reaction dynamics affecting materials under extreme conditions. Accordingly, this PRD addresses critical scientific questions such as the following.

- What is the interplay of long-range (nonlocal) and short-range (local) interactions in governing the energy landscape and associated dynamics in systems exhibiting multiple reaction pathways?
- To what extent does the energy contribution arising from local fields influence phase equilibria, microstructural stability, morphological dynamics, and atomic transport kinetics?
- To what extent can surface, subsurface, and/or bulk reaction pathways and the associated dynamics be predicted and ultimately controlled under extreme conditions?
- How can understanding atomic-scale properties/phenomena such as atom-atom and atom-defect binding energies, nearest-neighbor interactions, site selectivity, and changes in crystal structure enable control of structure selection and evolution?
- Can nontraditional approaches be developed to determine reaction pathways in extreme conditions to accurately describe the kinetics of phase selection, stable or metastable, and the corresponding advancement of new reaction laws and principles?

Our knowledge of chemical reactions at ambient conditions, particularly in gases, has advanced tremendously over the last decade through the advent of femtosecond time-resolved optical spectroscopy and ultrafast electron diffraction. Advances in analytical capabilities, neutron and synchrotron scattering, and ultrafast laser techniques can enable time-resolved studies of metastable phases and reactions in situ and provide fundamental probes of chemical dynamics and phase formation during reaction processes. Many of these capabilities have not yet been adapted to the reactions of solid materials in extreme environments. Furthermore, advances in terascale and upcoming petascale computing have opened the doors to more fundamental computational treatments of reactivity in complex environments. Thus, a coupling computational and experimental studies of fundamental reaction dynamics under extreme conditions has enormous potential for providing key knowledge required for the discovery of new materials. Traditionally, aggressive chemical environments have been distinctly viewed as either high temperature or high pressure and have been addressed by separate communities. It is now clear that bringing together skills of different scientific disciplines is required to address these problems, recognizing that the extreme environment involves several variables—stress, temperature, and chemical potentials—that can strongly perturb the reaction pathways. These perturbations, however, can be used as variables to produce new materials. The application of these variables to design new materials with extreme resistance to chemical environments represents a huge opportunity in materials research.

Potential Impact

The discovery of new forms of chemical behavior anticipated by this PRD would be profound, as witnessed by recent observations that have given a glimpse of a new world of chemical phenomena under extreme environments. The impact will include advancing our understanding of fundamental reactions such as hydriding, corrosion, and hydrolysis over a broad range of conditions. Overall, understanding reactions at solid-solid and solid-fluid interfaces will lead to breakthroughs throughout materials chemistry.

Future energy production systems will necessarily involve highly reactive, extreme conditions. Success in this proposed research will lead to understanding more complex reaction processes under extreme reactants and development of methods to mitigate real problems associated with processes such as hydrolysis or corrosive degradation in aggressive environments. It will also lead to the discovery of new classes of chemically resistant materials. These materials will offer breakthroughs in energy production and use. Examples include the use of more extreme temperatures in highly efficient steam plants, future generations of industrial and utility turbines, fuel cells, and thermochemical production of hydrogen. Furthermore, understanding the mechanisms of reactions under extreme conditions will lead to new, energetic, high-strength, and chemically resistant materials.

NOVEL MATERIALS BY DESIGN—WHAT IS POSSIBLE BEYOND WHAT WE KNOW

Abstract

Discoveries of novel forms of matter by manipulating electrons under extreme pressures, temperatures, strain, and strain rate are leading to new classes materials having unique properties both under extreme conditions and after recovery at ambient conditions. Many results and products of these explorations can be beneficially exploited to advance materials science in revolutionary ways. The overarching goals of this effort are to establish the guiding principles and rules to understand, predict, and create structures over multiple length scales from the atomic to macroscopic; extend our understanding of chemistry beyond the familiar to new extremes; establish and then retain at ambient conditions equilibrium and non-equilibrium states in materials transforming under extreme conditions; synthesize new crystalline materials that can withstand large stresses, variable temperature, and strain rates; and extend our abilities to pressurize and characterize materials over a wider range of thermomechanical extreme conditions.

Background and Motivation

Recent studies of materials under thermomechanical extremes reveal remarkable and unexpected behavior not anticipated just a few years ago. Familiar materials adopt unexpectedly complex structures under pressure that are not envisioned by extrapolating conventional theory or textbook models. We are taught that the “inert” gas xenon and the alkali halide cesium iodide are very different; one is a rare gas solid, and the other is an ionic salt with distinct crystal structures. However, under pressure both become metals with the same density and structure, and cesium iodide becomes a superconductor. Although low-pressure experience would suggest that xenon does not alloy with cesium iodide, the possible existence of such metallic alloys at extreme conditions exhibiting emergent behavior remains an open, unexplored question.

Some unexpected structures of these materials are ordered but have very large unit cells; other structures span a gamut of partially ordered/modulated self-clathrates to extraordinarily complex structures *in a single element* (Figure 20). The underlying principles that give rise to this “exotic” structure are unknown. Moreover, this complex structure is not an oddity; similar structures have been discovered in more than 20 elements.

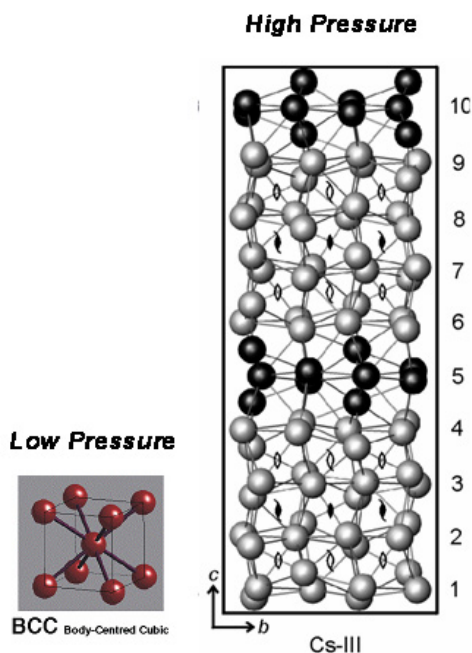


Figure 20. Effect of pressure on structures of simple metals. The crystal structure of a high-pressure form of cesium III, which consists of a framework of atoms surrounding by one-dimensional channels occupied by chains of “guest” atoms. The periodicities of the host and guest sublattices along the chain direction are different and incommensurate with each other. Source: M. I. McMahon and R. J. Nelmes, “High-pressure structures and phase transformations in elemental metals,” *Chem. Soc. Rev.* **10**, 943–963 (2006).

As described in the Panel 3 report, other new types of unusual crystalline materials can be accessed with thermomechanical extremes, such as polymeric forms of matter made from molecules as simple as CO and N₂. Compression also changes the spacing of electronic energy levels. Thus, at high pressures the alkali metals can take on characteristics of transition metals to form unusual alloys [1]. Further, compression is often associated with unexpected properties, such as superconductivity that persists to relatively high temperatures in compounds [2, 3], ferroelectrics with colossal dielectric properties [4], and new super-hard materials [5]. Under more extreme conditions (>300 GPa), exotic new forms of matter emerge that may reveal entirely new physics, such as the above-room-temperature superconducting hydrogen that may also be a super fluid (Figure 21). We need to develop the fundamental principles that will allow the structures of elements and compounds to be manipulated to form new, practical materials under extreme pressures.

The general principles that describe these transformations and permit extrapolation to design new, even better materials currently are unknown. They go beyond extensions of models developed from more familiar conditions. New classes of experiments, theory, and simulation are needed not only to describe this novel behavior but, more importantly, to provide a framework making useful and accurate predictions. By studying materials with such unexpected properties under extreme conditions, we can learn how to predict where electrons and nuclei will go and how they can be manipulated to design new, useful, novel, and improved materials that cannot be predicted by the current “conventional” approaches.

This PRD is focused on developing an underlying basis for the design and synthesis of new materials with enhanced performance under extreme pressures and temperatures and the development of a new paradigm for creation of new classes of useful materials in the coming decades. With the new rules to be developed, we will be able to use high P-T conditions to make materials for producing, storing, and transporting energy and super hard structural materials for cutting technologies, steam turbines, jet engines, and other industrial applications; for optical and electronic applications that include novel photoconductors, superconductors, colossal magneto-resistance materials; and for improved understanding of nuclear materials and fuels. The research will also develop new technologies for making materials that can withstand large stresses, variable temperature, and strain rates (e.g., large-volume, multifunctional pressure devices). Key to achieving these goals is extending our abilities to characterize crystalline materials by static and dynamic (e.g., neutron, electron, x-ray, lasers) diagnostics and to analyze these phenomena by simultaneously probing with smaller, faster, variable-energy, higher-resolution analyzers.

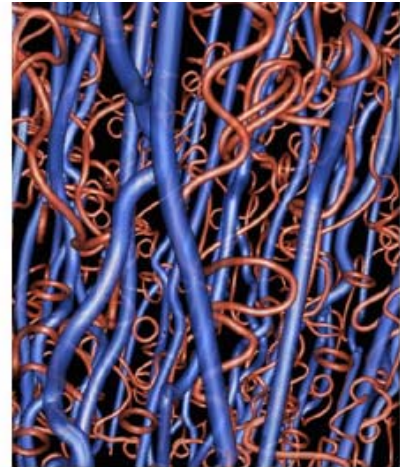


Figure 21. Snapshot of the magnetic state in the interior of predicted metallic superfluid hydrogen. The electronic (blue) and protonic (red) vortices. Source: E. Smørgrav, E. Babaev, J. Smiseth, and A. Sudbø, “Observation of a metallic superfluid in a numerical experiment,” *Phys. Rev. Lett.* **95**, 135301 (2005).

Research Directions

The state of our current understanding of the principles governing the behavior of materials at extreme pressures is still in its infancy. The key issues are as follows:

- What fundamental principles govern the behavior of electrons under high pressure when compression alters the electronic shell structures familiar under ordinary conditions?
- How do electronic structures give rise to unusual transport properties?
- What are the rules that govern the design of new materials with novel properties and functions?
- Can the principles governing structures of materials be understood over length scales from the atomic to the bulk? These changes may well encompass a significant fraction of materials science under extreme conditions. Properties of specific materials under extreme thermomechanical environments challenge current concepts of condensed matter science. These extreme environments also open intriguing pathways for making revolutionary new materials for future applications in energy and security.

In general, predictive rules do not exist to rationalize the myriad polymorphic transitions of materials at high pressures and temperatures. We thus need to establish guiding principles to predict structures and properties over a broad range of length scales. The effects of kinetics and non-equilibrium in transforming systems for broad classes of materials under extreme environments need to be understood. To accomplish this, experimental capabilities for large stress, variable temperature and strain rates, and the provision of other extremes need to be developed. An important experimental approach for defining this new behavior involves extending scattering spectroscopy with neutrons, x-rays, electrons, or other particles to matter under variable or multiple extremes. It is also imperative that smaller, faster, variable-energy, higher-resolution analysis with several simultaneous probes be carried out. Data from such experiments are needed to characterize changes of the structures and other physical properties. These data for unique materials under extreme conditions should be matched with first-principles simulations of the structure and dynamics. Calorimetry provides thermodynamic information on the transitions. Theory, simulating, and modeling are essential to understand the origin of phenomena and to build an accurate, unified, and completely predictive framework that is currently lacking.

Scientific Questions and Opportunities

Recent research has given us a glimpse of a new world of materials and materials behavior that can be accessed under extreme pressures and temperatures. For many materials, changing the temperature only varies structures and properties to modest degrees because minimizing distances between relatively “rigid” atoms is a driving force for establishing behavior and properties. Compression usually has a much greater effect (in some cases by tenfold) and changes atomic structures to much greater degrees. By understanding the changes in crystal structure, bonding properties, and electronic structures, it may be possible to exploit thermomechanical extremes to create entirely new classes of materials.

Once materials are formed under thermomechanical extremes, the materials must be sufficiently stable to allow recovery under ambient or near-ambient conditions. Diamond is perhaps the most well-known high-pressure material that can be recovered for a broad range

of applications but remains metastable under ambient conditions (i.e., the stable structure is graphite). Other materials are not stable when returned to ambient conditions. The development of a comprehensive understanding of how to produce and stabilize these novel materials is needed. It may even be possible to synthesize materials which are achieved using high-pressure techniques by alternative methods once the structures of these new materials are understood. For example, originally diamond was synthesized only in large high-pressure devices; now schemes have been developed to produce the material without pressure, that is, by chemical vapor deposition at pressures well below an atmosphere.

The ability to predict the structures and physical/chemical properties of materials under extreme conditions reliably is critically important. Most of the experimental discoveries already achieved under thermomechanical extremes were unanticipated by theory, yet theory has been useful for understanding the experimental observations. On the other hand, selected theoretical calculations such as the research on polymeric nitrogen and colossal ferroelectricity in oxides have provided guidance for key experiments and led to new discoveries. A robust and reliable framework for predicting behavior of all the elements of the periodic table over the widest range of conditions is needed. A new set of “chemical rules” need to be developed in order to understand bonding and reactivity of both familiar materials and those produced under thermomechanical extremes. Experimental input on crystalline and electronic structures are needed to extend fundamental theory of chemical bonding, which will also allow a new paradigm of chemical bonding to be developed for extreme conditions where conventional orbital descriptions of electrons (i.e., distinctions among s-, p-, d-, and f-electrons) break down. While current theoretical methods can explain the behavior of materials near ambient conditions, significant advances are needed to describe properties of the atoms and solids strongly perturbed by extremes in temperature and pressure. Achieving this goal will require great synergy between experiment and theory.

New experimental facilities and instrumentation are just now becoming available that will enable the study of these novel and complex phenomena for the first time. These developments are making possible direct comparison of experimental results for extreme conditions with accurate theoretical predictions. However, there is a major gap in current capabilities. Existing techniques limit the quality and quantity of experimental data available for complete analysis and comparison with computational data. High-quality diffraction patterns extended to high-momentum transfer are needed to extract accurate electron densities in order to test predictions that emerge from new theory. Inelastic scattering techniques that probe the electronic structure, bonding, and vibrational dynamics are needed to unravel the origin of structural changes and the onset of novel properties such as superconductivity, magnetoresistance, and ferroelectricity. A new generation of high-pressure cells (e.g., multi-anvil and large volume diamond anvil cells) needs to be developed for collecting data of a quality commensurate with the accuracy obtained from theory. Experimental apparatus must incorporate multiple analytical techniques simultaneously to allow integration of several experimental measurements under the same environment. New calorimetric methods are needed to measure thermochemical properties directly on small samples at very-high-pressure conditions. Current and future synchrotron, neutron, electron, laser, gas gun, and pulsed power facilities must be equipped for providing and characterizing

adequately simultaneous multiple extremes to understand the atomic-scale nature of the controlling mechanisms.

Complementing these new experimental capabilities, innovative methods for analyzing electronic wave functions are needed to define the effects of electronic structure, such as the stability/instability of structures formed under extreme pressure. Despite advances in first-principles methods, new computational techniques are needed to predict stable and metastable structures at arbitrary pressures and temperatures. Efficient and accurate methods for calculating transport and optical properties must be developed, improved, and implemented. Algorithms for the high pressure and temperature melting relations and combinations of other extreme must be developed. More accurate density functionals are needed to describe systems with large variations of electron density, from hydrogen to actinides. High-performance computational simulations must encompass multiple length scales. Moreover, advances in fundamental theory are needed that go beyond standard approximations that separate the electronic and atomic degrees of freedom. All of this is essential in order *to bring theory and experiment into agreement*.

Potential Impact

This Priority Research Direction will develop novel materials with superior properties that will have broad impact in many important applications. New polymeric forms of matter created from pressurizing molecules will lead to new high-energy-density materials with unprecedented energy content. These structures and related compounds could be essential for advanced energy production, storage, and transport applications. Improved structural materials with ultrahigh strength and hardness will impact technologies ranging from the creation of lighter weight vehicles as well as longer component lifetime. New optical, electronic, and magnetic materials are possible, including the design of new photoconducting, superconducting materials, and novel colossal magneto-resistance materials tuned by pressure. There will also be enhanced understanding of actinide and other materials crucial for national security materials and nuclear science. New classes of matter could ultimately be discovered, including the predicted new physics of metallic hydrogen.

The elucidation of the underlying guiding principles that govern materials under extreme pressures is essential for exploiting the novel electronic behavior that can be achieved. This knowledge will lead to designing a broader range of materials with specific tailored properties and/or for recovery for economically valuable uses near ambient conditions. First-principles theory and the availability of high-performance computing facilities tested against new highly precise determinations of structures and dynamics will provide a new paradigm for understanding condensed matter. The convergence of theory and experimental will provide an opportunity for understanding a broader view of electron structures of materials under extreme conditions. Predictive rules derived from experimental data and rigorous theory will finally be developed to guide the search of novel and useful states of matter and the design of a new generation of materials with unique/optimal functionalities.

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DISORDERED, NANOPHASE, AND COMPOSITE MATERIALS

Abstract

Disordered, nanophase, and composite materials exhibit enhanced performance that complements bulk crystalline materials over a broad range of extreme thermomechanical conditions. Materials in this class have untold potential for future applications in energy efficiency, production, and storage. However, we currently lack the fundamental knowledge necessary to describe, understand, design, and process these materials. We need to understand the underlying origin of transitions from crystalline to amorphous materials. In addition, we need to characterize the complex structures of these materials, including defining defects and their distributions. This information will enable new materials to be designed with tailored properties for use under extreme conditions. In addition, this knowledge will allow the use of extreme environments for surface or spatially distributed modification of materials to tailor properties. Recent advances in synthesis, characterization, and simulation tools offer important new opportunities for understanding the behavior of such chemically or structurally heterogeneous materials.

Background and Motivation

Traditional crystalline materials have dominated applications in extreme environments, yet requirements of future energy technologies demand performance far beyond their current limits. Glasses, polycrystalline ceramics with significant amorphous phases, amorphous metals, and new polymer composites exhibit behavior at high pressures, temperatures, and strain rates that offers the promise of breakthrough performance. Moreover, new classes of amorphous, semi-crystalline, and composite materials are being created under extreme pressures, temperatures, and strain rates [1–3]. However, realizing the full potential of this class of materials requires understanding their complex structures over a broad range of length scales, together with knowledge of the underlying energetics and kinetics of formation and subsequent behavior. Recent advances in materials characterization tools and multi-scale materials modeling, simulation, and theory capabilities for quantifying and linking atomic structure to predicting the properties of materials offer exciting opportunities for understanding and designing new types of these extraordinary materials. This fundamental knowledge will add new dimensions in the science of materials synthesis and processing by harnessing complexity to design materials with tailored properties.

The knowledge gained through fundamental studies of disordered, nanophase, and composite materials will enable the development of new materials with greatly improved functionality. Controlled materials synthesis and processing requires understanding the microstructural reorganization that occurs in materials strongly driven from equilibrium states to extreme conditions and under well-defined extreme conditions. Developing this control requires understanding the dynamics and atomic correlations during transformation and external process parameters, which requires real-time in situ measurement combined with advanced computational tools. Once this fundamental knowledge is obtained, a combination of experimental and modeling approaches can be developed to design materials with specific characteristics that can perform under extreme conditions. This research will open new pathways for enhancing performance (strength, fatigue, etc.) as structural materials; designing refractory and highly structured materials for use in erosive, wear, and high-stress

environments; and tailoring novel materials with advanced functionality by high-energy processing methods.

Realizing improved performances and new functionalities in amorphous, semi-crystalline, and disordered materials will have tremendous impact on future energy technologies. The knowledge gained by the fundamental research outlined in this PRD will produce advances in the ability to design multi-phased, smart, and multifunctional materials for a wide range of future energy generation, storage, and utilization technologies that require performance in extreme environments, such as lightweight yet strong materials for transportation, efficient solar cells, improve batteries, and many others.

Research Directions

Unlike crystalline systems, where the average atomic positions are readily fixed, the structure of a semi-crystalline and amorphous system is much more complex and requires a different framework for its description. Diffraction experiments can provide accurate measures of one-dimensional, pair-wise correlations that define the average structure [4], but such descriptions need to be coupled with short-range, many-body correlations from accurate atomistic simulations to yield thermodynamically self-consistent, three-dimensional structural models [5]. Accurate descriptions of liquid and amorphous structures need to go beyond the conventional concept of average packing of nearest neighbors and incorporate clusters of atoms which may have medium-range chemical and structural ordering [6].

To meet the needs of future energy technologies, performance is required in regimes beyond current limits set by conventional (e.g., crystalline) materials. Disordered materials have received less attention, especially under extreme environments, and their potential has not been adequately explored. Early studies measured the dependence of internal structure on static pressure [4–6], and more recent experiments have shown that the shock loading response of polymers is different from that observed in metals. Glasses and polycrystalline ceramics with significant amorphous phases also show response at high pressure and temperature that offers the promise of high performance in energy conversion applications. Clearly, to evaluate the full potential of these non-traditional materials for potential applications in advanced energy applications, additional fundamental studies are needed.

The driving force for many novel transitions in disordered systems under extreme conditions is not understood. Crystals can be transformed directly to glasses by application of pressure at low temperature—a novel transformation that can be described as pressure-induced melting in ordinary ice. Many more observations of such pressure-induced disordering have been reported in a large variety of systems, including the amorphization of quartz on static and shock compression (Figure 22). The nature of this transformation has challenged classical theory and is not fully understood. Emerging capabilities of high-flux neutron and x-ray sources, as well as other advanced characterization tools, can provide unique information on order/disorder phenomena in such materials, especially when applied in situ. These transformations between amorphous “structures” represent a new phenomenon in condensed matter now called “polyamorphism.” The nature of transitions between

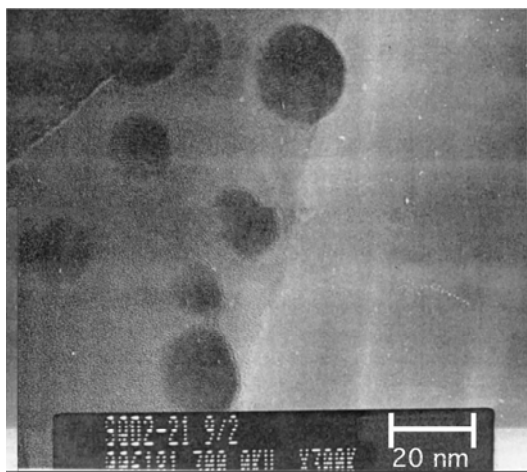


Figure 22. Transmission electron microscope (TEM) image showing shocked quartz at ~45 GPa to form an amorphous composite structure has been recovered to ambient conditions. The dark circles are nanocrystalline silicon, which photoluminesces in various colors within the matrix of the amorphous silica. The result demonstrates how novel composite structures can be made by shock compression. Source: P. S. Fiske, W. J. Nellis, M. Lipp, H. Lorenzana, M. Kikuchi, and Y. Syono, “Pseudodachylites generated in shock experiments: Implications for impact cratering products and processes,” *Science* **270**, 281–283 (1995).

liquid or solid phases is not yet understood. Understanding these transformations will play a crucial role in advancing both our knowledge of phase transitions in general as well as in the creation of new dense glasses and composites that will lead to novel functionalities and enhanced performance.

Self-organization at the nanoscale of materials under pressure can lead to remarkable properties such as high hardness combined with unique combined electronic and strength (Figure 23). Moreover, mechanically deformed materials often tend to show a high level of

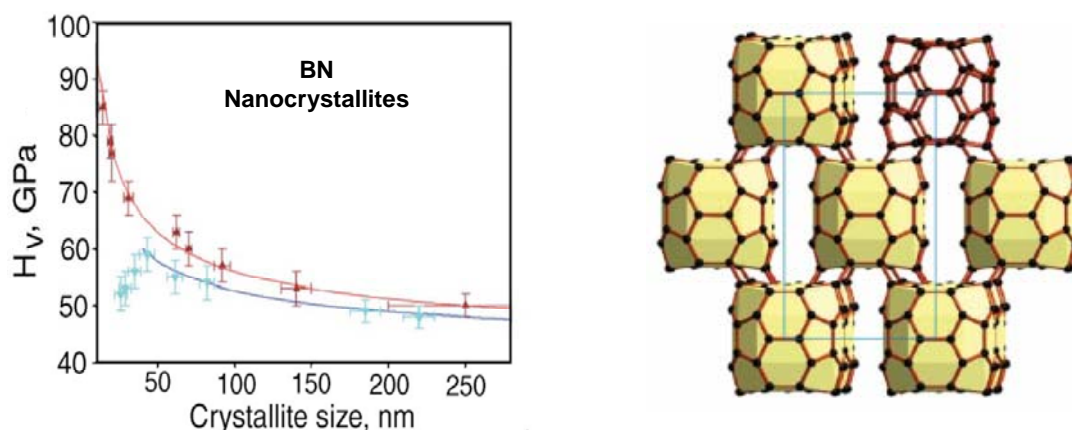


Figure 23. Left: Hardness of cubic-BN as a function of the crystallite size, showing that the hardness of the nanocrystalline material (red) greatly exceeds that of bulk material (blue) for small crystallites. Source: N. Dubrovinskaia, V. L. Solozhenko, N. Miyajima, V. Dmitriev, O. O. Kurakevych, and L. Dubrovinsky, “Superhard nanocomposite of dense polymorphs of boron nitride: Nanocarbon material has reached diamond hardness,” *Appl. Phys. Lett.* **90**, 101912 (2007). **Right: A novel three-dimensional metallic polymer predicted to form from C₆₀ under anisotropic stress.** Source: [S. Okada](#), [S. Saito](#), and A. Oshiyama, “New metallic crystalline carbon: three dimensionally polymerized C₆₀ fullerite,” *Phys. Rev. Lett.* **83**, 1986 (1999).

atomic spatial periodicity over extended length scales while simultaneously exhibiting little or no spatial periodicity across grain boundaries and at interfaces. The mechanisms leading to these phenomena are not understood, including the increasing complexity with loading stress [7]. There are only qualitative observations relating the scale of the microstructural perturbation (e.g., subgrain cell size) to the fundamental properties of the metal or alloy (e.g., stacking fault energy) and the imposed deformation conditions (e.g., total strain, strain rate). A similar picture appears in alloys driven by ion irradiation where self-reorganization, spontaneous organization into new, often novel, non-random structures, has been observed [8]. Nanostructured materials, metallic alloys, oxides, and other multi-component materials can give rise to complex self-organization behavior, including possible solid-solid phase changes that are not yet understood.

Self-reorganization has generally been explored by first stressing the system to an extreme state and recovering or removing the samples from the formation environment and studying the properties *ex situ*. This is now possible only for a narrow range of currently accessible parameters like pressure, stress, alloy composition, initial microstructure, and temperature. Experiments that significantly expand the ranges and types of parameters studied, take advantage of new capabilities in *in situ* real-time measurements, and eventually control the resulting dynamic and atomic correlations will lead to revolutionary classes of tailored materials to serve current and future needs. By understanding the dynamics and the interplay of the extreme conditions driving the material, different periodicities and therefore different properties, will be obtained for the self-organized structures from the nanometer to the micron scale.

To achieve this level of understanding, experiments that push the limits of current approaches are required. Scalable algorithms will be needed to guide and to interpret experiments. Recently, large-scale molecular dynamics simulations of shocked solids have captured the solid-solid phase transformation of iron [9] and a change in the plasticity of copper [10]. Results of these simulations compare well with current dynamic x-ray diffraction experiments. Continuum-level modeling continues to improve the connection between atomic-level understanding and experiments, such as for grain boundary evolution in nanocrystals [11] and phase transformations [12]. Of particular importance is the need to expand the sizes of the systems that can be modeled in practical times.

Materials with various novel nanoscale and microstructure features need to be designed for enhanced performance under a wide range of chemical, electrical, and strength requirements. For instance, under shock loading, nanocrystalline structures may evolve into dislocated nanostructures that exhibit ultrahigh strength [13, 14]. Understanding the physical basis behind the properties of superhard materials strengthened by chemical and defect-induced approaches could provide new avenues to produce a wide range of novel materials for future energy applications.

Amorphous metals offer high hardness and superelastic response combined with high free volume that impacts a diverse array of applications spanning from coatings, to vibrational damping, strength reinforcements, and hydrogen storage. Absence of fundamental understanding of the spatially and temporally dispersed structure of this class of material

currently precludes physically based structure-property models, which greatly inhibits our ability to understand and model their behavior under extreme conditions. Increased understanding will allow innovative processing using extreme fields, such as using intense laser pulses to introduce patterned amorphous structures for tailoring surface properties, for example.

Polymers exhibit characteristics of packing, chain folding, free volume, and interaction between adjacent chains at the atomic scale, yet many thermoplastics are semi-crystalline, comprising crystalline domains exhibiting a high degree of order both along the polymer backbone and between the chains. New characterization tools must be developed beyond their present state to define fully the types of ordering that can exist within such a malleable microstructure. Such microstructural complexity gives rise to mechanical properties that will vary over a large range. In semi-crystalline polymers, the elastic modulus is different in the amorphous and crystalline domains. Our current understanding and ability to control the tremendous variation in properties is still in its infancy for polymers. Similar advances are needed to fully understand polymer matrix composites and other amorphous and semi-crystalline systems.

In addition to the mechanical effects discussed above, the electrical response of these complex materials is also expected to change at high pressure-temperature conditions and under the constraints applied by transient loading. Electrical fields established in polymeric and semi-crystalline materials under shock produce a piezoelectric response that can be utilized for simple sensing applications, and control of the geometry of these complex materials may yield sophisticated electronic sensors.

Finally, disordered materials also can provide unique processing media for synthesis of other materials such as growing particles confined in polymer-based structures (Figure 24). For example, after formation of particles with tailored sizes, the polymer matrix can be removed to employ the particles themselves. Alternatively, the resulting nanocomposite can be used for a variety of novel applications of relevance to energy storage and structural applications.

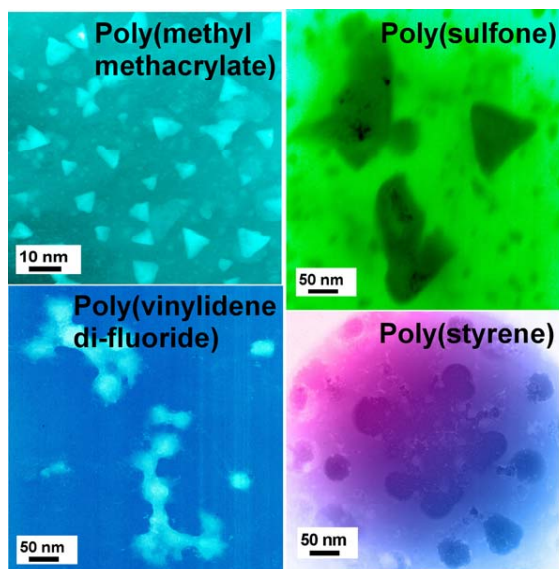


Figure 24. The size and shape of iron oxide nanoclusters are controlled by interfacial interactions with polymers having various functional groups. Source: <http://gtresearchnews.gatech.edu/newsrelease/polymer-sizing.htm>.

Scientific Questions and Opportunities

Key scientific questions and opportunities for discovering, characterizing, developing, and using new disordered, nanostructured, and composite materials under extreme thermomechanical conditions include the following.

- What is the underlying origin of transitions between crystalline to amorphous forms of materials, and between different amorphous forms? *Do these transitions have thermodynamic origins or can they be explained only in terms of kinetic barriers to change? Can a thermodynamic theory be constructed to describe phase transitions in such non-equilibrium, disordered systems? Can phase boundaries separating high-pressure crystalline phases be extrapolated into the liquid regime? In general, will the amorphous phases recrystallize upon further compression and processing? What governs the novel phenomena of high-pressure amorphitization? Under what conditions will recrystallization occur and what structures will result?*
- *How can we quantify and categorize the microstructure and defects and their distribution in disordered materials? What new diagnostics are needed to characterize disordered materials?* The current lack of a clear quantitative description of the atomic structure of disordered materials greatly inhibits development of the processing-structure-property relationships that govern their response.
- Designing materials from across the structural spectrum requires consideration of a range of material states. *How can we develop a theoretical paradigm for the design and synthesis of these complex materials with target properties?* A fundamental understanding in terms of statistical and structural thermodynamics is needed through the quantification of the local order, free volume, and mechanical state (e.g., chain length and folding of polymers) of the building blocks of these materials.
- *What are the potential opportunities to use extreme environments (e.g., transformations induced by fast lasers) for surface or spatially distributed modification of materials to tailor properties for enhanced performance? What new techniques are needed to probe these complex systems in situ?* Experiments must probe deformation mechanisms using available techniques in new integrated approaches (i.e., combined diffraction and spectroscopy) while also developing revolutionary new diagnostics and analysis. We need to identify the degrees of order, both structural and chemical, over an unprecedented range of length scales, from atomic to mesoscopic to macroscopic, and to develop imaging quantification of the atomic structure, defect distribution, and buried interfaces.

Answering these questions and thereby accessing the potential benefits of these complex materials will require the development of comprehensive tools for interrogating their structure and response under extreme environments. The understanding gained by these fundamental studies will add an extraordinary new dimension for the control materials synthesis and processing with predictable, tailored properties by use of extreme conditions. The goal of such an effort should endeavor to understand complex heterogeneous systems at a level commensurate with that available for bulk materials. Finally, the challenge of multiscale modeling and simulation must encompass the analytical descriptions of material response, to allow physically based prediction of the performance of designed

microstructures or composites on the one hand but also the prediction of constitutive and thermodynamic response to match to the loading envisaged in future use. Given the difficulty in probing the evolving structure of disordered materials, it is important that models are inspired by accurate atomistic, molecular, and defect scale modeling. Such benefits can only come with advances in accessing the parameter space available with modern testing methodologies, and recent advances in such technologies make this an opportune time to address these questions. The knowledge obtained will provide application across not only materials physics but also other branches of science.

Potential Impact

The knowledge to be gained through such studies is an exciting prospect for understanding both the physical and mechanical behavior of these complex and poorly understood systems and indeed represents a scientific grand challenge. This knowledge will enable the development of new materials with greatly improved functionality over existing materials. The introduction of tailored microstructures allows the ability to affect and enhance the functionality of disordered materials. The application of extremes in pressure, temperature, and/or deformation rates will enable introduction of predictable local order tailored control of the statistical distribution of the disorder, and alteration of structural motifs to produce a wide range of new materials.

Advanced amorphous, semi-crystalline, and disordered materials developed as a result of these fundamental studies have significant for use in future energy applications. For example, nanoporous polymers have the potential to yield new membranes selective to ionic or molecular transport and/or separation. These new membranes may also enable discrete sensors for dynamic chemical reaction studies that underpin synthesis, plasma formation, and energy release mechanisms. They will be critical to revolutionary improvements in lightweight battery performance and safety utilizing polymeric materials such as in lithium-polymer batteries. Coupling of structural and energy storage multi-functionality in future lightweight transportation platforms also offers revolutionary promise leveraging advances in polymeric materials. Fundamental understanding of the response of disordered materials to extreme chemical environments will lead to improved survivability of these materials for critical applications that include pipelines for transport of highly reactive energy materials such as hydrogen and ethanol. Design of new disordered, nanophase and materials with tailored microstructures will facilitate the production and fielding of lightweight and strong structural materials for aerospace, wind turbine, and automotive applications. Further, smart technologies could be designed within these materials to enable multifunctional uses for these structures impacting safety and efficiency in use and design of transportation platforms. Such benefits, applied to energy generation and storage, will increase in-service lifetimes and reduce operational downtime and have the potential for lowering production costs. These advances could also provide revolutionary new photovoltaic and dielectric materials. New capabilities in composite design will also enable advances in coating technologies for multi-phase, smart, and multifunctional materials for use in extreme environments.

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EXPLORING THERMOMECHANICAL LIMITS OF MATERIALS

Abstract

Although the ideal strength limit of materials has been known for decades, currently available bulk materials achieve maximum strengths that are only on the order of a few percent of this limit. Fundamental understanding of mechanisms that contribute to strength at the nanoscale has the potential to produce a new generation of high-performance materials that approaches this ideal strength limit. This advance would have significant and broad impacts on future energy applications, such as stronger, longer-lived, and safer transportation and power-generation systems. These new materials would also enhance energy efficiency and demonstrate significantly higher performance in a variety of extreme operating environments that will be required in future energy applications.

Background and Motivation

Structural materials are the backbone of the industrial infrastructure that is key for sustaining and enhancing the quality of life in technologically advanced countries. The myriad applications of structural materials range from building structures where we work and live to the automobiles and other transportation vehicles used every day to the power generation facilities and associated infrastructure (pipelines, etc.) that provide the energy for our industries and homes. Most of the structural materials commercially available today were developed as the result of rather empirical discovery techniques. This empirical approach to alloy development has resulted in marked improvements in the strength of materials, albeit at relatively high cost and at a slow rate of progress. For example, the history of steelmaking dates back over 30 centuries, but the strengths of most present-day commercial steels are less than a factor of two higher than the steel used for swords and other medieval-era applications. The strengths of commercially available steels are on the order of 1 to 5% of the ideal strength limit. The current paradigm is that it takes one or more decades and many millions of dollars to achieve an incremental improvement (e.g., 5% increase in strength) in the performance of a structural material such as a superalloy.

Achievement of higher strength materials can directly translate into large energy savings for transportation vehicles (trains, planes, automobiles, etc.) due to weight reduction and can enable improved high-efficiency power generation systems (fossil, nuclear, wind, etc.). There are constant new demands in the energy and transportation sectors for ever-stronger materials that are capable of operating at temperatures beyond the capabilities of existing materials. If the fundamental mechanisms that control the deformation and fracture behavior of structural materials can be understood, revolutionary new materials could be designed at the nanoscale with strengths approaching the theoretical limit.

Research Directions

An underpinning theme for discovering the practical thermomechanical strength limits of materials under quasi-static conditions involves understanding the role of dislocation generation and propagation. Dislocations were theorized to be the cause of low strength (relative to the ideal strength value) in materials over 70 years ago, and subsequent experiments have demonstrated the pervasive influence of dislocations on strength reductions (via dislocation glide and thermal creep mechanisms) and strength increases (via work-

hardening processes involving dislocation multiplication and pinning). Traditionally, most attention has been focused on impeding the propagation of dislocations since inhibition of dislocation generation at sources was considered to lead to undesirable brittle behavior. This traditional perception needs to be reexamined for new materials systems which are designed at the nanoscale to achieve strengths approaching the ideal strength limit. This knowledge will help answer such questions as what is the maximum temperature and stress under which new nanostructured materials can ultimately function in future energy applications.

Fundamental issues that must be addressed include defining possible critical dimensions for dislocation generation and multiplication, as well as potential length-scale or architecture effects on elastic strain relationships in composite materials. Recent deformation studies on nanocrystalline materials [1–3] and nanoscale multilayered films [4] have demonstrated that pronounced improvements in strength may be achievable in these nanoscale materials compared to conventional materials. These studies, along with corresponding investigations of nanoscale geometries such as micropillars [5], have shown considerable use for probing length-scale phenomena for dislocation generation and multiplication. In parallel, there are emerging discoveries of super-hard materials based on nanoscale aggregates of materials that have only moderate strength in bulk crystalline form. Tailored assembly of the scaffold architectures in composite materials may in some cases lead to materials systems that are stronger and stiffer than the constituent materials [6], which defies traditional simplistic “rule of mixture” estimations. It is critical to understand these various effects at the nanoscale because such knowledge would enable us to design new materials with superior thermomechanical strength. Advances in in situ characterization tools, such as those becoming available at advanced light and neutron sources, and those being developed based on imaging, spectroscopy, and other techniques, are critically needed to provide new insight on deformation and fracture mechanisms that have heretofore not been considered.

An overarching challenge in structural materials research is whether it is possible to defeat nature’s traditional linkage of high strength with poor ductility and low toughness. For example, diamond is nature’s hardest material but it is not an attractive candidate for most structural applications due to its brittle properties. However, diamond can be synthesized in the laboratory with enhanced toughness by introducing a dislocation microstructure not found in the natural material [7]. Fundamental research is needed to investigate and understand these phenomena and evaluate whether the traditional paradigm of high strength and low toughness can be overcome with science-based design of new materials systems.

Scientific Questions and Opportunities

Key scientific questions and opportunities that may lead to transformational advances in the knowledge of materials performance under extreme thermomechanical conditions include the following.

1. *What are the critical length scales that control deformation and fracture? What are the ultimate strength and temperature performance limits for structural materials?* The fundamental phenomena that control dislocation generation and multiplication over a broad temperature range need to be identified and quantified. This will require a broad range of theoretical and experimental studies, including single-effect and synergistic

combined-effect in situ characterization studies during controlled deformation at different temperatures.

2. *What are the roles of crystallinity and lattice structure on the fundamental processes of deformation and fracture? What new techniques are needed to probe these phenomena in situ?* Experiments must probe deformation mechanisms using available techniques in new integrated approaches (i.e., combined diffraction and spectroscopy) while also developing revolutionary new diagnostics and analysis. We need to identify the degrees of order, both structural and chemical, over an unprecedented range of length scales from atomic to mesoscopic to macroscopic, and to develop imaging quantification of the atomic structure, defect distribution, and buried interfaces.
3. *Is it possible to break the historical paradigm that high strength is only achieved at the expense of reduced ductility? What are the key experiments and modeling advances that will provide insight into the potential for simultaneous dramatic improvements in strength and ductility?*
4. *What are the physical mechanisms controlling plasticity, damage evolution, and failure in disordered, nanostructured, and composite materials? What are the kinetic and thermodynamic bases of deformation mechanisms that give rise to the rate-determining steps in material response? This understanding, and the development of advanced analytical and theory tools, will lay the groundwork for the development of physically based models of mechanical response across conditions of extreme temperature, pressure, and strain rates. How can material composites be utilized to radically evolve their properties? What is the proper description of crystalline and amorphous composite materials; that is, how can their macroscopic properties be predicted from their components?*

Investigation of these fundamental questions will require the development of a comprehensive set of computational and experimental tools for probing length-scale, structure, and composite architecture effects.

Potential Impact

Breaking nature's traditional paradigm of high strength and low toughness would be of enormous benefit for a wide range of applications, including the energy-intensive fields of transportation (commercial and personal), power generation (fossil, fission, fusion, and renewable energy), and industrial manufacturing (steelmaking, automotive components, etc.). Improved knowledge of the fundamental mechanisms controlling deformation and fracture (length-scale effects, influence of temperature and strain rate, architecture influence in metal-metal, metal-ceramic, and ceramic-ceramic composite systems) may lead to dramatic advances in the performance capabilities of these and other industries that are critical for the future economic success of the United States.

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HIGH-PERFORMANCE ELECTRIC AND MAGNETIC MATERIALS

Abstract

Increasing the capacity and decreasing the footprint of the electric power infrastructure to meet the growing demand for electricity in urban and suburban areas requires operation at higher electric and magnetic fields. Electric fields are limited by dielectric breakdown of insulation in high-voltage transmission lines and in the windings of coils for motors, generators, and transformers; magnetic fields are limited by the dipole strength of permanent magnets and by the strength and current-carrying capability of resistive and superconducting coils. These macroscopic limitations are controlled by the creation, interaction, and aggregation of atomic and nanoscale defects in materials. Emerging capabilities in materials design, synthesis, characterization, and modeling offer unprecedented opportunities to observe, understand, predict, and control the atomic and nanoscale defects and structure that define the limits of extreme electric and magnetic fields and the response of materials to them. This knowledge is critical for the development of new classes of materials required to meet future electrical energy needs.

Background and Motivation

To meet the ever-increasing demand for electric power, we must develop innovative new electrical technologies with higher capacity, smaller size, greater efficiency, and safer operation. Meeting the requirements of future electrical power systems requires operation at much higher electric and magnetic fields. High-voltage wires that reduce resistive losses enable long distance transmission of power; the present voltage limit of 765 kV is determined by the dielectric breakdown strength of insulators. The capacity of generators to produce electricity and of motors to produce mechanical motion is limited by the magnetic force that can be produced between a spinning permanent magnet and a surrounding coil, or between two coils. The existing fields of permanent magnets are well below intrinsic materials limits, and the field of coils in motors, generators, and transformers can be significantly increased by applying higher currents to resistive windings or by using superconducting windings that carry substantially higher current at low voltage and low loss. Increasing the dielectric breakdown strength of insulators, the magnetic field strength of permanent magnets, and the current-carrying capacity of conductors and superconductors are the fundamental basic research challenges for meeting U.S. and global electrical power demand through 2030 and beyond.

Producing higher electric and magnetic fields requires discovering new materials by design and understanding their electric and magnetic behavior. Such materials and phenomena are found in highly correlated electron materials such as insulators, magnets, metals, and superconductors at extreme electric and magnetic fields. The quantum critical points, metal-insulator transitions, phases displaying charge, orbital and spin order, and high-temperature superconducting behavior that are induced or affected by extreme electric and magnetic fields are the foundation of promising new materials behavior. Exploring the rich behavior of these fundamental states of correlated electron matter is central to finding and understanding the materials for next-generation electrical power technology.

Research Directions

Higher electric fields: dielectric

breakdown. The primary factor preventing use of higher electric fields in electrical technology is the lack of insulating materials capable of withstanding extreme electrostatic forces. Insulators fail dramatically by a sudden electric discharge when the electric field reaches the dielectric breakdown strength (Figure 25). This sudden discharge is thought to be the culminating event of a long incubation period during which electrons driven by the electric field are thought to penetrate the insulator and collect at atomic and nanoscale structural defects. As the number and density of charged defects grows over months or years, a few of them eventually come close enough together to form a continuous percolation path across the insulator that allows the trapped charges to jump from defect to defect in a sudden violent and destructive discharge.

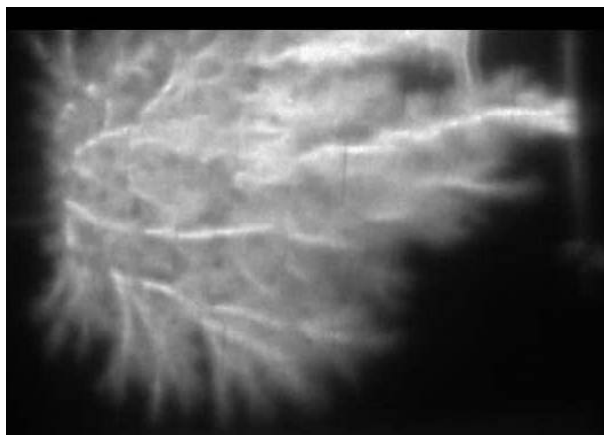


Figure 25. An arc in water insulator. Courtesy of Jane Lehr, Sandia National Laboratories.

Although the discharge itself is the dramatically obvious outward sign of insulation failure, the nature of the defects that collect charge, the slow charging process, and the trigger for the sudden discharge have never been observed. Thus the breakdown scenario described above, while plausible and widely discussed, needs much more observational detail before it can guide the development of new insulators with higher breakdown strength.

Understanding the atomic and nanoscale defects and the local charge trapping processes that occur during the incubation period would provide insight that could open the door to the development of new classes of insulating materials. Until recently, the ability to observe these defects has been outside the reach of our best imaging and spectroscopic characterization tools. The advent of high-intensity sources of electrons, neutrons, and x-rays, however, allows these tiny, formerly invisible defects to be seen. Forefront scattering and imaging experiments have the sensitivity to characterize these defects and the charging process itself, including small-angle x-ray and neutron scattering, single-crystal diffuse scattering, aberration-corrected transmission electron microscopy, and scanning probe microscopies. Ultrafast experiments that will be made possible by free electron lasers such as the Linac Coherent Light Sources (LCLS) promise an even more dramatic opportunity: observing the trigger mechanism and dynamics of the sudden discharge jumping between neighboring charged defects. Resolving these two breakdown events—the slow charging of ultrasmall atomic and nanoscale defects during the incubation period and the ultrafast discharge of these defects across a continuous percolation path spanning the insulator—are the keys to understanding dielectric breakdown behavior and finding new insulation materials that will operate at significantly higher electric field.

Beyond characterization, a theoretical understanding of high-field aging and breakdown over a wide range of thermal and mechanical stresses is required for the development of new

materials with higher dielectric breakdown strength. A theory for high-field conduction in solid insulation systems is at the root of such understanding, and no such theory exists at present. Recent advances in computational quantum mechanics provide a tool with which to understand high-field conduction at the atomic and molecular level, while transient nonlinear finite-element analysis makes possible high-field modeling at larger length scales [1, 2]. The multiscale challenge of the dielectric breakdown problem—understanding macroscopic failure in terms of atomic and nanoscale events—is emblematic of many fundamental problems in condensed matter and materials physics. Linking cause and effect across the length scales is a central challenge that is beginning to come within reach of modern multiscale modeling. Dielectric breakdown is fertile ground for developing multiscale models as well as a high-payoff target for their application.

In-depth characterization and modeling are needed to explore new classes of candidate materials for high field dielectrics. For example, polymer dielectrics such as cross-linked polyethylene (XLPE) filled with nanoparticles such as silicon or TiO_2 show substantial promise for improved breakdown strength and durability at extreme electric fields [3]. Experiments show that improved performance of nanofilled polymer dielectrics is the result of several factors including the interaction of electrons across the filler-polymer interface, the surface treatment of the filler particles, and the size of the filler particles. The dependence on size is especially striking: micron-size fillers *degrade* dielectric breakdown strength and raise the charge absorption rate compared with the bare dielectric, while nanoscale fillers significantly *enhance* breakdown strength by a factor of 2 or more at 80°C and reduce charge absorption. However, a fundamental understanding of the mechanisms for such improvement as well as a basis for engineering such systems is lacking. Characterization of the physical and electronic structure of the filler–host composite coupled with quantum mechanical modeling will allow filler surface states, including the effects of surface treatments, to be studied quantitatively and optimized. In cases where nonlinear fillers (e.g., ferroelectrics) are employed, Ginzburg-Landau theory for such materials can be coupled with transient nonlinear finite-element analysis to quantify macroscopic system performance, while computational quantum mechanics can be used to optimize system performance at a molecular level. This information will reveal the root causes for the degradation and enhancement of dielectric breakdown at atomic and nanometer length scales, allowing new polymer composites to be designed with structures tailored for improved resistance to extreme electric fields.

Higher magnetic fields: permanent magnets. The highest known field strength in a permanent magnet, 1.6 T in $\text{Nd}_2\text{Fe}_{14}\text{B}$, is remarkably small compared to fundamental limits imposed by materials strength needed to contain the magnetic energy density. Fields an order of magnitude higher, up to 17 T, are known in superconducting trapped field magnets where the elementary magnetic moments are nanoscale vortices trapped on structural defects (Figure 26) [4]. Even this field value, 17 T, requires only a modest material strength, ~ 100 MPa. This value is well below the 1-GPa strength of copper-silver composites used for steady field-resistive magnets producing 35 T, and even farther below the strength of the strongest materials known such as carbon nanotubes at 63 GPa [5]. The limiting factor for permanent magnets is not strength of materials. The challenge is basic materials design of a structure accommodating a high density of strong atomic magnetic dipoles such as iron or

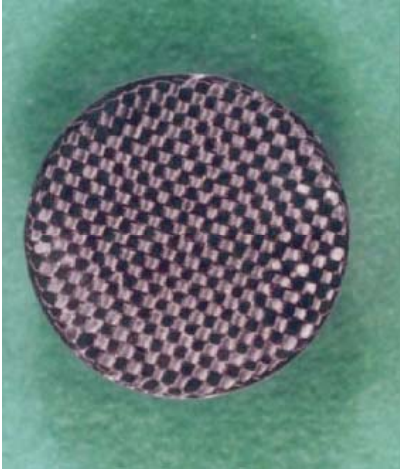


Figure 26. Trapped field superconducting magnet producing 17 T at 29 K. Source: Masaru Tomita and Masato Murakami, “High-temperature superconductor bulk magnets that can trap magnetic fields of over 17 tesla at 29 K,” *Nature* **421**, 517 (2003).

their magnetocrystalline anisotropy is weak. Rare earth moments are smaller than transition metal moments, but they have a very strong magnetocrystalline anisotropy and tend to lock their moments along a single axis. Strong permanent magnets such as $\text{Nd}_2\text{Fe}_{14}\text{B}$ are a fortuitous composite of the transition metal and rare earth elements.

The search for new high-field permanent magnet materials takes advantage of complex crystal structures, as in $\text{Nd}_2\text{Fe}_{14}\text{B}$ with 68 atoms per unit cell. Such complex structures enable a wealth of possible new materials. The sheer number of possibilities requires effective search strategies to focus on the most promising candidates. The most important criteria are high magnetic moment, high magnetocrystalline anisotropy, and strong ferromagnetic coupling. Theoretical calculations of the electronic and magnetic structure of complex materials from first principles are becoming possible with dedicated multi-node computer clusters, as shown in Figure 27 [7]. Such calculations provide valuable guidance in searching for promising new permanent magnet materials and eventually may enable numerical design of high-field-strength permanent magnets.

nickel and with sufficient orbital anisotropy to force the dipoles to point in a common direction. This progress in exploring and understanding correlated electron materials since the discovery of $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnets provides a broad base and wide horizon for pushing the limits of permanent magnets [6]. The variety of new correlated electron phase transitions and phenomena that are found at extreme magnetic fields provides fertile ground for discovering new interactions among orbital and spin magnetism and chemical bonds that can stabilize high-field permanent magnets. The discovery or design of substantially higher field-strength permanent magnets is a scientifically ripe challenge that would dramatically increase the capacity and reduce the space required for motors and generators in the electric power infrastructure.

Creating higher field permanent magnets requires a large atomic moment and strong magnetocrystalline anisotropy, two properties that do not coexist among the elements.

Iron and other transition metals have large moments, but

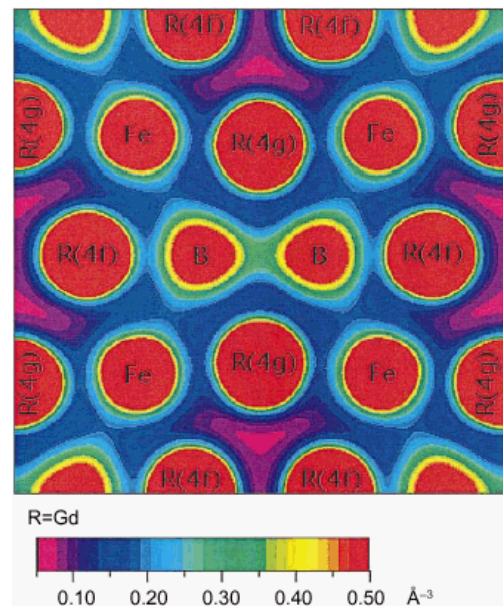


Figure 27. Electronic structure of $\text{Nd}_2\text{Fe}_{14}\text{B}$. Source: M. Yamaguchi and S. Asano, “Calculations of the magnetic properties of $\text{Y}_2\text{Fe}_{14}\text{B}$ and $\text{Gd}_2\text{Fe}_{14}\text{X}$ ($\text{X} = \text{B}, \text{C}, \text{N}$) by the full-potential linearized augmented plane wave method,” *Physica B* **254**, 73 (1998).

Higher magnetic fields: resistive and superconducting coils. Like the field of permanent magnets, the magnetic field of coils that surround spinning magnets is a limiting factor in increasing the capacity and reducing the footprint of motors and generators. The easiest way to produce higher fields in coils is simply to pass higher current through their windings. In resistive coils this increases the voltage levels linearly with current, and the resistive losses with the square of the current. Higher voltages can be accommodated by better insulation with higher dielectric breakdown strength, an immediate application of the basic research on dielectric breakdown described above. Superconductors provide an alternate route to higher currents and larger magnetic fields in coils. Superconductors carry high current at zero resistivity in DC applications, producing neither voltage nor heat. In AC applications such as the power grid, superconductors are about 100 times lower in resistivity than copper wire, the commonly used resistive conductor. Thus superconducting windings can accommodate much higher currents at much lower voltages than copper windings, producing higher power output in motors and generators, while reducing size requirements by a factor two or three and losses by a factor of two.

The fundamental challenge for superconducting wire is its current-carrying ability. The maximum current that can be carried by a high-temperature superconductor falls dramatically with magnetic field, losing 90% of its value in only 1 T. To realize significant gains in power capacity and efficiency, motors and generators must operate in fields of 5 T or more. Basic research is needed to raise the current-carrying ability of superconducting wires in magnetic fields by an order of magnitude.

The current-carrying ability of superconductors is determined by nanoscale defects that attract and trap superconducting vortices, tiny tubes of magnetic flux surrounded by circulating supercurrents. If the defects successfully trap the vortices, current flows without resistance or loss through the superconductor. If the vortices break free of their pinning defects, however, energy is dissipated and current flow encounters strong resistance. Recent progress in scanning tunneling microscopy (Figure 28), Lorentz imaging by transmission electron microscopy, and scanning Hall probe microscopy now let us see individual defects and vortices so that we may observe directly the interaction between them. Sophisticated nanoscale fabrication techniques based on top-down lithography and bottom-up self-assembly enable creation of complex defect structures and patterns on demand. By clever design, such defect structures accomplish remarkable feats, such as selectively manipulating individual vortices on the basis of commensurability with a defect pattern or direction of motion. The ability to see the action of individual defects on individual vortices and to create defects of arbitrary complexity opens new doors for designing and fabricating much more effective pinning structures [8]. Like the

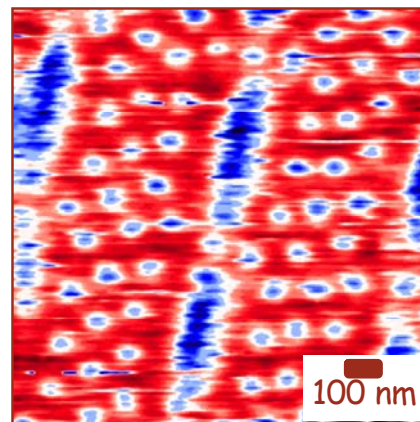


Figure 28. Scanning tunneling microscope image of vortices (circles) and pin sites (ellipses) in the superconductor NbSe₂. Source: G. Karapetrov, J. Fedor, M. Iavarone, D. Rosenmann, and W. K. Kwok, "Direct Observation of Geometrical Phase Transitions in Mesoscopic Superconductors by Scanning Tunneling Microscopy," *Phys. Rev. Lett.* **95**, 167002 (2005).

sudden discharge of dielectric breakdown, depinning of vortices from defects is an abrupt and catastrophic event that is difficult to catch in real time. To do so will require ultrafast techniques and monitoring of the precursor conditions that trigger it, bringing exciting new possibilities to model, understand, and control the current-carrying capability of superconductors. The best pinning structures and current-carrying abilities that we now achieve are a factor of ten below the intrinsic thermodynamic limits set by the condensation energy of the superconducting phase transition. Achieving this order-of-magnitude improvement in current-carrying ability of superconductors is a basic science challenge that will have a transforming effect on electrical power technology.

New materials. Currently the synthesis of new materials exploits the variables of temperature, pressure, and composition, the same phase space that mankind has been exploring for millennia. Deliberately applying electric and magnetic fields to materials with the intent of synthesizing new materials is a new approach still in its infancy. A small number of effects have been observed and published and a few are in use by industry at very small fields, but there is little understanding of the underlying mechanisms or the range of phenomena that may be induced.

The magnitude of the observed changes on material properties is surprisingly large. Changes of 30% in solubility of nickel in iron in the Fe-Ni alloy system have been observed [9] as shown in Figure 29, a much larger effect than can be accounted for by the relatively small magnetic energy of a spin moment in an applied field. The magnetic degree of freedom is not an incremental change in the toolbox of materials synthesis and processing; rather, it is a transformational opportunity. It provides a path to control the physics and chemistry of materials that is as powerful as changing the temperature or pressure.

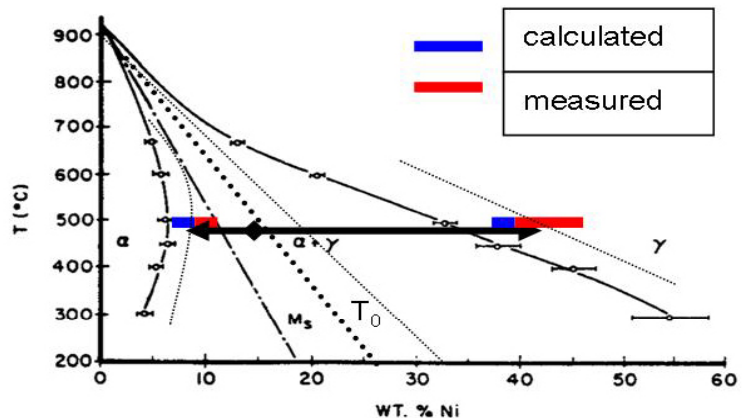


Figure 29. The solubility of Ni in Fe processed at 500°C at 29 T increases by as much as 30%. Calculations using Local Spin Density functional theory predicts the increased solubility. Source: D. M. C. Nicholson, R. A. Kisner, G. M. Ludtka, C. J. Sparks, L. Petit, Roger Jaramillo, G. Mackiewicz-Ludtka, J. B. Wilgen, Askar Sheikh-Ali, and P. N. Kalu, “The Effect of High Magnetic Field Annealing on Enhanced Phase Stability in 85Fe-15Ni,” *Journal of Applied Physics* **95**, 6580 (2004).

The small energy scale associated with spins in a magnetic field has an important advantage: it allows anomalous states of many materials synthesized in a field to be recovered at room temperature. Magnetic fields can orient diamagnetic or paramagnetic materials, favor one phase over another by changing the free energy, affect the kinetics of reactions by changing the chemical potential, and select valence states of multivalent ions. In all cases the fundamental limits of these effects on final material properties are unknown.

There has been no systematic investigation of materials synthesis using magnetic fields, and because of this, several basic research gaps must be overcome for magnetic fields to be used as a synthesis tool. The most pressing underlying need is for greater understanding of the limits of magnetic fields in affecting materials synthesis. A few surprisingly large effects have been discovered, suggesting that many more await exploration. Predictive capability of the effects of magnetic field on synthesis needs to be developed, even if the models are initially very simple and empirical. Finally, facilities are needed that allow extreme magnetic fields to be applied to sophisticated synthesis techniques so that this new direction can be systematically explored. Some of these facilities must specifically target in situ observation of synthesis under extreme magnetic fields to observe the mechanism by which magnetic fields affect materials growth.

Beyond the synthesis of new materials, extreme magnetic fields play a central role in the discovery and exploration of new phenomena that define the horizon for materials behaviour. Today's energy technologies are based on conventional metals, semiconductors, ferromagnets, and superconductors, many of them traditional materials that have been in use since the middle of the last century. Modern condensed matter research, however, suggests that these traditional materials are but a small subset of the novel phases that can be formed by the collective interactions of correlated electrons with spins, charges, and structural distortions.

Insulators, for example, display a panoply of phases beyond conventional ferromagnetism and antiferromagnetism. The phase diagram of one such insulating system is shown in Figure 30, where application of a magnetic field up to 50 T induces Bose-Einstein condensation of magnetic excitations, indicated by the red region [10]. The enhanced magnetic response of the condensate to applied magnetic fields could enable a new class of smart materials that respond to changes in their magnetic environment.

Materials with variable valence such as the cuprate high-temperature superconductors, the manganite colossal magnetoresistance compounds, and the cobaltate exotic magnetic materials show a remarkable variety of new magnetic, metallic, superconducting, and high thermopower phases, all related to their layered oxide structures and to strong spatial and temporal electronic correlation among the variable valence states. These materials are in the vanguard of a host of unexpected and as yet largely unexplored correlated electron phenomena that promise a revolution in superconducting and magnetic behavior.

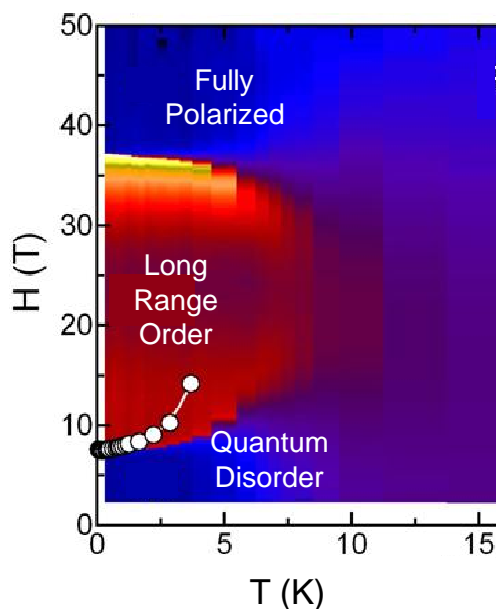


Figure 30. Field-induced Bose-Einstein condensation (red) of magnetic excitations in the insulating polymer piperazinium hexachlorodicuprate, a state that can only be reached in extreme magnetic fields.

Source: M. B. Stone, I. Zaliznyak, D. H. Reich, and C. Broholm, "Frustration-induced two-dimensional quantum disordered phase in piperazinium hexachlorodicuprate," *Phys. Rev. B* **64**, 144405 (2001).

The actinide compounds of uranium and plutonium and the rare earth compounds of cerium and ytterbium, especially in combination with the transition metals of variable valence such as manganese, rhodium, ruthenium, and iridium, show even more variable valence than the oxides, with up to five valence states observed in plutonium. Magnetic fields are uniquely powerful in probing the rich and still unexplored behaviour of the actinide multiple valence states, revealing a wealth of coupled charge, spin and structural phase transitions at extreme fields. Figure 31 shows an example of the breakdown of the standard model of metallic behavior in YbRh_2Si_2 , where magnetic field quenches the conventional metallic behavior and triggers a new phase with anomalous resistivity, heat capacity, and magnetic susceptibility [11]. Progress in this field requires the study of materials under high magnetic fields with multiple characterization capabilities, such transport, spectroscopy (neutron, x-ray, optical),

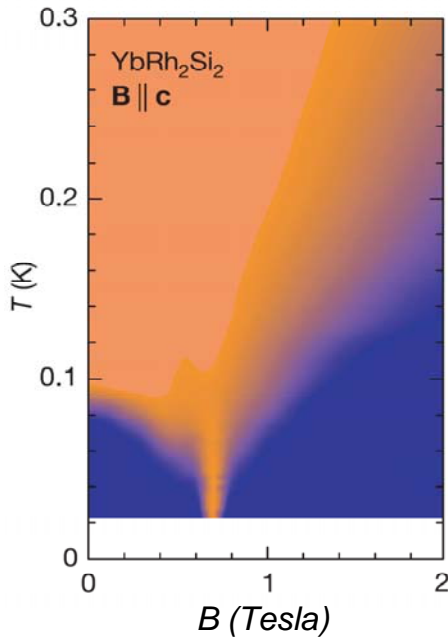


Figure 31. The exponent x in the resistivity $\rho = \rho_0 + AT^x$ of YbRh_2Si_2 , color coded to show its rapid change with magnetic field to an anomalous phase where conventional Fermi liquid theory suddenly and dramatically breaks down. Source: J. Custers, P. Gegenwart, H. Wilhelm, K. Neumaier, Y. Tokiwa, O. Trovarelli, C. Geibel, F. Steglich, C. Pépin, and P. Coleman, “The break-up of heavy electrons at a quantum critical point,” *Nature* **424**, 524 (2003).

and thermodynamics, as well as the application of multiple extreme environments such as high magnetic fields combined with high pressure and low and high temperatures. Synthesis of new materials requires precise control over material purity, doping, and homogeneity in the polyatomic compounds likely to exhibit novel forms of quantum order. This will require real-time, in situ analysis of these materials as they are synthesized and computational tools for understanding dynamic mechanisms in material synthesis and processing.

Scientific Questions and Opportunities

The existing limits of dielectric breakdown, of the magnetic field of permanent magnets, and of the current-carrying ability of resistive and superconducting coils are determined by atomic and nanoscale defects that have remained tantalizingly just beyond the reach of our best characterization tools. As discussed in the section on cross-cutting research, the advent of high-intensity sources of electrons, neutrons, and x-rays at user facilities and of scanning probe microscopies at the benchtop has broken through traditional barriers in space and time resolution of nanoscale behavior. These tools offer unprecedented opportunities to see directly the atomic and nanoscale behavior that controls macroscopic properties like dielectric breakdown, the strength of permanent magnets, and the current-carrying ability

vortices in superconductors that controls current-carrying capability. These observational challenges, too difficult for conventional scattering and imaging techniques, are coming within reach of new generations of intense sources and innovative scanning probe techniques. Designing new instrumentation to exploit these unprecedented opportunities for in situ measurements of the ultrasmall and ultrafast behavior of dielectric breakdown of insulators, magnetic structure, and moment reversal of permanent magnet materials and trapping and de-pinning of vortices in superconductors, is a central challenge for basic science.

The exploration of correlated electron behavior in extreme electric and magnetic fields and the use of extreme fields to synthesize new materials will enable powerful new directions for the discovery of new materials and phenomena. The richness of electronic and magnetic behavior in magnetic fields reveals a wealth of new phases and phase transitions that couple valence, spin, charge, and structure. These new phases and phenomena are the prototypes for new materials whose properties are controlled by strong correlations of valence and conduction electrons. Extreme electric and magnetic fields are crucibles for new materials that will extend the performance limits of magnets, superconductors, metals, and dielectrics.

Potential Impact

The dielectric breakdown of insulators, the need for high-field permanent magnet materials, and the limited current-carrying capability of superconductors are major technology gaps required for a secure energy future. Bridging these technology gaps will only be realized by fundamental research. Observing, understanding, predicting, and controlling the atomic and nanoscale behavior of defects and their emergent effect on macroscopic performance will lead to new generations of robust materials that will significantly increase the capacity and reliability and reduce the footprint of our electric power infrastructure.

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CROSS-CUTTING RESEARCH THEMES

CROSS-CUTTING RESEARCH THEMES

This workshop established a compelling picture of the current limitations and significant scientific challenges that are required for the development of new materials needed to address the most demanding requirements of future energy technologies. The development of new materials that operate at the theoretical limits of performance represents the most important challenge to be addressed by materials research. Success in this context would have truly transformational impacts on areas critical to securing the energy future of the nation. Addressing the challenges posed by extreme environments—energetic photon and radiation flux, chemical reactive conditions, high temperatures and pressures, extensive mechanical deformations, and electromagnetic fields—represents a high priority area of need, one that will only be resolved by significant advances in fundamental scientific understanding. The workshop identified Priority Research Directions, described in the previous sections, which illustrate the unique opportunities for improving both materials properties and processes involving extreme environments (Figure 32).

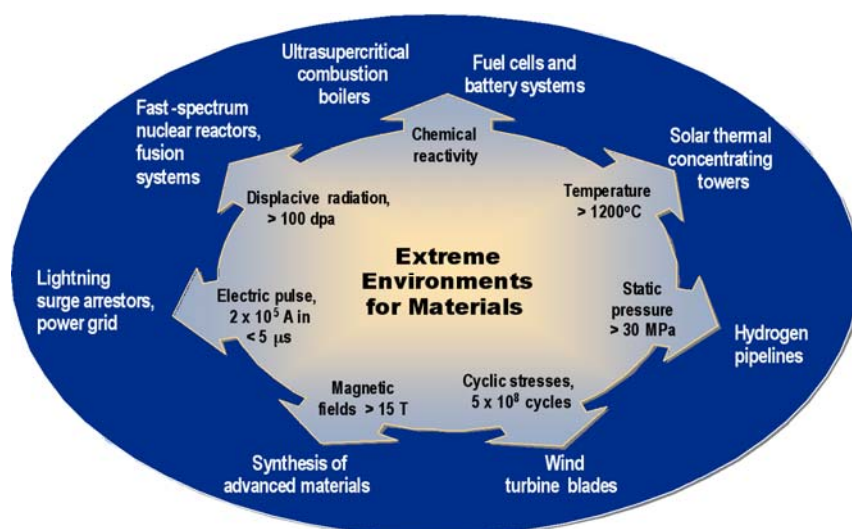


Figure 32. Materials in extreme environments cross-cut a wide range of energy technology needs, while sharing common theoretical and experimental approaches.

During the course of the workshop, the following four recurring science issues emerged as important themes:

1. Achieving the Limits of Performance
2. Exploiting Extreme Environments for Materials Design and Synthesis
3. Characterization on the Scale of Underlying Fundamental Interactions
4. Predicting and Modeling Materials Performance

These themes are summarized in the following sections.

ACHIEVING THE LIMITS OF PERFORMANCE

All of the workshop panels emphasized the need to understand the complex and inter-related physical and chemical processes that control the various performance limits of materials subjected to extreme conditions, identifying this as a major bottleneck in meeting future energy and security technology needs. This knowledge will lead to revolutionary breakthroughs in the design and synthesis of new materials for extreme environments. By understanding various mechanisms by which materials fail, it may be possible to increase the performance and lifetime limits of materials by an order of magnitude or more and thereby realize the full potential of a new generation of materials specifically designed for high performance under the most extreme conditions.

Compounding the difficulty of this challenge is the fact that in most energy technologies, more than one extreme environment exists, such as high temperature and pressure, high temperature and harsh chemicals, and many other combinations of environments. In today's fission reactors, for example, structural materials experience operating temperatures of about 300°C and damage levels up to about 30 displacements per atom. The relatively low operating temperatures limit thermodynamic efficiency to well under 40%. To extract substantially higher levels of electrical energy from the same amount of nuclear fission events, higher operating temperatures are needed. Understanding the atomic basis of defect creation and localization is needed to determine the intrinsic temperature and displacement dose limits of structural materials in radiation fields to meet future requirements for fission reactor materials.

Obtaining the required fundamental knowledge will require advances in characterization and computational tools, which together will provide unprecedented capabilities for observing physical and chemical processes at wide time and length scales. Recent developments in these areas demonstrate the exciting potential for even further advances that will, for the first time, allow us to observe, model, and predict changes in materials and associated processes at the atomic and molecular level. These capabilities set the stage for the design of a new generation of materials to meet future energy technology requirements.

Scientific Challenges: Future energy technologies will require operation at high efficiencies and with high reliability. This means that ultra-performance materials will be needed that can be subjected to extremes in temperatures, mechanical stress, electromagnetic fields, particle and electromagnetic fluxes, and chemical environments. The atomic- and molecular-scale mechanisms that define the fundamental performance limits of materials operating at these extremes (including combinations of extremes) need to be understood. This fundamental knowledge will enable accurate prediction of materials failure and lifetime and will provide the basis for the design of materials specifically tailored to be resistant to failure in extreme environments. For example, it may be possible to design new synthetic routes to strengthening materials. The distinct differences in structure, bonding, and physical properties of graphite and diamond are well known in nature for carbon. It may be possible to create altogether new carbon-based materials with properties of both (i.e., having both kinds of chemical bonds). Moreover, it may be possible to design materials with self-healing or adaptive characteristics that are tailored for the specific application environment. For example, it may be possible to design structural materials that have self-healing capabilities

by incorporating inclusions that terminate cracks. Understanding how high electric fields impact materials may lead to a new generation of wide gap semiconductors and insulators. Finally, this fundamental knowledge has the potential for opening the door to the discovery of new materials with designed functionality that combines durability and functionality, such as structural components that self-report stress.

Impact: Materials lie at the heart of energy technologies, and future energy technologies, will place unprecedented demands on materials as they are exposed to extremes in temperature, pressure, stress, photon and radiation flux, electromagnetic fields, and chemical environments. Understanding the fundamental mechanisms of how these extreme environments impact materials at the atomic and molecular level and cause changes that eventually result in materials failure is required to form a basis for designing transformational new materials for applications in future energy technologies. Examples of such energy technologies include

- Higher temperature behavior for improved thermodynamic efficiency of boilers
- Higher stress resistance for vehicle weight reduction
- Higher radiation field performance for fission and fusion reactor components
- Higher EM field behavior for motors and generators
- Reduced chemical reactivity for efficient hydrogen conversion and energy storage

EXPLOITING EXTREME ENVIRONMENTS FOR MATERIALS DESIGN AND SYNTHESIS

An ultimate goal in materials science is to develop control strategies for synthesis in which the precise details of atomistic arrangements can be essentially programmed with any arbitrary level of complexity and hierarchy of length scales. Extreme environments offer a unique opportunity to develop new strategies for controlling the atomic- and molecular-level structure of materials in unprecedented ways. Extreme conditions provide an effective forcing strategy—essentially new “knobs” that can be manipulated for the synthesis of revolutionary new materials. These “knobs” can be in the form of high temperatures, pressures, strain rate, radiation fluxes, or external fields, alone or in combination, and can follow two paths. The first path is that of thermodynamic equilibrium, in which case the dissipation of free energy drives the material towards a thermodynamically determined outcome. In such instances, the complexity of kinetic constraints and metastability can be overcome and well-defined structural outcomes engendered. The second path relies on “kinetic” control. Here the dynamics of energy dissipation within a material leads to a non-equilibrium outcome. Controllable non-equilibrium phenomena represent a novel approach to manipulating both structure and properties in materials over broad ranges.

It is becoming possible to shape intense fields—optical, electric, and magnetic—in ways that were heretofore unimaginable; this in turn offers an opportunity to use them as a new tool for designing structures in complex three-dimensional forms. Physical extremes, such as extreme pressure and temperature, also offer new opportunities to control structure. Strongly driven processes—such as those provided by intense particle fluxes—can profoundly disrupt atomic-scale structure, doing so in ways that provide new means to control it—to render a structure with specific nanoscale textures, glassy or amorphous forms, or precise non-

equilibrium organizations of more longer-ranged (mesoscopic) architectures, as specific examples. Using one or more of these extreme environments provides exciting new capabilities with which novel materials with specific structures and properties can be synthesized.

Scientific Challenges: Fundamental advances in understanding the atomic-level effects of the interaction of extreme environments with materials will give rise to entirely new abilities to control the synthesis and processing of materials and drive the functional performances of materials to their most fundamental (intrinsic) limits. For example, it may be possible to develop new materials with extraordinary temperature resistance using synthetic conditions that combine extremes in temperature, pressure, and chemical environments. Employing tailored pulses of photons matched to a specific vibrational mode of the material may be used to enhance surface stress and lead to increased hardness, thus producing a material with improved wear resistance and possibly better corrosion resistance. High magnetic and electric fields affect phase stability, phase solubilities, diffusion barriers, dislocation cores (magneto- and electro-plasticity), stacking fault energies, phonons, and magnons, and application of these fields can alter phases in materials to produce new materials with novel functionalities. Higher microwave and radio frequency fields used in combination with high gas pressures of strongly reactive species hold the promise of dramatically increasing material growth rates and creating new materials by chemical vapor deposition. Taking advantage of these extreme environments, combined with emerging capabilities in nanoscience, has the potential to revolutionize the field of materials synthesis.

Impact: Progress in energy production is, in general, ultimately limited by materials. Materials created in extreme environments, especially multiple extreme conditions, can be radically different from those produced at ambient conditions and can provide another “knob” that can be changed to synthesize materials with specific properties. The ability to use these conditions to design new materials with extraordinary properties could have enormous impact on the development of new materials for future energy technologies. The key to this vision is understanding the fundamental processes that form the foundation of the interaction of extreme environments with materials.

CHARACTERIZATION ON THE SCALE OF UNDERLYING FUNDAMENTAL INTERACTIONS

The ability to characterize the structure and function of materials on the atomic and molecular scale—the scale of the underlying fundamental interactions—is an exciting new opportunity for understanding materials under extreme environments. Continued advancements in analytical tools are making it possible for the materials community to observe changes in structure and dynamics over broad timescales (femtoseconds to many seconds) and length scales (nanoscale to macroscale). Advances in characterization tools, including diffraction, scattering, spectroscopy, microscopy and imaging, are needed. Of particular importance is the need to combine two or more of these characterization tools to permit so-called “multi-dimensional” analysis of materials and surfaces in situ. These advances in characterization capabilities will enable the elucidation of fundamental chemical and physical mechanisms that are at the heart of materials performance (and failure) and

catalyze the discovery of new materials required for the next generation of energy technologies.

Scientific Challenges: Advances in analytical tools are critically needed to understand the behavior of materials under extreme conditions from the nanoscale to the macroscale. For example, new tools are needed that will provide unprecedented capabilities to probe materials on the atomic and molecular length scale. This requires the ability to observe materials and defects in materials on unprecedented short length scales (sub-Angstrom) and short timescales (femtoseconds). Advances in ultrafast lasers and synchrotron light sources will enable us to watch chemical bonds being formed and broken. On the Angstrom and femtosecond scale, the processes that give rise to nucleation and chemical kinetics as well as the first glimmers of phase transformations begin. Connecting these observations to their macroscale consequences is an experimental grand challenge. Measurements on these scales also enable studies of extremely non-equilibrium and excited-state phenomena that are not accessible at “ambient” conditions. In addition to observing these processes, it is critical to be able to measure these effects quantitatively.

Complementary in situ, multi-scale tools are required to reveal the mesoscale and macroscale consequences of processes that occur at the atomic and molecular level. New imaging and spectroscopic techniques, as well as other techniques that probe materials behavior, are needed to understand the many complex and interrelated physical and chemical phenomena that underlie materials performance under extreme environments. To meet these goals, it is critically important to probe materials properties associated with different controlling physical and chemical mechanisms under all types of extreme conditions. This will require designing special experimental environments in which materials can be studied in situ. For example, a high-pressure, variable-temperature instrument dedicated to extreme condition studies at the Spallation Neutron Source has been completed (Figure 33). Similarly, new analytical tools need to be co-located at other major facilities and in the laboratories of

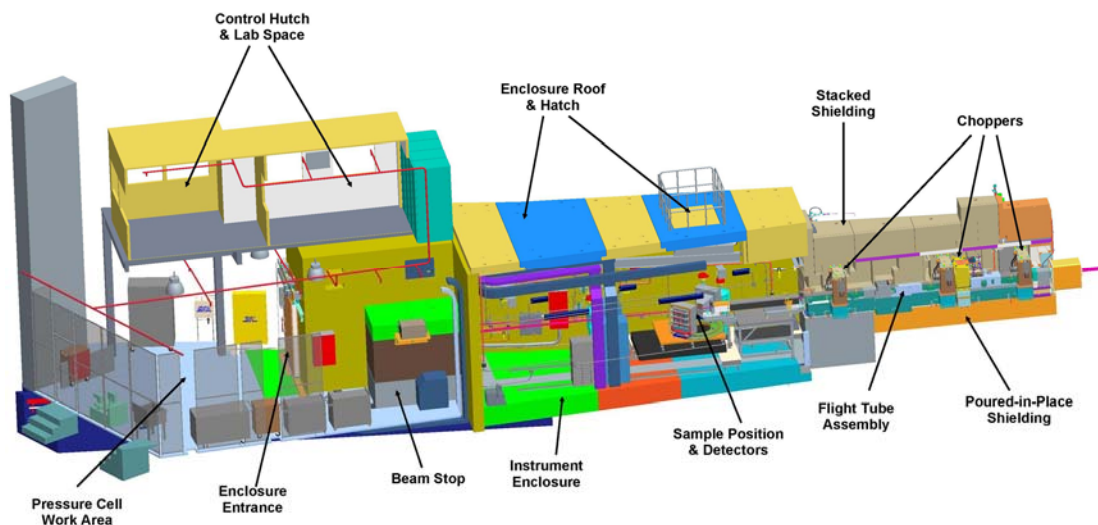


Figure 33. SNAP (Spallation Neutrons at Pressure), the high-pressure, variable-temperature instrument at the Spallation Neutron Source, is the first neutron scattering instrument in this country dedicated to in situ studies of materials extreme conditions. Courtesy of Chris Tulk and Jamie Molison, Spallation Neutron Source.

individual investigators to take advantage of conditions generated at thermomechanical, electromagnetic, chemical, and photon and radiation flux extremes.

When coupled with advances in theory and simulation (next section), the challenge will be to perform “experiments on the scale of simulation” and/or “simulations on the scale of experiments.” This convergence of characterization and simulation capabilities represents an unprecedented opportunity for understanding the complex physical and chemical phenomena which occur at the atomic level in materials under a wide range of extreme conditions.

Impact: These new analysis capabilities, which will enable the study of materials from the nano- to macro-length scales and from femto- to many-second timescales under realistic conditions, will revolutionize our ability to understand the performance of materials under extreme environments, provide unprecedented capabilities for understanding the effects of extreme conditions on materials performance, and open new vistas for designing new materials for future energy and security needs.

PREDICTING AND MODELING MATERIALS PERFORMANCE

All four panels in this workshop noted that significant progress in addressing current technical bottlenecks facing materials under extreme environments will require that theory and simulation be closely coupled with experiment. Recent advances in theory and algorithms, coupled with enormous and growing computational power and ever more sophisticated experimental methods, are opening up exciting new possibilities for taking advantage of predictive theory and simulation to design and predict the properties and performance of new materials required for extreme environments. For example, there has been enormous progress in the last decade in using quantum mechanical approaches to predict and analyze many important systems in materials science. Indeed, first-principles density functional theory-based electronic structure calculations have become the basis upon which to discuss materials properties at the fundamental atomic level. At longer length and time scales, large atomistic molecular dynamics simulations based on classical potentials and new continuum and quasi-continuum approaches (dislocation dynamics, phase field methods) have also undergone rapid development, as has the integration of these approaches within so-called multiscale simulation approaches (Figure 34).

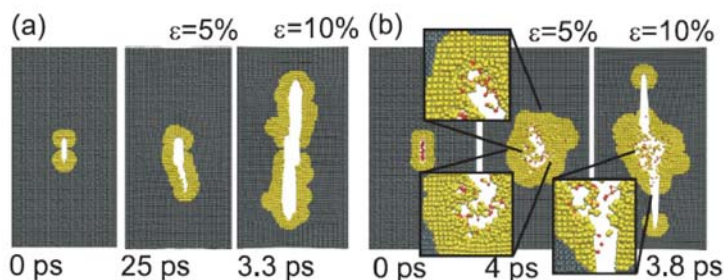


Figure 34. Recent simulations demonstrate the importance of chemical reactivity on crack tip propagation. The simulation combines reactive and nonreactive classical treatment of the atomic forces to efficiently represent the complicated dynamics and chemistry at the crack tip. The figure shows simulated crack tip propagation in silicon without (a) and with (b) chemical reactions. Reactive silicon is gold, nonreactive silicon is grey, and reactive oxygen is red [6]. Sources: A. van Duin et al., “ReaxFF: A reactive force field for hydrocarbons,” *J. Phys. Chem. A* **105**, 9396–9409 (2001) and M. J. Buehler et al., “Multiparadigm Modeling of Dynamical Crack Tip Propagation in Si Using a Reactive Force Field,” *Phys. Rev. Lett.* **96**, 095505 (2006).

There is a surprisingly wide diversity of phenomena encompassed by the response of materials to extreme environments. Here extreme implies that the energy of the environment—high pressure, thermal energy, chemical energy; kinetic energy of incident particles, electron beam, and photon flux; as well as interaction energy with applied electrical and magnetic fields—approaches the energy of the chemical bonds of the material. Such extreme environments then result in the disruption of the electronic structure (as in the application of intense photon, magnetic, or electric fields), the nuclear positions (as in radiation damage), or both (as in high-temperature phase transformations, microstructure evolution, fracture, and corrosion). Because so much of the functionality of real materials is ultimately controlled by the properties defects—point defects, defect clusters, stacking faults, antiphase boundaries, grain boundaries, compositional modulations, dislocation structure, and microstructure—it is clear that methods that can not only deal with the interaction of ideal materials with extreme environments but also with the influence of extreme environments on the defected structure of real materials will be required in order for theory and modeling to have maximum impact.

When discussing the modeling and prediction of materials properties in extreme environments, it is important to distinguish situations where currently available approaches can already have significant impact from situations where current theory is either inadequate to deal with extreme environments or is relatively unexplored and new theoretical advances are required. For example, modern first-principles electronic structure methods can be readily used to identify structures and screen properties of the presently unknown materials that can be formed under extreme conditions. When closely integrated with experiment, this alone could help facilitate the discovery of new materials which themselves have extreme properties—novel high-density phases with exceptional mechanical properties and new functional materials with highly enhanced ferroelectric, magnetic, and superconducting properties. Conversely, first-principles approaches can provide insight into possible synthesis routes under extreme conditions. However, powerful as modern first-principles techniques are, they are not equally applicable to all classes of materials. In particular, standard approaches fail to properly describe many strongly correlated systems, including such important materials as transition oxides and materials containing 4f- and 5f-electron rare-earth and actinide elements; thus, development of robust parameter-free electronic structure methods for such materials is a prerequisite for exploiting such materials. Furthermore, new approaches will be needed for extreme environments where electronic excitations and/or quantum dynamics of nuclei are important in the chemistry. An example of the latter is provided by the expectation for next-generation free electron laser-based facilities to deliver extremely intense and short (femtosecond to attosecond) photon pulses. Because such pulses have the capability to drive the electron (and material) system far from equilibrium, new theory will be required to understand what such experiments tell us about the dynamics of conventional materials properties (e.g., in pump-probe experiments to study chemical reactions or magnetic switching) or, conversely, how such extreme excitations can be used to produce unconventional or extreme materials and materials properties. Similar arguments are also relevant to the application of intense electric and magnetic fields.

Despite the recent rapid progress in first-principles simulations, the time and length scales of accurate quantum simulations (typically 100 to 1000 atoms) fall woefully short of the scales

required for designing and understanding experiments at the microstructural and system levels; as a point of reference, a 20-nm cube of material contains ~1 million atoms. Thus it is important to further develop the full spectrum of approaches—quantum, atomistic, continuum—such that they are each able to treat increasingly complex materials and extreme environments as well as to integrate them into sophisticated multiscale simulation strategies. Generally, multiscale modeling strategies can be divided into two groups, those based on parameter passing, in which data obtained at a particular length scale is parameterized and used as input to simulations at progressively increasing length scales (Figure 35), and embedding strategies, in which a theoretical method capable of representing physical phenomena at one length scale is seamless, embedded within the next highest length scale. The former generally leads to disjoint simulations at the different length scales, while the latter leads to a single simulation and as such is typically best suited to dealing with localized phenomena, for example the physics associated fracture and motion of a crack tip. As with first principles, there is a need both to apply these approaches to studies of extreme environments as well as to develop new approaches for dealing with some of the additional complexities attendant to extreme environments. Additionally, combining the effects of multiple extremes through coupled models will pose some important challenges but is critical in assessing the performance of materials in conditions that are required for future energy and security applications.

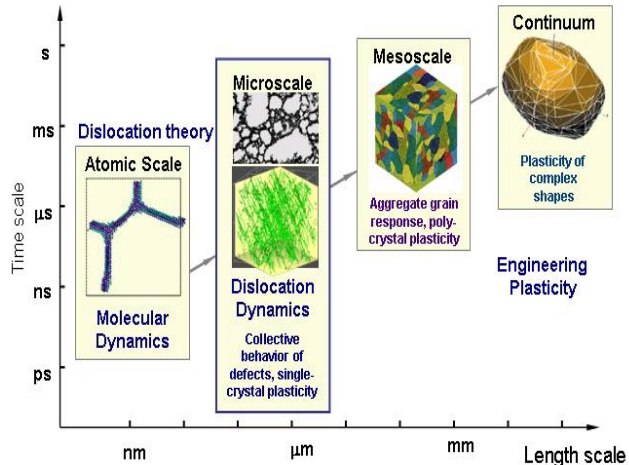


Figure 35. Understanding materials under the full suite of extreme conditions requires information on their behavior over length and time scales spanning orders of magnitude—from atomic, micro, meso, and continuum levels. The accurate theoretical treatment of this response requires altogether new “multiscale” modeling approaches.

While the availability of relatively inexpensive but powerful cluster computers and continued development high-performance computers—now rapidly approaching the petaflop/s scale—make it possible to model ever larger (and complex) systems they are generally of little help in addressing the timescale over which simulations can be performed. At the quantum level, state-of-the-art simulations are typically limited to a few picoseconds, even for quite simple systems; for classical potential atomistic molecular dynamics simulations, typical simulation times rarely exceed nanoseconds. Given the need to address the long time stability of materials under extreme conditions, there is a clear need for the development of new theoretical techniques that can include the necessarily fast time scales of electronic and nuclear motions that accompany bond rearrangements on the one hand and the slow diffusion-limited process that results in microstructure evolution and structural stability of real materials on the other.

Scientific Challenge: Extreme environments occur when external stimuli strongly couple to the properties of the material. This strong coupling challenges our ability to use well-

established simulation methodologies that have been developed for ambient conditions. The clear challenges are threefold: to develop the theoretical tools necessary to describe new phenomena and processes that occur under extreme conditions, to integrate these methods across length scales to model and predict the properties of real materials response to extreme environments, and through integration of theory and model with experimental synthesis and characterization, to accelerate scientific discovery and shorten the development cycle from discovery to application across the field.

Impact: The development of new predictive models of materials under extreme environments has the potential of dramatically accelerating the discovery and development of breakthrough materials, which are required to meet future national needs in energy and security. Successful models are critical for realizing a new generation of materials whose behavior approaches theoretical limits of performance or materials with yet unimagined properties that may result from synthesis and characterization under extreme conditions. In particular the development of a new generation of theory and modeling tools will be critical to success in the other three crosscutting themes. Simulations, ranging from quantum simulations of local atomic/chemical processes to multiscale simulations of real microstructures and failure modes, will be critical in achieving the limits of performance. The use of existing and yet to be developed first-principles methods for describing the equilibrium and excited-state properties will be an invaluable tool for both screening new materials synthesized under extreme environments and for studying and suggesting novel synthesis routes. Finally, quantum theory and simulation of static and dynamic response will be indispensable for the exploitation of atomic-level characterization tools and will provide the natural language for understanding the fundamental interactions that control materials properties in extreme physical environments or that give rise to new physics and chemistry when stimulated by intense external fields.

CONCLUSION

Although materials under extreme environments are central to energy and other technologies, we know relatively little about how and why materials respond under these conditions. Most of our information about materials under extreme environments is indirect—it is obtained after, but not during, exposure. Particle irradiation, for example, produces a dynamic steady state of atomic displacements due to collisions, recombination of displaced atoms with the vacancies they have just created, and migration of the displaced atoms and vacancies to form larger clusters. The energy deposited by particle irradiation heats the material, a key factor affecting the rate of damage creation, relaxation, and migration. Measurements in ambient conditions see only the static configuration of atoms left after the exposure, a faint shadow of the rich mixture of dynamic interactions that causes the damage. To understand the mechanisms and learn to mitigate the effect of particle damage, we must develop in situ experiments that see the dynamics in real time. Such experiments are coming within reach, as ever brighter sources of electrons, x-rays, and neutrons with ever higher spatial and temporal resolution allow sensitive measurements on ever smaller sections of materials.

A second reason for our limited knowledge of materials under extreme environments is the enormous complexity of the damage such environments cause. Chemical corrosion of stainless steel, for example, proceeds by a multitude of reactions, the mix depending on

changing conditions of temperature, pressure, surface structure, and chemical composition. This complex environment is far from equilibrium, and far from the ideal controlled conditions of the perfect experiment where each variable is separated and studied in isolation. In chemical corrosion, the variables are hopelessly entangled, a change in one inducing dramatic changes in the others. Corrosive damage is a unique amalgam of all the variables, a prime example of *emergent behavior* that defies simple explanation.

Unraveling the emergent behavior of materials under extreme environments requires more than observing the response of the material in situ. We must understand and model this behavior to see how extreme environments damage, degrade, and ultimately disable materials. One of the most pervasive and difficult challenges blocking this understanding is the diverse range of time and length scales that govern the behavior. Often the initial damage seems negligible: a few atoms displaced from their equilibrium positions in the crystal lattice in a few picoseconds. These isolated damage sites, however, are the seeds of ultimate materials failure. With time the number of damage sites grows, the defects move about within the crystal, cluster into extended defects like voids or dislocation loops, and these clusters themselves begin to interact through the long-range strain fields they induce. Macroscopic performance is degraded on length scales of millimeters, and failure such as cracking can develop on centimeter or meter scales over timescales of hours or months. The challenge of such extreme multiscale behavior is connecting the diverse scales. Although the damage proceeds continuously through the length and time scales, the structure and dynamics at small scales is virtually invisible at large scales. The challenge is the same in biology: visible functions like breathing or eye blinking are completely determined by invisible interactions of nanoscale genomes and proteins. Capturing the multiscale damage evolution of extreme environments in a single computational format is a daunting challenge that is just now coming within reach.

Finally, the knowledge gained from these studies will reveal new avenues to design materials at the nanoscale that will result in greatly enhanced performance and functionality. Further, once the cascade of events that results from the interaction of the environment with the materials is understood, the door will be opened to using these extreme environments as another parameter to synthesize new materials and process materials with extraordinary properties. The impact of these new materials on future energy technologies will be enormous and will be felt across a broad range of applications such as security, industry, construction, and electronics and consumer goods.

CONCLUSION

CONCLUSION

Among the pressing challenges facing the world today, none are more universal and daunting than energy, environment, and security. Global demand for energy will double by 2050, and triple by the end of the century, putting ever more pressure on science and technology to find new energy sources and more efficient ways to use them. Global warming, accelerated by greenhouse gas emissions from fossil fuels that make up 85% of our energy supply, threatens the stability of our environment. The energy and security technologies that address these global challenges depend critically on materials operating in extreme environments. Boosting the efficiency of coal-fired power plants from 35% to 60% with ultra-supercritical steam requires raising operating temperatures from 540°C to 760°C and operating pressures from 16.5 MPa to 37.9 MPa. Such environments are extreme not only for thermomechanical stress but also for severe corrosion from steam at high temperature and pressure. The operating temperature of next-generation nuclear reactors will jump from 350°C today to over 1000°C for Generation IV systems, with neutron fluxes an order of magnitude higher than today. Fusion requires first wall materials operating at equally high temperatures and neutron fluxes ten times larger than Generation IV fission reactors. Megawatt lasers for igniting fusion pellets are currently limited by the optical materials for focusing and directing high-intensity photon fluxes, which fail a factor of ten below their intrinsic flux limits. Delivering electric power at high density in crowded urban areas requires raising the current-carrying capability of superconductors by a factor of ten and their operating temperatures by a factor of four. Next-generation semiconductor electronics requires dielectric materials that can withstand the extreme electric fields of nanometer-thin gate geometries and still operate in the high-radiation environments of space, fission, and fusion reactors. Understanding chemical reactions in entirely new domains of extreme conditions using new classes of materials for energy storage and release is required for future transportation and propulsion needs.

Materials that can operate reliably in extreme environments are a critical roadblock to energy and security technologies needed to move into the future. These extreme environments are no longer on the exotic fringes of science and technology; they have entered our everyday world. Despite their importance, we have relatively limited scientific knowledge of their effect on materials performance and failure modes. We now face the critical challenge of understanding why, for example, dielectrics fail catastrophically after years of service under the same electric field; high-temperature superconductors fail at one-tenth the current they can theoretically carry, and metals and thermoplastics under tensile stress crack and fail when exposed to corrosive chlorides or nitrides. Extreme corrosion, temperature, and radiation are critical environments associated with our aging nuclear stockpile. Achieving a predictive understanding of materials performance in these and other extreme environments is essential to a wide range of applications of importance to this nation.

The Basic Energy Sciences' Basic Research Needs Workshop on Materials under Extreme Environments examined four extreme environments and their effect on materials: energetic flux extremes, chemically reactive extremes, thermomechanical extremes, and electromagnetic extremes. The workshop found remarkable similarities in the effect of these four extremes on materials performance and failure. One common feature tying all these

extremes together is atomic and nanoscale defects. Performance degradation and materials failure begin when tiny, isolated defects such as vacancies and interstitial atoms appear in the crystal structure of materials. Under ordinary conditions, these defects peacefully coexist in equilibrium with their perfect crystal hosts. Under extreme environments, however, these tiny defects continue to form, migrate, coalesce, and grow into larger clusters that assemble into networks. Eventually the network of defect clusters dominates the material, degrading macroscopic performance and potentially leading to materials failure. The multiscale progression of damage from atomic and nanoscale defects to macroscopic networks of defect clusters spans a wide range of space and time—picoseconds to years (or millennia in the case of radioactive waste) and subnanometers to meters.

To overcome the challenge presented by materials under extreme environments, fundamental research is needed in two critical areas. The first is characterizing and understanding the multiscale progression of defect structures from the nano to macro scales. New characterization tools based on scanning probe microscopies and on scattering of electrons, neutrons, x-rays, and light sources are making it possible to detect ever-smaller signals with nanoscale spatial resolution and femtosecond time resolution. These existing and emerging characterization tools will dramatically enhance the power of experiments to see atomic and nanoscale defects and watch their dynamics as they migrate, coalesce, and assemble in macroscale networks. In situ experiments that can observe defect evolution, as it occurs, will supply the critical missing links between defect structures on different length scales. These missing links have, until now, precluded understanding the complex chain of nano-to-macro defect evolution.

Beyond characterization, multiscale theory is needed to describe the evolution of defect structures and predict their effect on macroscopic performance and failure. Capturing multiscale evolution in a consistent computational framework is a major challenge, not only for materials under extreme environments but across all of materials physics. We are just now learning how to organize multiscale simulations by rolling up the output of calculations at a given length scale and passing it as input to calculations at the next higher length scale. The use of density functional theory for electronic behavior and molecular dynamics for atomic positions and motions would enable, in principle, a complete description of defect behavior in an unprecedented range of length scales. The challenge is to integrate these two techniques to predict macroscopic performance from nanoscale behavior. The nano-to-macro defect evolution of materials under extreme environments provides not only a compelling challenge for multiscale theory but also a stringent test of its validity.

The second critical fundamental research area needed to overcome the challenge of materials under extreme environments is innovative synthesis. Over the last half century, the vast majority of materials we have synthesized have been made and are used under near-equilibrium conditions. Traditional synthesis manipulates temperature, composition, and sometimes pressure to access an equilibrium phase in the material's phase diagram and then recovers this phase to ambient conditions by slowly or rapidly changing the thermodynamic variables. This traditional near-equilibrium approach cannot access the immense untapped conditions that are inherently far from equilibrium. Delivering energy to materials by energetic particle or photon beams, or changing pressure, electric, or magnetic fields faster

than equilibrium can be established, opens entirely new avenues to materials synthesis. These far-from-equilibrium conditions create novel atomic configurations within the solid that dramatically alter its properties and functionalities. Using extreme environments to produce new materials that are inaccessible from traditional near-equilibrium approaches presents an immense opportunity to meet future energy needs. Exploration of materials under extreme environments is also leading to the discovery of new physics and chemistry, thereby deepening our understanding of matter in the broadest sense.

Many of the materials now used in energy and security technologies had their origins in the last century. However, the need for materials that can withstand and reliably perform in extreme environments goes far beyond the vision of the last century. Traditional materials are now the limiting factor in developing new energy technologies, seriously restricting efficiencies and output capacities. The emerging capabilities in nanoscience, characterization, and computation are providing fundamental scientific knowledge that has enabled the recent discovery of whole new families of materials with remarkable properties, such as the high-temperature cuprate superconductors, the manganites showing colossal magnetoresistance and other unconventional correlated electron behavior, and the artificially layered oxides where targeted properties such as multiferroic functionality can be programmed in. These examples show the power of innovative synthesis to create entirely new classes of materials with unprecedented properties enabled by fundamental science. Extreme environments offer a novel dimension with which the properties and functionalities of materials may be tuned. This “knob” represents an exciting prospect for developing a new generation of materials required for future energy technologies.

The knowledge imparted by research in the two areas described above will also provide insight into how complexity can be harnessed to design new materials functionality. Complexity brings with it additional degrees of freedom that interact to produce emergent behavior. High-temperature superconducting materials require four or more elements to exist; the phenomenon is unknown in materials with fewer components. The complex oxide family of materials is remarkable for the range of behaviors it contains, sometimes switched by only a subtle change in composition. Ferroelectrics, magnets, semiconductors, insulators, metals, and superconductors are all represented within a single structure type, and understanding the atomic-level basis for this emergent behavior will unlock the rule set required to design materials with novel functionality.

The search for new materials that operate at extreme environments is a major scientific challenge, but only one of many materials challenges that are basic to progress in science and technology. While we are seeing dramatic progress in creating incisive new characterization tools using scattering of electrons, neutrons, and x-rays at intense sources, much less progress is being realized in the synthesis of new materials displaying exotic new behavior worthy of these characterization tools. The remarkable development of forefront characterization tools has created a “synthesis gap” that is now the bottleneck in materials science and engineering. Major emphasis on creative materials synthesis using innovative near-equilibrium and far-from-equilibrium approaches is critically needed to bridge this gap.

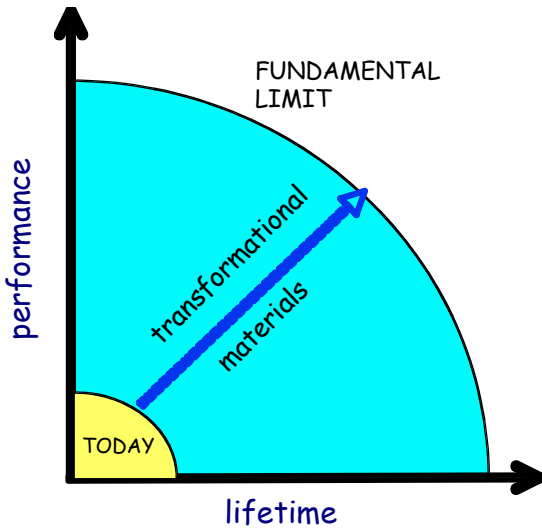


Figure 36. Today's materials typically fail at one-tenth of their fundamental limits. Finding the root causes of this early failure using emerging characterization and simulation tools enables design and discovery of transformational materials that will achieve the fundamental limits of performance and lifetime.

The workshop found a second commonality spanning extreme environments: materials typically fail at one-tenth the performance and lifetime levels they can intrinsically achieve, as illustrated in Figure 36. This early failure of materials is the primary factor limiting the growth of new technologies for energy and security. Although early materials failure is a major challenge and roadblock to progress, it is also an enormous opportunity. Because the root causes of early failure are not intrinsic, they can be overcome with sufficient knowledge of their genesis and growth. We know in broad outline that the root causes of early failure are tiny atomic and nanoscale defects that evolve over multiple time and length scales and ultimately disable macroscopic performance. The challenge is to use emerging characterization tools such as scanning probe microscopies and scattering from intense sources combined with

innovative multiscale modeling to capture the entire range of defect formation and evolution across all the relevant length and time scales. Armed with this fundamental knowledge, we are prepared to face the ultimate challenge of intentionally interrupting the multiscale evolution of defect structures to eliminate early materials failure. The workshop identified several promising opportunities to accomplish this goal by creating defect tolerant or self-healing microstructures in known materials and by synthesizing entirely new classes of materials that are intrinsically resistant to defect formation and evolution. These innovative approaches have the potential to unlock orders-of-magnitude improvement in the performance and lifetime of materials under extreme environments that will transform the efficiency and capacity of today's energy and security technologies to the much higher levels required to meet tomorrow's needs.

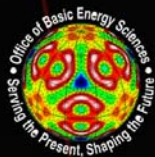
APPENDIX A:

**TECHNOLOGY AND APPLIED R&D NEEDS FOR MATERIALS
UNDER EXTREME ENVIRONMENTS**

Technology and Applied R&D Needs for Materials Under Extreme Environments

Resource Document for the Workshop
on Basic Research Needs for Materials
Under Extreme Environments

May 2007



Cover image: Modeling combustion in a gas turbine engine. Gas turbine combustor liners operate in high-temperature combustion gas environments and are often damaged. Work performed by Suresh Menon, Georgia Institute of Technology, under the sponsorship of the Army Research Office.

TECHNOLOGY AND APPLIED R&D NEEDS FOR MATERIALS UNDER EXTREME ENVIRONMENTS

Resource Document for the Workshop on Basic Research Needs for Materials Under Extreme Environments

May 2007

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ABBREVIATIONS, ACRONYMS, AND INITIALISMS

a-Si:H	amorphous hydrogenated silicon
AFE	antiferroelectric
<i>B</i>	high magnetic
<i>BT</i>	high magnetic fields coupled with high temperatures
BWR	boiling water reactor
CMC	ceramic matrix composite
COHMAG	Committee on Opportunities in High Magnetic Field Science
CRA	corrosion-resistant alloy
CS	central solenoid
CVD	chemical vapor deposition
D-T	deuterium-tritium
DFT	density functional theory
dpa	displacements per atom
DOE	Department of Energy
DOE/FE	DOE Office of Fossil Energy
E-85	15% gasoline, 85% ethanol
EBC	oxide-based coating for environmental protection
EDLC	electric double layer capacitor
ELM	edge-localized mode
EM	electromagnetic
EMAT	electromagnetic acoustical transducer
EMP	electromagnetic pulse
FE	ferroelectric
GaN	gallium nitride
HAWT	horizontal-axis wind turbine
HEV	hybrid electric vehicle
ICF	inertial confinement fusion
IGCC	integrated gasification combined cycle
IL	ionic liquid
ITER	International Thermonuclear Experimental Reactor
J	induced surface current
LSD	local spin density functional theory
MEMS	microelectromechanical system

NMR	nuclear magnetic resonance
NNSA	National Nuclear Security Administration
NSF	National Science Foundation
ODS	oxide dispersion strengthening
PEM	proton exchange membrane
PEMFC	proton exchange membrane fuel cell
PF	poloidal field
PFC	plasma-facing component
PIL	protic ionic liquid
PMI	plasma-material interaction
PV	photovoltaic
PWR	pressurized water reactor
R&D	research and development
rf	radio-frequency
RTIL	room temperature ionic liquid
SGEMP	system-generated electromagnetic pulse
SI	sulfur-iodide
SIA	self-interstitial atom
SiC	silicon carbide
SOFC	solid-oxide fuel cell
T	Tesla
TBC	thermal barrier coating
T_c	transition temperature (to a superconducting state)
TF	toroidal field
TWIP	twinning-induced plasticity
USC	ultrasupercritical

1. INTRODUCTION

New materials are critically needed to realize the full potential of any advanced energy system, whether it is based on solar, fossil, hydrogen, nuclear, or other energy sources. These new materials must have significantly enhanced capabilities that will allow them to operate robustly for prolonged periods of time in extreme environments, such as photon or radiation flux, corrosive chemicals, stress, strain, and high or low temperatures or pressures—as well as combinations of these environments. For example, solar energy conversion requires new materials that can withstand intense photon and thermal flux for many years of operation. High-performance batteries designed for use with plug-in electric vehicles must be fabricated with new electrode materials that can withstand extremes in reactive chemical and high electrical current environments without breaking down. Materials employed in the generation of fission and fusion energy need to perform reliably at extremes of radiation flux and temperature. Even relatively simple energy systems, such as wind turbines, require materials that can withstand extraordinarily high, and cyclic, loadings.

It is widely recognized that today's materials will not meet the demands of tomorrow's energy applications.¹ In addition to energy applications, the development of new materials that can perform in extreme environments is essential to other applications within the Department of Energy's (DOE) mission, such as national security, and to broader applications in defense, space, and earth science. Developing an entirely new generation of materials that can meet the requirements for future energy needs will be achieved only by investing in fundamental research. This research would allow us to unravel the complex effects that occur when materials are exposed to extreme conditions. This knowledge would then enable the design of new materials that will exhibit optimum performance in extreme environments. In addition, this knowledge may enable us to exploit these same extreme environments of temperature, pressure, chemical composition, and external fields to tune the intrinsic properties of materials and even create altogether new materials for future applications in energy and other fields.

This document was produced in preparation for a DOE Office of Basic Energy Sciences workshop, "Basic Research Needs for Materials Under Extreme Environments." This workshop will identify key, basic research directions that could provide breakthroughs needed for developing next-generation materials. This document is intended to provide a high-level assessment of current technology needs, primarily in energy applications, that require operation under extreme conditions. Because the range of applications in which materials are exposed to environmental extremes is so broad, this document is not intended to be comprehensive. Rather, it is intended to provide some common background for participants in the "Basic Research Needs for Materials Under Extreme Environments" workshop and to set the technological basis for the workshop. Sections of this report have been organized to a specific extreme environment that can cut across many energy technologies. For example, extreme chemical environments can apply to

¹ Basic Energy Sciences Advisory Committee, *Basic Research Needs to Assure a Secure Energy Future*, Proceedings of Basic Research Needs to Assure a Secure Energy Future, John Stringer, chair, Gaithersburg, MD, February 2003.

fossil energy, electrical energy storage, nuclear energy, and the synthesis of new materials critically important for many energy systems. The document was prepared by Oak Ridge National Laboratory in consultation with numerous subject matter experts from other national laboratories, universities, and industry.

2. ADVANCED ENERGY AND NATIONAL SECURITY SYSTEMS AND THEIR EXTREME ENVIRONMENTS

2.1 NUCLEAR ENERGY: FISSION AND FUSION

Fission power, in the form of nuclear power plants, currently supplies 18–20% of U.S. electricity and is expanding worldwide. However, both the disposal of intact spent nuclear fuel and the management of the separated fission products that result from fuel reprocessing present major technical and institutional challenges that must be met if nuclear power is to continue to be a major energy supply technology in the future. Two advanced technologies are the focus of worldwide research activity: the high-temperature gas-cooled thermal reactor and the fast-spectrum liquid metal-cooled reactor for burning transuranic waste elements.

Nuclear fusion is a possible long-term complement to fission power and has the potential to provide an environmentally attractive, practically inexhaustible, and reliable source of energy. The leading technology option for future fusion power plants involves magnetically confined plasmas, commonly termed magnetic fusion; and the latest major undertaking is the ITER, shown in Fig. 1, which aims to demonstrate the feasibility of fusion power. (More information about ITER is available at www.iter.org.) The other major fusion option is inertial confinement fusion (ICF), in which deuterium-tritium (D-T) pellets are compressed by use of very intense laser beams, ion beams, or electromagnetic (EM) fields. The National Ignition Facility at Lawrence Livermore National Laboratory is the leading ICF test system; its mission is to increase the understanding of the relevant high-energy-density physics.

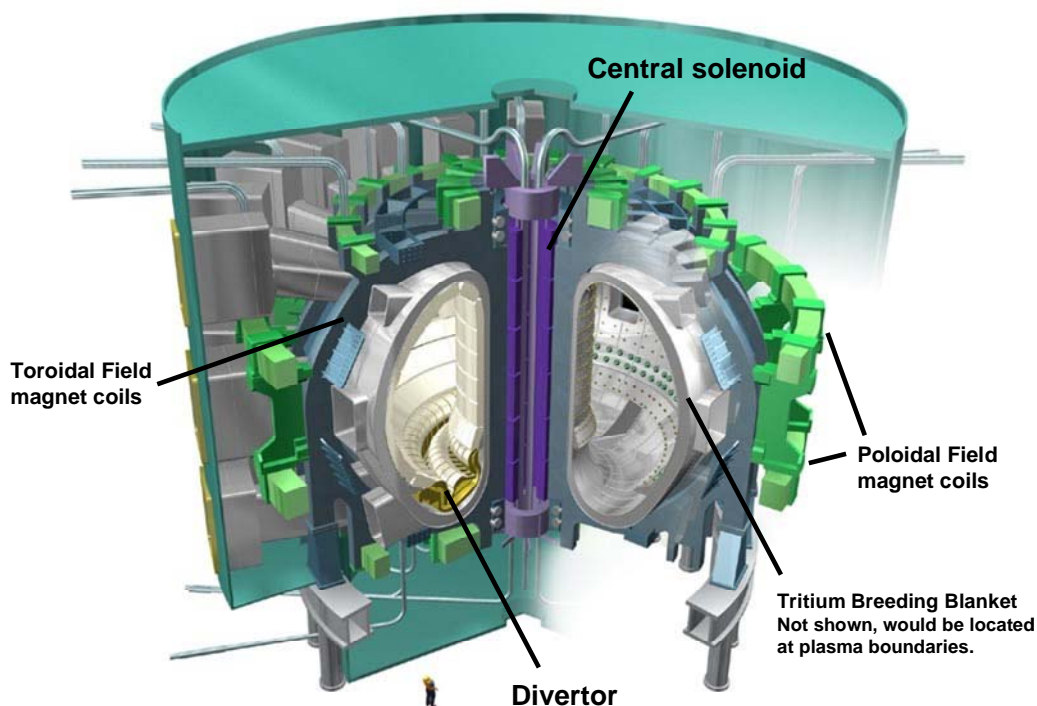


Fig. 1. The ITER tokamak system. Subsystems with the most extreme environments for materials are highlighted.

The development of advanced nuclear energy systems will require materials to operate reliably and predictably within much harsher environments. Three general areas are discussed:

- Structural materials
 - The radiation environments in both fast-spectrum reactors and fusion energy systems will be more severe than those found in current commercial systems.
 - Structural materials and power conversion components will be subjected to higher temperatures and thermal heat load fluxes to achieve greater thermal-to-electricity conversion efficiencies.
 - Both fission and fusion energy systems will use advanced coolants, some of which will create chemically reactive environments for structural materials.
 - Fusion systems will be exposed to intense fluxes of energetic particles and high mechanical stress environments resulting from EM forces.
- Highly robust waste disposal packages that can reliably contain radioactive materials within a geochemical environment for 10,000 years or more.
- Materials for pipelines to transport high-grade heat for distances on the order of 1 km to enable thermochemical production of H₂.

2.1.1 Structural materials for nuclear power systems

Fission systems. Two broad categories of advanced fission reactors are thermal-spectrum reactors (or thermal reactors) and fast-spectrum reactors (or fast reactors). Advanced thermal reactors are designed to produce very-high-temperature heat so as to improve the efficiency of conversion of thermal energy to electricity. Commercial light-water reactors operate at <300°C and convert thermal energy into heat at about 33% efficiency; high-temperature thermal reactors are expected to operate at 850–1000°C and convert thermal energy to electricity at 45–52 % efficiency. Engineering researchers are also proposing the direct application of the high-temperature heat from advanced thermal reactors to other energy-related missions, such as thermochemical production of hydrogen. Liquid metal fast reactors present more severe radiation conditions for structural metals because of their higher neutron flux level and more energetic neutrons.

The structural materials environments posed by advanced fission reactors and magnetic fusion systems are summarized in Table 1.

Advanced thermal reactors are usually considered to be constructed of dense, high-grade graphite, carbides, and advanced steels or refractory alloys. They employ coated microparticle fuels that are compacted into pellets or pebbles and are cooled either by high-pressure helium gas or by molten fluoride salts. Thermomechanical stresses at the reactor outlet manifold, where outlet flows of many reactor coolant channels are combined into a single coolant channel, present a difficult technology challenge. In the reactor's power conversion system, advanced high-temperature structural materials are needed for heat exchangers (in which materials must be thin and highly conductive) and turbine blades (where rotational forces are high). Helium gas has the advantage of being chemically nonreactive, but it is erosive and, at a pressure of 20 MPa, poses a significant stress on components. Molten fluoride salts have the advantage of low-pressure operation at <1300°C, but their chemical reactivity with structural metals is an issue.

Table 1. Extreme environments for structural materials in fission reactors and magnetic fusion power systems

	Fission reactors			Magnetic fusion power systems	
	Commercial light-water reactors	Gas-cooled thermal reactors	Liquid metal fast reactors	Tritium breeding blanket and first wall	Divertor system
Structural materials	Zirconium alloys, stainless steel, Incaloy	Graphite	Martensitic steels	Advanced ferritic steels, V alloys, SiC/SiC composites, refractory alloys (Ta, Nb, Mo, W)	Tungsten, graphite
Maximum thermal power load				5–7 MW/m ²	15–20 MW/m ²
Structural alloy maximum temperature	<300°C	~1000°C	<600°C	550–700°C (1000°C for SiC)	>1000°C
Maximum radiation dose	~1 dpa	~1–2 dpa	~30–100 dpa	~150 dpa	~150 dpa
Maximum transmutation helium concentration	~0.1 appm	~0.1 appm	~3–10 appm	~1500 appm (~10,000 appm for SiC)	~1500 appm (~10,000 appm for SiC)
D,T ion flux				1 W/cm ² (at 10 keV/ion)	~2–3 W/cm ² (at 10 keV/ion)
Magnetic field strength				~6–7 T	~6–7 T
Chemical reactivity	Water/steam	He gas or fluoride salt	Na, Pb/Bi	Molten Li/Pb alloy	
Peak steady state stresses	6–15 MPa (coolant pressure)	20 MPa for He; 1 MPa for salt (coolant pressure)	~1 MPa (coolant pressure)	50 MPa (EM forces)	50 MPa (EM forces)
Dynamic stresses (tokamaks only)				Edge-localized modes: 100 MJ for several milliseconds, at a local instantaneous rate of ~100 MW/m ² and a repetition rate of 10–100 Hz. Plasma disruption: 50 MJ/m ² , corresponding to 100–1000 MW/m ²	

The development of corrosion-resistant alloys (CRAs) for molten salt coolants at temperatures approaching 1000°C is a long-term need.

Advanced fast reactor technologies pose yet a different set of extreme conditions. The higher neutron fluxes and higher energy of the neutrons result in a higher radiation dose to materials (see Table 1) Sodium liquid metal coolant technology is relatively well developed and involves intermediate temperatures and relatively low pressures. Use of liquid lead and Pb/Bi alloys as a coolant has been a recent research direction in the United States, where the focus has been on

controlling performance-degrading chemical reactions between structural materials and the Pb/Bi liquid metal.

Magnetic fusion systems. Magnetic fusion systems have a design aspect that drives the need for extremely high levels of surface power loading on materials: the requirement to remove all of the generated fusion power through the edges of the plasma. By contrast, heat loads in fission reactors are relatively low because coolant tubes can be placed in the fission core without disrupting the fission chain reaction. The requirement that all fusion power must flow out of the plasma by streaming across materials at the plasma's external boundaries leads inevitably to high thermal surface loads and charged particle loads for structural materials.

As indicated in Table 1, the components subjected to the most extreme environments are the tritium breeding blanket and first wall and the divertor system. The development of materials that can withstand the high heat loads, radiation doses, and EM forces of the plasma environment is a major challenge.

Another challenge is presented by the antennas and related metallic structures used to launch large amounts (10–20 MW) of 50- to 5000-MHz radio-frequency (rf) wave power through a region of 1–2 m² into the plasma to heat it to ignition and tailor the profile of the plasma current. The launching of high-power waves in the plasma is achieved by imposing a spatially tailored pattern of very large (10- to 50-kV) rf potentials ~10 cm outside the plasma. These field structures can accelerate ions and electrons in the edge plasma to very high kinetic energy, which can lead to surface erosion and sputtering of metal impurities when they strike antenna, wall, or divertor surfaces. Understanding and mitigating sputtering-induced modifications of the thermomechanical and EM properties of antenna materials will be important.

Finally, magnetic fusion systems such as ITER have three major magnet systems: the toroidal field (TF) coils, the poloidal field (PF) coils, and the central solenoid (CS). The D-shaped TF coils operate with a constant current and a maximum magnetic field at the coils of 13 T and provide the bulk of the field to contain the plasma. The CS and PF coils are operated with specific current-vs-time profiles, selected so that the combined action of the fields is consistent with the conditions necessary for plasma initiation, control, and shutdown. The bulk of the flux change for a pulse of ITER operation is caused by the CS, which achieves a maximum field level of 13 T and then swings through zero to a field of –13 T. This requirement subjects the CS system to two large stress peaks for each operational pulse of the ITER plasma and makes it the most highly stressed of the coils.

The conductor material currently proposed for all ITER coils is Nb₃Sn superconductor. Dielectric (insulator) materials and structural materials are integral parts of the coil design. Table 2 provides electromechanical environmental data for the ITER coils; a full power system has not yet been designed.

2.1.2 Robust waste package materials

A key consideration in nuclear-waste management is the development of highly durable waste containers, particularly for those wastes that are to be emplaced in deep geological formations

Table 2. Electromechanical environment for fusion magnet coils

	TF coils	CS system
Maximum magnetic field, T	13	13
Total current, MA	10	~125–150
Current per conductor turn, kA	40–50	~ 40
Total inductance, H	1–2	15–20
Total stored energy, GJ	~100–150	10–15
Maximum voltage between layers, kV	1.25	4.2
Maximum voltage to ground, kV	±5	±15

for very long time periods. For the Yucca Mountain Repository, the nation’s proposed repository for high-level waste, the containers are relied upon to provide substantially complete containment for a minimum of 10,000 years. However, the lifetime of iodine-129, the principal source of health effects from the Yucca Mountain Repository, is $>10^7$ years. In principle, geologic disposal strategies for spent fuel and separated wastes would benefit greatly from container materials that would be physically and chemically stable within the deep geologic formation for time periods of 1×10^6 to 1×10^8 years. The “extreme environmental factor” to be confronted by the materials scientist is the extraordinarily long time frame for ensuring material integrity.

Understanding, simulating, and mitigating very slow degradation effects in waste container materials that might be important over very long time frames would be of benefit to nuclear waste technology.

2.1.3 Structural materials for transport of high-grade heat

The potential for advanced thermal reactors and fusion reactors to produce very high grade heat, 900 to 1000°C, has led to a number of proposals for direct utilization of the heat for purposes other than electricity production. Thermochemical production of hydrogen at high efficiency is a prominent example of a proposed application for direct use of high-grade nuclear heat.

One of the principal challenges for use of high-grade heat is the capability to transport the heat away from the immediate reactor site. Currently, nuclear regulations would make it essential to transport reactor heat more than 0.25 km from the reactor vessel; in practice, distances of 0.5 to 1.0 km appear to be a minimum requirement.

The fluids that are the leading candidates for economic transport of high-grade heat are molten fluoride salts. Interest in fluoride salts is due to their very low pressure, their high thermal capacity, and their lack of reactivity with air (in scenarios where a pipe breach occurs). Other alternatives for heat transport media, such as pressurized gas or liquid metals, pose very difficult cost and safety problems. The development of low-cost, high-temperature structural materials for kilometer-scale “pipelines” of 100°C fluoride salts is a crucial challenge.

The development of heat exchangers that can transfer high-grade heat between a high-pressure fluid (such as 3000-psi helium) and a low-pressure fluid (such as an atmospheric pressure molten salt) is another outstanding materials challenge. In heat exchangers, the interface structure between two streams is designed to be thin so as to minimize conductive drops in temperature

during heat transfer. For a high-pressure to low-pressure heat exchanger, the thin metal interface must also be designed to maintain mechanical integrity against the large pressure drop. Additionally, the high-temperature heat exchanger material must be chemically compatible with the two fluids.

Direct use of high-grade heat for hydrogen production or for other purposes will hinge upon developing materials for these extreme environments.

2.1.4 Inertial containment fusion materials

Much of the current research focus for ICF is on issues of high-energy-density physics rather than on engineered systems for power production. Thus ICF materials environments are somewhat less characterized and are discussed here only briefly.

In the areas of structural materials and secondary power conversion, ICF systems will face issues that are somewhat similar to those for magnetic fusion. The fusion chamber environment will involve intense bursts of 14-MeV neutrons, X-rays, and gamma radiation, occurring at tens of hertz in electricity-generating systems based on laser fusion and at 0.1 Hz in the electrical discharge-based Z-pinch concept. The pulsed nature of the power output of an ICF system can be expected to cause dynamic stresses and thermomechanical shocks on the fusion chamber that further complicate materials engineering requirements. Chamber walls consisting of molten LiBeF salt in a waterfall arrangement have been described as one option; low-activation carbon composites cooled by molten ceramics are another prominent concept, designated SOMBRERO.

For laser-driven fusion systems, the lifetime of the final optical components of the laser system will be a crucial materials issue. The materials in the final optics must survive the highest laser energy flux/fluence of any component within the laser system and must also, by definition, have a direct line of sight to the fusion targets, meaning that they will be exposed to the extremely harsh ionizing radiation created by the fusing target.

Achieving ion-driven or Z-pinch-driven fusion power systems will also involve advancing the frontiers of materials performance in pulsed, extremely high-power electronics systems.

2.2 RENEWABLE ENERGY SYSTEMS

Renewable energy systems harvest the energy content of sunlight, wind, water flow, tides, geothermal heat, and plants (biomass) to produce heat, electricity, or chemical fuels in forms that can be beneficially used by society.

2.2.1 Wind turbines

Several different turbine configurations are under development for wind power systems. The most common form of wind power system is the horizontal-axis wind turbines (HAWTs) that are mounted atop vertical towers. HAWTs are discussed here as an illustration, but all wind turbine configurations have similar issues.

Wind turbines have been increasing in size, with rotor blades now exceeding 60 m in length. The turbine blades must be made of a material that is high-strength and lightweight. Glass fiber laminates have been the standard material for turbine blades; but within the past decade, turbines with blades constructed of carbon fiber composites and polymeric laminate materials have become available. Wind turbines are subjected to an extremely high number of stress cycles, up to 5×10^8 cycles for 30 years of life. As a result, cyclic stress fatigue is often the life-limiting phenomenon for wind power systems and a dominating design consideration in the development of more advanced wind power systems.

Cyclic stresses, which fatigue the blade and bearing material, have historically been a major cause of turbine failures, particularly in larger windmills with longer blades. Because wind velocity often increases at higher altitudes, the backward force and torque on a turbine blade peaks as it turns through the highest point in its circle. The tower reduces the airflow at the lowest point in the circle, producing a local dip in force and torque. These effects produce a cyclic twist on the main bearings of a turbine. The combined twist is worst in machines with an even number of blades, so that one blade is straight up when another is straight down (hence the design tendency for an odd number of blades).

When the turbine turns to face the wind, the rotating blades act like a gyroscope. As the turbine pivots, gyroscopic precession tries to flip it in either the forward or the backward direction. For each blade on a wind generator's turbine, precessive force is at a minimum when the blade is horizontal and at a maximum when the blade is vertical. This cyclic twisting can quickly fatigue and crack the blade, as well as the axle and hub of the turbine.

The momentary stress on the turbine from these forces is typically a fraction of a percent of the ultimate strength; but after a very large number of repetitions, cyclic fatigue failures are observed to occur. Advanced lightweight materials with higher ultimate strength and lower variability in strength are desired, as are better predictive capabilities for the cycle life of the materials.

2.2.2 Solar concentrating power

The goal of solar power research is to find more efficient ways to convert sunlight into electricity or other forms of useful energy. Solar thermal power is one such strategy in which the thermal heat of energy is either used directly or concentrated to produce high-grade heat for electric power generation or to drive chemical reactions. Large arrays of parabolic solar troughs can be used to concentrate sunlight onto a common receiver atop a solar thermal tower. A heat transfer fluid such as liquid sodium is heated in the receiver and used to generate steam to drive a conventional turbine generator. The Kramer Junction Solar Electric Generating System (Fig. 2) began operation in 1986 and now consists of nine individual electric power facilities clustered around Kramer Junction, California. These combined facilities have a peak power of 560 MWe.



Fig. 2. Array of parabolic troughs at the Kramer Junction Solar Concentrating Plant.

Peak material temperatures at the receiver of 450–600°C are typical for conventional concentrating solar plants. Recently, it has been suggested that solar concentrating systems may be capable of producing temperatures as high as 1500°C if suitable materials of construction, coolants, and power system components can be developed. At these very high temperatures, there is a prospect of driving thermochemical processes and producing electricity at very high levels of efficiency.

2.2.3 Electricity storage systems

In order to realize efficient, widespread use of solar and wind energy systems these systems must be capable of providing power generation in a reliable and predictable manner. The central challenge to attaining this capability is bridging and smoothing over the natural intermittency and variability of sunlight and wind speeds. Thus, rechargeable battery and/or ultracapacitor technology that can store and discharge electricity as needed in significant quantities and at acceptable cost is a major renewable energy research goal.

Development of stationary electrical storage technology has focused on sodium sulfur batteries, flow batteries (such as vanadium redox and zinc-bromine), and electrochemical capacitors, as well as vehicular battery systems such as nickel–metal hydride batteries, lithium ion, and lead acid. Various battery demonstration projects, ranging in power from 500 kW to 40 MW, are under way around the world.

In these electrochemical energy storage systems, the aggressive and complex chemically reactive environment constrains the system design and leads to degradation of performance. Improved corrosion-resistant electrode and structural materials with longer life and higher performance characteristics are a crucial need.

This subject was extensively addressed in the recent Basic Energy Sciences Workshop on Basic Research Needs for Electrical Energy Storage, and the conclusions and priorities are documented in the reports associated with that workshop.

2.2.4 Biofuels

The use of biomass to create ethanol, biodiesel, and other biofuels, as well as electricity, has great promise for reducing the net carbon emissions of society as well as reducing U.S. dependence on foreign sources of petroleum. Biomass must undergo several processing steps to be converted into transportation fuels. Process routes involving gasification are straightforward, albeit energy intensive, and are being pursued for the first generation of biomass-to-ethanol plants.

Biomass gasification. As with fossil fuel gasification, there are strong performance drivers for operating biomass gasification at higher temperatures. The need for high-temperature materials for gasification and post-combustion systems is discussed in Sect. 2.1.2.

Ethanol corrosion. Ethanol has been an additive to transportation fuels for over 30 years, and experience with E-10 (90% gasoline, 10% ethanol) is extensive. However, the introduction of E-85 (15% gasoline, 85% ethanol) will require that issues of materials corrosion be addressed. Ethanol is not compatible with soft metals (Al, Zn, Cu, Pb, and brass), certain polymers, or elastomers and adhesives (such as the adhesives used in fiberglass); furthermore, water inleakage to E-85 systems is known to lead to reaction products that corrode most standard steels. Catastrophic failures of fuel pumps used to transport ethanol have been reported in various industrial ethanol facilities, some after no more than 50 h of operation; this is believed to be due to corrosive pitting caused by ethyl sulfate.

The corrosion processes resulting from impurities are not completely understood, and the need for conversion of existing facilities to ethanol-compatible materials is becoming an industry-wide concern. A more complete understanding of ethanol corrosion mechanisms is urgently needed, and the development of inexpensive alternative structural materials, corrosion-resistant coatings, and/or chemical additives to inhibit corrosion would greatly benefit the future conversion to E-85 fuel

2.2.5 Geothermal energy

Geothermal energy system technologies consist of near-surface hydrothermal plants and deep borehole technologies. Deep borehole technologies are relatively immature and involve pumping and removing water at great depths so as to remove heat from the Earth's mantle. These deep borehole technologies are conceptual, have problematic economics, and have not been put into practice, but they are the technology associated with the very high levels of geothermal energy resource that are often claimed.

Near-surface hydrothermal technologies are in use in the western United States, Hawaii, Alaska, and elsewhere in the world. They represent only a small fraction of the overall geothermal resource but are the more near-term embodiment of geothermal energy systems and have received the most research attention. The near-surface power plant technologies are all based on the extraction of geothermal steam and the direct or indirect conversion of the steam's thermal energy into electricity.

Virtually all near-surface hydrothermal technologies use steam at fairly moderate temperatures (180–300°C). However, geothermal water sources typically contain dissolved minerals, sulfur compounds, and salts and are highly corrosive, leading to reliability and service life issues with down-hole equipment and pipes and with heat exchangers and other power system components at the surface. Process streams may also contain gaseous and particulate species that lead to surface abrasion and erosion. Corrosion-resistant materials and coatings with longer life and higher performance for processing brine at 200–300°C are a priority for virtually all geothermal plant process equipment and components.

2.3 EFFICIENT ENERGY END-USE TECHNOLOGY

2.3.1 Hydrogen fuel cell vehicles and infrastructure

Fuel cell membranes and catalysts. Proton exchange membrane fuel cells (PEMFCs) are being developed for vehicular power because of their capability to convert fuel and air into electricity with high efficiency. In H₂ PEMFCs, protons and electrons are catalytically produced from fuel at an anode and recombined with oxygen at a cathode, with the electrons performing work in an external circuit. Hydrogen as the fuel gas offers many advantages, including water as the only significant combustion product.

PEMFC membrane materials technology is quite challenging. H₂/O₂ cells must operate at low relative humidity and near ambient pressure to avoid plugging of gas-flow channels by combustion water. However, the proton conductivity of state-of-the-art membranes is strongly dependent on water content. This dependence also means that currently available membranes have an upper temperature limit, due to membrane dry-out, that is below the temperature range ($\geq 120^{\circ}\text{C}$) desirable for efficient catalyst operation and heat management. This limitation is one of the most severe materials issues limiting the viability of PEMFC systems. Several other performance issues that affect membrane efficiency include fuel and oxygen transport, which short-circuits the electrochemical cell; the flexibility of the membrane over its lifetime; and resistance to rupture over many thousands of hours of operation over highly variable temperature, humidity and load conditions. Finally, the high cost of the current industry-standard Nafion[®] membranes and Pt-carbon-Nafion catalyst inks, relative to their performance, is a major barrier to employment in the transportation fleet.

Furthermore, while membranes are fabricated from relatively abundant materials, the use of PEMFCs is currently constrained by the world's reserves of platinum and other precious-metal catalysts, which are insufficient to support widespread use. Viable alternatives to such catalysts have not yet been identified. Another incentive to develop nonprecious-metal catalysts is the significant loss of efficiency associated with very low levels of contaminants such as CO and H₂S in the fuel stream.

Other materials issues involve minimization of oxidative degradation of the gas-flow channel plates and gas delivery layers (typically dense and porous carbon, respectively); maximization of catalyst utilization, which requires a "triple junction" between catalyst surface, proton-conducting medium, and gaseous fuel and oxygen transport media; and effective seals for preventing fuel/oxidant mixing.

Compressed hydrogen storage. While many solid-state and chemical systems are being explored for possible use as hydrogen storage systems, compressed hydrogen gas tanks are the currently available technology that is used in hydrogen fuel cell-powered vehicles. The current state of the art is carbon-fiber-reinforced tanks that operate at 35 MPa (5,000 psi) and 70 MPa (10,000 psi). To maintain adequate safety factors, a 70-MPa tank must have a burst strength of 165 MPa (23,500 psi). The inner liner of the tank is a high-molecular-weight polymer that serves as a hydrogen gas permeation barrier. A carbon fiber-epoxy resin composite shell is placed over

the liner and constitutes the gas pressure load-bearing component of the tank. Finally, an outer shell is placed on the tank for impact and damage resistance.

The practical range of fuel cell vehicles with compressed hydrogen storage depends upon the amount and pressure of stored hydrogen, as well as the weight and wall thickness (volume) of the high-pressure tank. Conformability of the tanks to the available volume within a vehicle is also a design target; i.e., designing and fabricating tanks in shapes other than right cylinders with end caps.

Developing advanced systems with superior gravimetric and volumetric storage capacities is the current challenge. Material technologies to achieve pressures of 100 MPa (15,000 psi) with a safety factor of 2.5× (i.e., 250 MPa) would have significant benefits. Materials with higher specific strength (on a gravimetric and volumetric basis) than currently available composites are needed, as well as less expensive methods for fabrication of high-strength carbon fibers and carbon composites.

Hydrogen pipeline materials. Pipeline transmission is the most economical method for hydrogen delivery in large quantities from the point of generation to the points of use. It would be highly desirable to use the existing natural gas pipeline network to deliver hydrogen and/or mixed natural gas/hydrogen, but a new pipeline and distribution system will likely be required because of materials issues. Currently, long-distance high-pressure (500- and 1200-psig) natural gas pipelines are made of carbon steel, which is susceptible to hydrogen embrittlement. Cast iron, copper, steel, and plastic are the materials of construction for lower-pressure (100-psig) distribution gas piping systems. Plastics (i.e., PVC pipes) are known to experience a loss of ductility or reduction in other mechanical properties as a result of aging under certain high-pressure hydrogen conditions.

Therefore, a major goal for the future hydrogen infrastructure is the development of low-cost coatings or pipeline materials that are resistant to embrittlement, fatigue cracking, and degradation under a broad range of temperatures, pressures, gas impurities, and cyclic conditions. DOE targets for hydrogen pipeline materials include handling high-pressure hydrogen gas at up to 34 MPa (5 ksi) with less than 2% leakage per mile at costs of less than \$1 million per mile.

Current applied research on hydrogen pipeline materials includes development of high-strength polymeric materials, new metallic alloys, and coatings for conventional materials.

Structural materials for thermochemical hydrogen production. Efficient carbon-free production of hydrogen is an essential goal if hydrogen-powered vehicles are ever to realize their full potential. Thermochemical hydrogen production using high-grade heat produced from nuclear reactors is one of the major routes that researchers are exploring. Most of the viable thermochemical methods for hydrogen production require temperatures of >800°C to meet minimum efficiency targets. Structural materials challenges in transporting high-grade heat are reviewed in Sect. 3.3, but additional challenges exist for structural materials in the thermochemical plant itself owing to the chemical reactivity of the fluids.

For example, one of the leading thermochemical cycles is the sulfur-iodide (SI) cycle. The SI cycle requires structural materials, seals, welds, etc., that have acceptable life and performance characteristics for sulfuric acid streams at 800–1000°C. In addition, a heat exchanger material for transferring high-grade heat from molten fluoride salts to sulfuric acid at these high temperatures would be a crucial development for enabling thermochemical hydrogen production.

2.3.2 Advanced vehicular batteries

Electricity storage systems, and in particular battery systems, are central to the performance and design of hybrid electric vehicles (HEVs), all-electric vehicles, and the hydrogen fuel cell vehicle. In particular, batteries with higher volumetric and gravimetric energy density and power density and longer life are needed. Batteries are complex electrochemical architectures composed of many different materials. Thermodynamic stability of these materials is seldom achieved; as a result, there are parasitic reactions on the surface of electrodes that shorten life and compromise performance. Furthermore, when batteries are operated in a deep discharge mode over many cycles, as is required for plug-in HEVs and all-electric vehicles, various reaction products will form on the electrodes, further complicating the already complex and aggressive chemical environment. Development of longer-lived corrosion-resistant materials is a universal need for all battery systems.

This subject was extensively addressed in the recent Basic Energy Sciences Workshop on Basic Research Needs for Electrical Energy Storage and is documented in the reports associated with that workshop.

2.3.3 Industrial process efficiency

Industry consumes about 33% of all energy used in the United States. Equipment and processes involving very high temperatures, often coupled with corrosive environments, are encountered in many energy-intensive industries:

- Aluminum: melt temperature of 750°C
- Steel: Blast furnaces at 900–1300°C
- Metal casting: temperatures of 350–750°C
- Glass: furnace temperatures up to 1200°C
- Mining (blade tips)

Material failures lead to interruptions in process operations and loss of energy. Operational energy efficiency is often lost as materials corrode, wear, or otherwise degrade. Improved materials that perform better under corrosive, high-temperature, high-pressure environments would be expected to enable new industrial technologies to save more energy.

Priority materials technology needs for extreme industrial environments are

- high-temperature heat exchangers,
- corrosion protection methods for carbon steel,
- methods to clad corrosion-resistant metals on base metals,
- stronger reinforcements/fibers for polymeric composites,

- weldable, high-temperature ceramics ($>750^{\circ}\text{C}$), and
- improved high-temperature materials for thermal insulation ($350\text{--}700^{\circ}\text{C}$).

The energy efficiency of mining operations would be significantly improved if the cutting blades on boring equipment were constructed of, or coated with, “super-hard” materials with superior wear resistance. Joining and bonding of such materials is a major science challenge.

2.4 ELECTRICITY TRANSMISSION AND DISTRIBUTION GRID

The performance and cost of electric power equipment have always been limited by materials, mainly in terms of the ability of materials to tolerate heat, voltage, and mechanical stress. Electric equipment encounters relatively large electric and magnetic fields ($\sim 2\text{ T}$). Transmission conductors typically operate at a maximum voltage of 765 kV at around 1000 A.

2.4.1 Electrical insulation

Electrical insulating materials, or dielectrics, are an integral part of the transmission and distribution grid, from overhead lines to transformers, cables, and switchgear in substations. Virtually every electrical device must have dielectrics to isolate the current-carrying conductors from ground and to provide mechanical support as well as withstand the high voltage imposed. The insulation is expected to perform without failure over the design lifetime of the equipment, which is generally 25–30 years. Dielectrics are expected to perform under more demanding conditions, including high temperatures (transformer applications), pressure (compressed gas insulating cable), cryogenic temperatures (high-temperature superconducting applications), and mechanical stresses and thermal gradients.

2.4.2 Fault protection: Lightning strikes and line surges

Failure of electrical equipment can result from inadequate protection from lightning strikes and surges. Peak discharge currents in each lightning stroke vary from several thousand amperes to 200,000 A or more. The current rises to these values in only a few millionths of a second (microseconds), and the major part of each stroke usually lasts much less than a thousandth of a second.

Lightning strike and power surge protection are provided by materials such as ZnO. These ceramics are difficult to fabricate in large pieces while controlling the materials properties essential to surge protection. The inability to control the ceramic structure during processing results in variable and unreliable performance of the surge arrestors, leading to high levels of overdesign and redundancy. The net result is that the power systems industry cannot afford 100% of the equipment needed and is only able to supply the most critical equipment. Better processing technology for surge arrestor materials and advanced materials with superior properties would lead to greater levels of protection and higher reliability in grid operations.

2.4.3 Transmission power flow control

An increasing percentage of the electricity generated in the future will be processed by solid-state power electronic converters in utility applications. However, these applications require voltage-blocking capabilities in the tens and hundreds of kilovolts and need a series connection of many silicon-based power electronics devices to achieve the necessary voltage rating. Power electronic converters will eventually process gigawatts of power at some point between where it is generated and where it is ultimately used, emphasizing the need for highly efficient power electronic converters and systems in these utility applications.

Figure 3 illustrates the required voltage and current rating of power electronic devices for several different application sectors. At lower voltages and currents (light blue shading), individual power electronics devices exist; however, the combined voltage and current ratings of many high-power utility applications exceed those of today's power electronics technology, and several devices must be combined in series or parallel in order to achieve the required application rating.

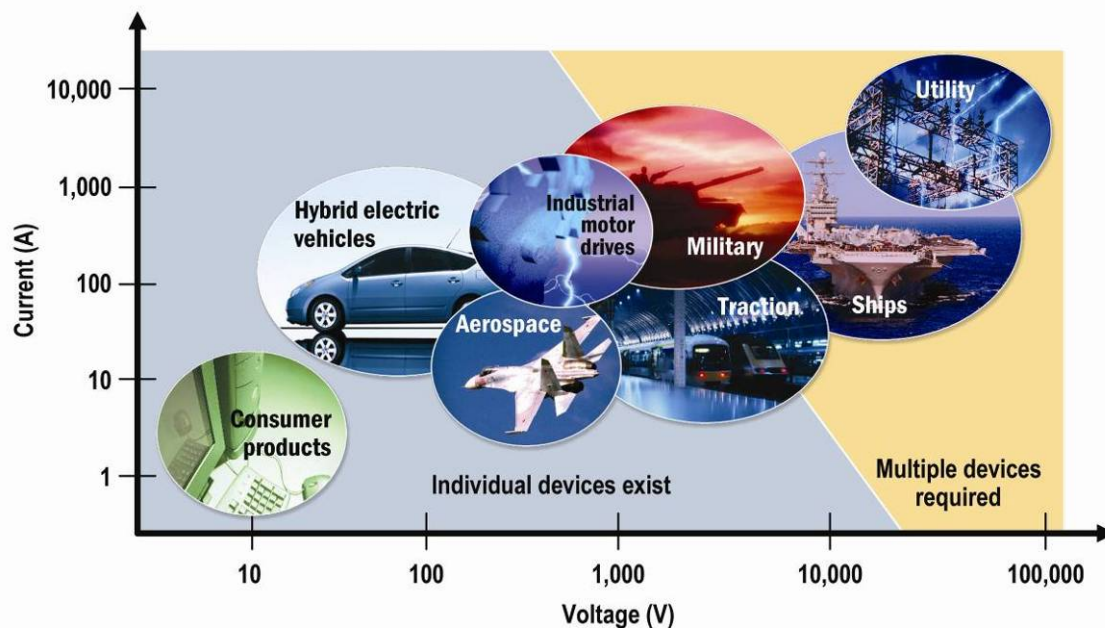


Fig. 3. The voltage and amperage requirements for power electronics and their materials. The yellow area of the chart signifies the current/voltage conditions that cannot be met by current materials, thus requiring the use of a large number of devices in combination.

It is desirable for high-power electronics to have switching speeds of >20 kHz; however, the switching speeds of the devices with the highest power ratings available today are limited to 2 kHz. Accommodating this slower switching speed involves large custom-built inductors, capacitors, and transformers that can add significant cost to converter installations, demanding filtering requirements. Switching speeds of >20 kHz would make it possible to reduce filtering requirements to levels at which they can be met with equipment of reasonable size and cost.

2.5 FOSSIL ENERGY

From extraction to use, fossil fuels occupy or create extreme environments. Decades of materials research and development (R&D) have succeeded in moving forward the performance of conventional fossil energy plants, and today, fossil fuels satisfy most of the world's energy needs. In the United States, coal provides approximately 56% of the power generation, and oil is overwhelmingly the principal energy source for transportation. Advanced power generation technologies have been and are being developed, primarily with planning, funding, and leadership of the DOE Office of Fossil Energy (DOE/FE).

An enduring technical direction of coal combustion research has been to develop technology that allows coal combustion units to operate at progressively higher temperatures, in order to achieve higher thermal-to-energy conversion efficiency and more favorable combustion process characteristics. The two major technology directions are Rankine cycle ultrasupercritical (USC) steam and integrated gasification combined cycle (IGCC) systems employing both Rankine and Brayton cycles. Both of these technology systems require materials for extreme temperatures and pressures.

A flagship demonstration project for advanced fossil energy technology is FutureGen, a public-private initiative to build the world's first integrated sequestration and hydrogen production research power plant. Although numerous configurations of technologies are possible and are still under evaluation, a likely configuration for FutureGen will include coal gasification leading to both hydrogen production and power production. The high-temperature gas-phase separations for CO₂ capture, hydrogen storage, and removal of sulfur and mercury all offer challenging temperature and chemical reactivity environments for materials.

There is an emerging interest on the part of private industry in investigating in-situ processing (refining and extraction) of deep deposits of coal, oil shale, or oil sands. These proposed techniques may open vast quantities of domestic fuel resources while significantly reducing environmental impacts from extraction and refining (by processing some of the refining operations underground where emissions are contained), but they may involve unusual combinations of elevated temperatures and geochemical conditions that require advanced materials.

2.5.1 USC steam technology

As steam technology continues to advance, the desire is to increase the steam temperature significantly, to 800°C. Systems now being studied include the so-called USC steam cycles with a target steam temperature of 760°C and pressures that may range up to 35 MPa (5000 psi.) Efficiency gains of at least 8–10% can be expected if these operating conditions can be attained. Steam is particularly aggressive on materials due to formation of volatile species and phase instabilities. However, current steam system materials for the boiler and turbine components are not capable of meeting lifetime requirements at 760°C and 35 MPa. In the USC boiler, the areas with crucial materials issues are the “thick section” structural parts, such as the main steam piping and steam headers. the capability of current steam system materials. In the USC boiler,

the areas with crucial materials issues are the “thick section” structural parts, such as the main steam piping and steam headers.

A longer-range research target is to develop materials for USC steam environments at 870°C and higher. Current ferritic steels and austenitic stainless steels do not have the requisite mechanical properties, particularly time-dependent properties such as creep rupture strength.

2.5.2 Coal gasification and gas turbine technology

Coal gasification involves the incomplete combustion of coal, i.e., the combustion is sub-stoichiometric in oxygen and does not elevate carbon to its highest oxidation state. The product of the gasification process is synthesis gas or syngas, which is principally CO and hydrogen (H₂) with minor amounts of other gaseous diluents and contaminant compounds such as CO₂, H₂S, H₂O, and NH₃. Coal consists of minerals and materials, and its hydrocarbon content is represented by a hydrogen-to-carbon ratio of about 1:1.

Numerous gasification processes are under evaluation for the planned DOE/FE FutureGen demonstration. Presently, in the United States, there are two demonstration-scale gasification plants devoted to power production via an IGCC system. Both of these plants, the Wabash Plant in Indiana and the Polk River Plant in Florida, use oxygen-blown slagging gasifiers; the oxidation of the coal is supported by pure oxygen rather than air, and temperatures are sufficiently high to fuse the ash, thereby creating a molten slag. Environments in gasifiers are extreme with respect to the gaseous atmospheres, temperature, particulate loading, and localized alternating oxidizing and reducing conditions. Although many major materials issues/problems have been solved, the materials of most concern are those that are used to line the gasifier vessels and the injector/burner nozzle.

Hot/warm gas cleaning. Gases emanating from the gasifier proper are very hot (flame temperatures may be 2400°C) and are always cooled either by quenching (rapid cooling through contact with a liquid, usually water) or by use of large gas-gas or gas-liquid heat exchangers. Purification of the combustion gases is required. Contaminants must be removed by chemical means and particulates by filtering or other physical methods. The gas cleanup systems themselves require materials that can survive in the high-temperature, chemically reactive environment of the 2400°C combustion gas.

IGCC gas-fired turbines. The efficiency of gas turbine-based power systems is a function of the temperature of the inlet gas stream. Currently available gas turbine technology is limited to rotor inlet temperatures of about 1300°C. In order to increase efficiencies to a target level of 60%, temperatures will need to be raised considerably. For state-of-the-art gas turbines, materials must have an operating temperature capability of 1400–1500°C and lifetimes of 30,000 h. It will be necessary to develop improvements in thermal barrier coatings (TBCs) and high-strength materials for components in larger turbines, such as combustor liners, which are desired to operate at 1600°C or higher.

Syngas presents special materials issues when it is combusted to directly drive a gas turbine. Syngas has a much lower heating value than natural gas, and burn characteristics such as flame

velocity may be considerably different than they are for conventional gas turbines fired with natural gas. The presence of contaminants and dissolved by-product gases can cause combustion gas to be far more chemically reactive. As an example, water vapor will almost always be present and can dissolve product gases such as H_2S , creating a corrosive environment. Additionally, the presence of small particulates can lead to erosion or modification of material surfaces due to energetic impacts.

The combustion gas contains diluent gases and entrains various contaminants as it travels along the “hot path” in the system, encountering a diversity of equipment temperatures. The formation of chemical impurity phases and thus material deposition mechanisms of materials obviously have a strong temperature dependence, and very significant differences in deposits are observed on equipment surfaces in different temperature regimes. As a result, different chemical degradation mechanisms are observed at different points in the system, complicating the selection and development of structural materials. Coupled with heterogeneity in source materials and impurities, the dependence of the materials corrosion environment at any one point on the entire upstream history of the combustion gas creates a complex challenge for developers of advanced combustion systems. Additionally, the development of different classes of materials for different locations in the hot path is required.

Rotating components of an advanced high-temperature gas turbine will require yield strengths in the range of 300–400 Mpa at 1300 to 1600°C, which have not yet been achieved by the current generation of composite materials.

Gas phase separations: hydrogen production and CO_2 capture. FutureGen, as noted, also includes hydrogen separation and purification. The purity of the hydrogen product will vary on the basis of intended use; the required purity for fuel for a turbine is much lower than that for hydrogen to be used in fuel cells, for example. The gas feed to the hydrogen separation devices may be syngas as it is produced in the gasifier, or the hydrogen content may be increased via so-called water gas shift reactions in which catalytic processes are used to react CO in the synthesis gas with water to create more hydrogen. The high-purity requirements for separated hydrogen will require hydrogen separation systems to operate outside of their normal operating windows, that is, at higher temperatures and gas with feed gas compositions that are more chemically reactive.

For CO_2 storage scenarios, the gas separation and purification systems must also separate CO_2 from the gas stream. The CO_2 stream should be separated at the highest possible pressure because subsequent operations will involve additional pressurization of CO_2 into a liquid phase for eventual placement (via hydraulic pumping) into deep geologic systems. Thus there is a strong operational reason to require that the gas phase separation systems for capturing CO_2 function at high temperatures and pressures. For the leading physical separation options, this requires advancing the capabilities of functional materials, such as membranes, with acceptable operational lifetime and control of pore size and other functional characteristics, at 1300 to 1600°C.

2.5.3 Sensor materials

Every aspect of energy conversion from fossil fuels depends on sensors for monitoring and control. Accurate and reliable sensors for high-temperature and/or corrosive environments would have multiple benefits for the thermal plant, such as avoidance of damage to heat-transfer surfaces, combustion controls for individual burners in utility boilers (which is not possible at present), reduction of noxious emissions, and structural health monitoring of critical components.

Standard sensors used for monitoring the operation of the combustion system and the emissions controls systems rely on optical techniques and fiber-optic technology. The materials in most of these optical sensor systems have a temperature dependence that makes them unsuitable for the extreme environments of advanced combustion systems. Advanced fiber optic and optical materials for high-temperature (1300–1650°C) environments are needed.

Corrosion of steam-plant materials is strongly influenced by the pH of the circulating water. Since the physiochemical properties of water are highly sensitive to temperature, there is a strong incentive to develop online pH sensors that can be used at system temperatures (360–400°C), rather than relying on analytical extrapolations from grab samples cooled to the ambient temperature (the current practice). However, sensor materials are degraded by hot water, and measured values are sensitive to impurities introduced by even slight dissolution of the sensor in the local cooling water.

2.5.4 Coal liquefaction systems

Two approaches are attractive for converting coal to liquid fuels: *indirect* coal liquefaction and *direct* coal liquefaction. Both are well developed and at commercial scale, but significant improvements are desired in materials performance in the extreme environments that prevail in these systems are needed.

Indirect coal liquefaction involves first the gasification of coal, followed by one of several available catalytic operations for conversion of a synthesis gas to a liquid product. The most common approach to catalytic conversion to liquids is Fischer-Tropsch synthesis, which has been commercialized in South Africa by Sasol to meet essentially all of South Africa's liquid fuel needs. The extreme environments in indirect liquefaction are mostly in the coal gasification element and are identical to those discussed in Sect. 2.1.2.

Direct coal liquefaction involves the conversion of coal directly to liquids via hydrogenation of the coal to increase the H:C ratio which, depending on the specific choice of catalysts and operating conditions, may yield a variety of liquid products. In the 1980s and early 1990s, the United States conducted a large coal liquefaction technology effort with four major coal liquefaction pilot plants, ranging in throughput from 5 to 600 tons of coal processed per day. In direct liquefaction processes, temperatures are ~800°C and pressures are 10–20 MPa (1,500–3,000 psi.) Liquid products formed during direct coal liquefaction range from aliphatic hydrocarbons (such as alkanes and cyclalkanes) to aromatic hydrocarbons (such as phenols and toluene) to heterogeneous compounds (such as aniline) and are highly corrosive, as well as carcinogenic and mutagenic. Mineral and maceral matter are also abundant in the liquids prior to

refinement, and these constituents create severe environments for materials because of their erosive and abrasive character.

Significant changes to coal liquefaction flowsheets can be expected as a result of research-improved catalyst materials that produce a slate of liquid products similar to those of hydrotreated petroleum. Several companies have indicated progress, with one advanced catalyst reportedly incorporated into the 50,000-ton/day plant constructed in China. These positive developments notwithstanding, direct coal liquefaction remains a very extreme environment and presents significant challenges for materials.

2.5.5 Solid oxide fuel cells

Stationary solid-oxide fuel cell (SOFC) systems are under development for use at advanced coal-fired power plants to convert by-product methanol gas to electricity, thus increasing the net power efficiency and output of the plants. SOFCs employ an oxygen-ion-conducting ceramic membrane, such as yttria-stabilized cubic zirconia, to complete an electrochemical circuit between streams of air or oxygen and a fuel gas. Porous anodes and cathodes must be multifunctional; they conduct fuel and oxidant to the membrane, catalyze the electron transfer reactions, and conduct electrons. These systems are an attractive technology route for conversion of chemical to electrical energy because of their very high efficiency (45–55% and up to 80% with use of exhaust heat to generate steam), their fuel flexibility (hydrogen, oil, natural gas, diesel, syngas, etc.), their benign environmental features (low noise, no vibration, low emissions), and their modularity for power stations in the watts-to-megawatts range.

Operating typically at 600–1000°C with a wide variety of input fuels, SOFCs are entirely dependent on specially designed ceramic and metallic materials. As with all fuel cells, efficiency and fuel flexibility improve with increasing operating temperature and power output; higher temperature improves the mobility and transport of the gaseous fuel to and within the cathode and anode, the selectivity and efficiency of ion transport across the membrane, and the reaction kinetics at electrode/electrolyte interfaces. One crucial set of fuel cell components is the *interconnects*, which deliver electrons to the cathode and separate the cathode and anode gas streams. For higher-temperature operation, electrically conducting ceramics replace metals for the interconnects, and the industry standard LaCrO₃ interconnect can cause problems due to volatilization of chromium during operation and leaching of highly toxic Cr(VI) after disposal. Effective seals are also needed to prevent fuel/oxidant mixing over many thousands of hours of operation and frequent on-off cycles. Virtually every aspect of SOFC operation has a major materials issue impacting both cost and performance (Williams 2007, Molenda 2006).

2.5.6 In-situ processing and extraction of hydrocarbon resources

Advanced processes are being proposed by the oil and gas industry for efficient, low-impact refining and extraction of solid hydrocarbon resources such as oil shale, coal, and tar sands. The most fundamental problem arises from the need for environmentally acceptable means of accessing vast concentrated deposits of oil shale in Wyoming and Colorado that are located at depths of 600–1000 m. Oil shale is a solid and thus cannot be straightforwardly pumped out of the ground as petroleum is. A fairly large number of techniques are reported in the literature for

dissolving the oil shale in a liquid solvent, or entraining the oil shale in pressurized water, that is pumped through the deposit and recovered via extraction wells. Several proprietary techniques are under development.

Some of the leading industry concepts involve releasing the liquid petroleum products from the kerogen in the shale by raising the temperatures of the oil shale deposits (and surrounding geology) to 350–400°C, over a period of several years. Several methods for providing heat are being explored, including microwaves, resistance heaters, and direct injection of pressurized steam. In general, approaches involving elevated temperatures have the potential to partially refine the hydrocarbon resource as part of the extraction method, thus trapping underground some of the undesirable emissions and effluents that normally result from refining plant operations. In principle, the in-situ processing approach would be applicable to coal deposits as well, including those coal deposits that are deep and presently unmineable.

The need for advanced materials in the in-situ extraction processes arises from the unusual high-temperature geochemical environment of in-situ processing in combination with the presence of reactive hydrocarbon materials.

More conventional concepts for extraction of deep geologic oil shale would also require advanced materials, albeit with different requirements. Long-lived corrosion-resistant materials that could be used with high-pressure caustic liquids would benefit from the proposed solvent extraction methods.

2.6 NATIONAL SECURITY SYSTEMS

The ability to predict the properties and response of materials under a wide range of extreme conditions is at the heart of the missions of the National Nuclear Security Administration (NNSA). These conditions include regimes of high pressure, high temperature, high strain, and high strain rates, as well as extreme radiation environments. Materials responses under these conditions encompass, but are not limited to,

- structural phase transformations, including melting and solidification;
- elastic and plastic deformation;
- fracture and failure; and
- radiation effects.

Materials of particular interest to NNSA include metals, foams, polymers, ceramics, ferroelectrics, piezoelectrics, nanomaterials, and gases, as well as plasmas at temperatures from 1 eV to many kiloelectronvolts. Radiation environments include self-irradiation from the decay of nuclear materials; 1- to 1,000-keV rays at $>1 \text{ J/cm}^2$ and $>1 \times 10^8 \text{ W/cm}^2$; and neutrons with energies ranging from 0.025 eV to $14.5 \times 10^6 \text{ eV}$ at densities of $>1 \times 10^{14} \text{ cm}^{-2}$. Also of interest are environments characterized by pressures of 0.1–10 GPa at strain rates greater than 1×10^3 and by pressures of 10–1,000 GPa at strain rates greater than 1×10^6 . The proposed transformation of the U.S. nuclear weapons complex, designated Complex 2030, will require a detailed understanding of the dynamics of materials in extreme conditions coupled with the physics of high-energy-density plasmas.

Among the critical materials issues for national security systems are the following.

- Understanding the thermodynamic and constitutive properties of materials.
- Predicting materials failure and fracture and understanding the subsequent responses of damaged components or systems. This issue spans both structural materials and electronics, including sensors, and also includes the effects of EM pulses (EMPs) generated by nuclear bursts on electrical components.

2.6.1 Thermodynamic and constitutive properties of materials

The response of materials under extreme conditions can be broadly categorized into two classes of properties: thermodynamic properties and constitutive properties. Generally, thermodynamic properties are fundamentally well defined at the quantum and atomic scales and include equation of state, melt and solidification, phase boundaries and structural transformations, etc. On the other hand, constitutive properties are governed by phenomena occurring across many length scales—from the quantum-level scale to the continuum scale—and are dominated by the collective behavior of defects and the evolution of the materials microstructure.

2.6.2 Materials damage and failure

Predicting materials failure and fracture is an extremely challenging scientific problem central to numerous NNSA-relevant applications, ranging from the performance of munitions to explosive-forming processes to predicting the long-time structural integrity of engineered structures. Conditions can range from quasi-static tensile failure to high-strain-rate dynamic (shock) loading. To predict component and system performance, safety, and reliability under this wide variety of conditions also requires the ability to understand the subsequent response of the damaged material. Experimentally validated models with the predictive power to describe both the failure process and the subsequent response of materials are thus important for a broad range of applications.

Exploration of the effects of radiation on system survivability directly supports NNSA's national security missions. Regimes of interest include ultrahigh total dose and dose rate environments, as well as low-dose-rate environments due to nuclear bursts, natural and enhanced space environments, or proximity to radioactive materials.

Radiation effects on materials: Displacement damage and electronic excitations. Past research on radiation effects in materials has mainly dealt with the damage produced by nuclear or atomic collisions in which energy is directly imparted to atoms, resulting in their displacement from regular crystal lattice sites. This displacement damage leaves behind crystal lattice defects that subsequently diffuse and aggregate into larger defects, causing changes in the properties of the irradiated materials. Radiation effects associated with electronic excitations can be separated into two categories: those associated with widespread but singular electronic excitations in dilute systems, and those associated with concentrated collective excitations in condensed matter. The first category encompasses low-radiation environments (e.g., atmospheric conditions and chemically reactive plasmas). The second involves passage of heavy ions at very high energy, which create showers of secondary electrons and tracks of charged and electronically excited ions in the material.

Radiation effects on electronics and sensors. The performance of transistors in national security systems can be degraded by a variety of environmental effects, including radiation damage from both X rays and neutrons. The radiation effects themselves also comprise a variety of mechanisms, including displacement damage, single-event effects, and total ionizing dose. In some instances, the exposed system is intended for a significant lifetime within a mixed radiation field. For instance, electrical designs may introduce intrinsic (on-board) sensing capabilities into the systems and devices themselves. These additional circuit elements and sensors can enable the system to react to the encountered radiation environment.

EMPs. Nuclear bursts give rise to a variety of EMP effects that can damage electrical components. Of particular interest to the survivability of NNSA systems is the system-generated EMP (SGEMP) induced by electrons created by the intense X-ray field.

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3. TECHNOLOGY NEEDS

3.1 ENERGETIC FLUX EXTREMES

3.1.1 Photonic interactions with materials

3.1.1.1 Introduction

The phenomena that occur when photons interact with materials include reflection, refraction, absorption, scattering, and transmission. One of the most desirable and important phenomena for the photonic processing of materials is absorption of the radiation. Absorption of radiation by materials results in such effects as heating, melting, vaporization, and plasma formation, which form the basis of several materials processing techniques.

The extent of these effects depends primarily on the characteristics of the EM radiation and the thermophysical properties of the material. The photon source parameters include intensity, wavelength, spatial and temporal coherence, angle of incidence, polarization, and illumination time; the materials parameters include absorptivity, thermal conductivity, specific heat, density, and latent heats. The interaction of a photon source with material is a complex interdisciplinary subject and requires knowledge from several branches of physics and materials.

3.1.1.2 Photon–materials interaction

High-energy photonic sources (e.g., lasers, flashlamps, other radiant sources) provide an EM oscillating energy field to a material surface. Any interaction between the wave and a surface is defined by the interaction of the electric field vector, the outer electrons of the material, and the interaction time.

The absorption of photon energy by electrons in the shell of the material results in one of four types of excitation (Bauerle 2000):

- interband transition
- defect transition
- coherent multiple photon transition
- intraband transition

These excitations then generally lead to one of four different mechanisms (Bauerle 2000; Ion 2005):

- photothermal (thermal)
- photochemical (nonthermal)
- photophysical (partially thermal)
- photoelectrical (nonthermal)

A comprehensive description of these thermal and nonthermal mechanisms requires a detailed knowledge of the fundamental interactions between light and matter and especially of the various interaction and relaxation times involved. This specific information is available only for selected systems that have been extensively researched.

As a simple model, these mechanisms can be understood as a competition between the relaxation of an electron, the energy transition to the lattice, and a chemical reaction due to the excitation of that electron. A photothermal mechanism exists when the electron can relax and transfer its energy to the lattice during the interaction of the EM wave with the electron. A nonthermal mechanism exists when the electron cannot relax during this time and either separates from the material (via ionization or the photoelectrical mechanism) or reacts in the form of a direct bond break or similar interaction (the photochemical mechanism). For example, in metals, the time between electron-electron collisions is on the order of 10^{-14} to 10^{-12} s, and electron-phonon relaxation times are on the order of 10^{-12} to 10^{-10} s. In contrast, interband electronic excitations in nonmetals can last much longer, with decay times of 10^{-14} to 10^{-6} s.

In general, the shorter the pulse duration compared with these interaction times, the more nonthermal the interaction becomes. Figure 4 presents a schematic of types of physical phenomena and resulting engineering processes for various combinations of photon energy and interaction time for engineering materials (mostly athermal processing (and structural steels (mostly thermal processing) is presented in Fig. 4.

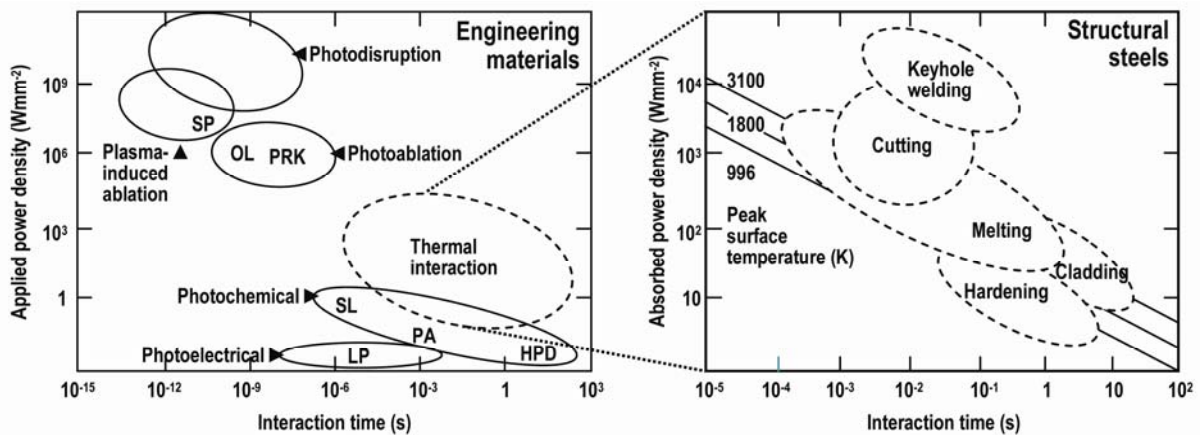


Fig. 4. Power–interaction time diagram for engineering materials (left) and structural steels (right) with thermal and athermal mechanisms. At left, athermal mechanisms of laser material processing are bounded by solid lines, while the region of interest for thermal processing is bounded by a dashed line. HPD: hematoporphyrin derivative; LP: laser printing; OL: optical lithography; PA: photochemical annealing; PRK: photorefractive keratectomy; SL: stereolithography; SP: shock processing. At right, experimental data are shown for five methods of laser thermal processing. *Source: J. C. Ion, Laser Processing of Engineering Materials: Principles, Procedure and Industrial Application, Butterworth-Heinemann/Elsevier, London, 2005.*

3.1.1.3 State of the art

With the advent of nanoscale processing of materials, ultrashort-pulse photon sources (femtoseconds, 10^{-15} s) are gaining prominence. Under such ultrashort pulses, the electron gas of a metal is excited but cannot sufficiently interact with other electrons or the lattice to transfer the energy. Initially, it was thought that during such processes, an absolutely nonthermal interaction, similar to photochemical interactions in several polymers, takes place. More recently, the existence of thermal processes at the nanoscale has been identified, leading to a new model that defines different temperatures for the electron gas (electron temperature) and the matter (lattice temperature). In this two-temperature model (Bauerle 2000), the electrons remain excited for a time much longer than the EM wave duration, leading to interaction times of up to 100 ps

(10^{-10} s) (Dausinger, Lichtner, and Lubatschowski 2004) and providing more contributions through thermal interaction to the photophysical effect. This is a further indication that the current understanding of photon energy–material interactions must be extended beyond the time-based phenomenon.

3.1.1.4 Future direction

Work is needed to take into account the complex interactions between photon energy parameters and material parameters. Such efforts will extend the applications of photon energy–based processing of materials from conventional processes, such as bulk processing (cutting, joining, and surface modification), at the macro- and microscale to submicron-scale processing for electronics and telecommunication and for biomedical applications. These applications involve a wide range of materials: metals, ceramics, polymers, composites, and biological materials. Studies of the interaction of photon energy with these materials are required to gain a fundamental understanding of the energy distribution and its effects within the system. This can be approached by capturing the phenomena (heat conduction, light transport, interfacial effects, etc.) at multiple scales.

Basic research on short-duration interaction of high-energy photons with materials should be focused on four technologically important classes of materials: conductors (metals), semiconductors (amorphous or crystalline semiconducting ceramics), and two types of isolators (polymers and ceramics). During interactions with high-energy, short-duration photon sources, these materials experience circumstances and processes that are currently far beyond the well-studied and understood thermodynamic equilibrium. Thermal and nonthermal effects in these materials during high EM impact are not well understood. Phase transitions and microstructural phase transformations need to be examined, as do melting, evaporation, ablation, and direct bond breaking. These studies could provide knowledge for more efficient and faster material synthesis and processing.

Metals. Work is needed to take the treatment of metals, especially in electronic and functional applications but also in microelectromechanical system (MEMS) devices, to the next level: ultrafine, low-dimensional treatment to form and rapidly prototype structures. At this scale, any nonintended mechanism (thermal or nonthermal) disturbs the structures. The availability of photonic processes over time frames from the ultrashort (femtoseconds) through short (nanoseconds) to pseudocontinuous (microseconds) and continuous wave treatments enables detailed studies of time and energy conversion mechanisms. For metals with high melting points, such as tungsten; intermetallics, such as nickel aluminides or ruthenium aluminides; and high-conducting but low-melting metals, such as copper, a complete understanding of the processes involved in treatment is needed. Thermally and nonthermally activated processes need to be studied in metals with a variety of properties, using photonic processes across a range of time scales and wavelengths, to determine the impacts of these effects.

Semiconductors. The use of amorphous hydrogenated silicon (a-Si:H) for photovoltaics (PVs), thin-film transistors, and other microelectronic devices is a mature technology that is economical. However, its material properties such as mobility are low compared with those of polycrystalline silicon; in addition, a-Si:H undergoes a light-induced degradation known as the Staebler-Wronski effect. This phenomenon reduces the optoelectronic properties, and thus the

conversion efficiency, of a-Si:H solar cells as a result of the high diffusion coefficient of hydrogen and changes in the local bonding coordination. Several theories have been proposed to explain this effect; a commonly accepted explanation is that weak bonds break, forming dangling bonds that act as recombination centers for electron/hole pairs. There is a great need to understand the fundamentals associated with this effect in order to improve the performance of a-Si:H PV material systems. A basic understanding of photon-materials interactions may lead to increased conversion efficiency through photon-based processing techniques.

Polymers. Because of the low electron density and low electron mobility in polymers, it was previously believed that the electron field vector would interact only with free electron pairs in functional groups and with binding electrons at certain binding energies corresponding to the laser wavelength. For this reason, it was assumed that any interaction mechanism would be purely photochemical, with direct bond breaking and no thermal contribution. On the contrary, recent high-resolution microscopy studies have shown that melting and thermally activated phase transformations and chemical changes also occur in this class of materials. Hence, thermally activated processes such as crystallization or cross-linking can be achieved using high-energy photonic techniques in polymers such as polymethyl methacrylate, polyethylene terephthalate, or polycarbonate for applications in industrial areas. Basic research to explore laser-induced changes in polymers could lead to new industrial applications and to more efficient processes for manufacturing.

Ceramics. Ceramics with high stiffness, controlled toughness, and high thermal conductivity, such as silicon and tungsten carbides, are increasingly used in automotive and other applications. These ceramics often need to be extensively machined (e.g., by drilling or grinding) to meet specific needs; but because of their extremely high hardness, machining can result in surface cracking and subsurface damage. The use of ceramics in industry is typically limited not by material properties or cost, but rather by the high cost of finished part manufacturing. Photonic processing offers a potential noncontact solution. The high thermal conductivity of these ceramics, however, interferes with the delivery of high energy density to localized regions for removal of material (e.g., through ablation or melting); it can also lead to steep thermal gradients with crack initiation and ultimate fatal fracture. Further studies of laser-materials interaction mechanisms at the molecular level and the precise mode and amount of energy delivered in thermal activation could lead to substantial process improvements.

3.1.2 Technology needs for extreme plasma environments

Plasmas exist at widely varying densities and temperatures. Low-temperature plasmas are used extensively in industrial applications, particularly for deposition on plastic substrates; plasma-based surface processes are an indispensable tool for manufacturing integrated circuits. Plasma processing is also used in the aerospace, automotive, steel, biomedical, and toxic waste management industries.

The principal driver for the investigation of extreme plasma environments is the possibility of generating useful energy from fusion reactions. As discussed in Sect. 2, the two main technology options for future fusion power plants are confinement of a D-T plasma using magnetic fields, commonly termed magnetic fusion; and compression of D-T pellets by intense laser beams, ion

beams, or EM fields, known as ICF. In both magnetic fusion and ICF systems, extreme plasma environments are created. The development of materials that can withstand the energy and neutron fluxes of the fusion environment presents an enormous technical challenge. These materials must survive for long periods, release minimal impurities into the plasma, and exhibit favorable activation characteristics (i.e., be minimally radioactive).

Plasma-based propulsion systems are being explored as a possible replacement for chemically based rocket engines. Using electric or magnetic fields to accelerate ionized propellant, exit velocities of >30 km/s may be achieved with these devices, compared with 4 km/s for the most efficient chemical thrusters. Sputtering of thruster electrodes, which are exposed to energetic ions, limits the service life of these devices.

These environments are characterized by highly energetic ions, electrons, and photons, which interact with the surrounding materials in a variety of ways. Energetic ions transfer their kinetic energy to materials through electronic and nuclear processes, which can result in erosion and damage. Electrons and photons deposit energy into materials and cause both heating and secondary effects such as desorption, evaporation, and radiation-enhanced diffusion. In fusion plasmas, neutrons are also produced and can heat, damage, and activate materials. These processes are collectively referred to as plasma-material interactions (PMIs), and they critically affect the performance of materials in plasma environments.

3.1.2.1 Characteristics of the plasma environment

A number of processes can occur simultaneously when materials are exposed to plasmas. (For a comprehensive review of PMIs in fusion reactors, see Federici et al. 2001.) The most prevalent are schematically diagrammed in Fig. 5 and described below.

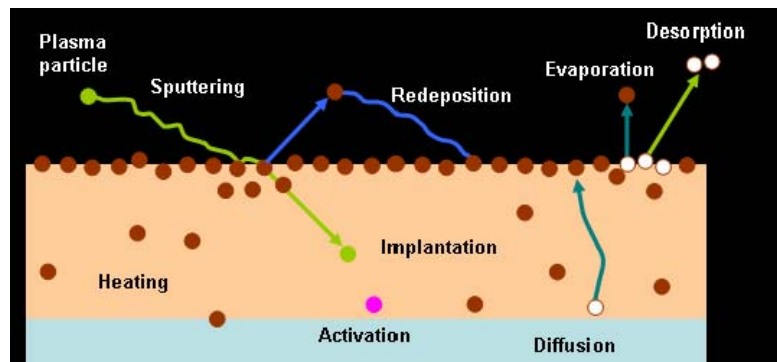


Fig. 5. Representation of various processes occurring in materials exposed to plasmas. Sputtering leads to erosion, while transport of sputtered atoms and their subsequent deposition can redistribute the material. Ion implantation causes damage and alters the material. Large radiative fluxes of ions, electrons, photons, and fusion neutrons heat the material and can produce strong thermal gradients and secondary effects such as evaporation, desorption, radiation-enhanced diffusion, and activation. (Source: R. Bastasz, Sandia National Laboratories.)

Sputtering and erosion.

Physical sputtering produces erosion when incident particle energies exceed a threshold value determined by the incident species, energy, and direction and by the material's composition and morphology.

Cascades of displaced atoms, when they intersect the surface, can produce large sputtering yields (sputtered atoms/incident ion >1). Chemical erosion occurs when incident species react with substrate atoms and produce volatile products. Accurate description of sputtering is essential to quantify PMIs and has already been the subject of much experimental, theoretical, and modeling work. Physical sputtering is well understood in simple situations, such as low-dose bombardment of pure targets in the linear cascade regime. At high incident fluxes and in complex materials,

sputtering and erosion are much less well understood, as nonlinear processes can dominate cascade dynamics.

Transport and deposition. Sputtered material can be transported some distance from its point of origin and deposited on adjacent material, where it leads to the formation of surface layers with properties that often differ from those of the original material. The transport process depends on several factors, such as local field strengths, the charge state of sputtered atoms, the ionization rate of sputtered neutral atoms, and surface geometry. Roughening, smoothing, and the development of ripples or other features may occur over the range from nanometers to the macroscopic scale. Understanding how deposited layers form and characterizing their properties is an active area of research.

Implantation and retention or release. Implanted particles can alter a material's electronic and mechanical properties, depending on the particle type, concentration, and range. Trapping of atoms (e.g., the hydrogen isotopes and helium) to damage sites can occur and can result in significant retention of foreign atoms in the plasma-facing material. The condition of the material, notably its temperature and surface composition, affects the degree to which damage persists and implanted material is retained or released. In the D-T plasmas of fusion energy systems, retention of tritium may drive up fuel cost and result in tritium inventories that are unacceptable from a safety point of view. Oxidized surfaces or surfaces with other characteristics slow the recombination of the hydrogen atoms into molecules at the surface and hinder release. Materials with high trapping rates (resulting from lattice imperfections or impurities) may also lead to enhanced retention. Measurements and modeling of the retention and release of implanted particles have received significant attention in the last 20 years.

Thermal processes. Intense PMIs may result in high heat loads on materials, leading to mechanical stresses, evaporation, and melting. For example, carbon blooms can result from radiation-enhanced sublimation when carbon surface temperatures exceed about 1600°C and from carbon vaporization above 2300°C. The hot spots associated with such blooms can result in an enormous amount of plasma contamination. High-density vapors formed in front of a plasma-facing component (PFC) can actually shield the PFC from further damage due to particle irradiation. Hot spots often result in enhanced arcing due to higher localized pressures at the PFC surface that produce further material evaporation. The area of experimental testing, simulation, and modeling of PFCs subjected to high heat loads is receiving considerable current attention in the fusion PMI community.

3.1.2.2 State of the art for plasma-facing components

Material requirements for PFCs in magnetic and inertial confinement energy systems and propulsion systems differ in detail but share many similarities. In all cases, a key requirement is the ability of materials to withstand bombardment by high fluxes of energetic particles.

Most tokamak PFCs fall into three generic classes: the first wall, limiters, and divertor. In ITER, these components will be subjected to fluxes of deuterium, tritium, α , γ , X-rays, neutrons, and electrons; pulse lengths will range from 0.1 s to steady state, and duty cycles will extend from 0 to 0.5 Hz. Other physical conditions surrounding these three classes of components for ITER are summarized in Table 3.

Table 3. Typical PFC conditions in ITER

	Particle energies (eV)	Temperature ^a (°C)	Heat flux (MW/m ²)	
			Normal	Off-normal
First wall	<200	<350	0.1–1.0	<50
Limiters	<200	<600	1–15	<50
Divertors				
Vertical targets	<50	<1000	10–30	<50
Baffles, domes	<50	<350	1–10	<50

^aUnder off-normal conditions, the melting point of the material can be reached.

First-wall PFCs. The first wall, which forms the innermost surface of the plasma vessel, is the PFC with the largest area. In addition to being durable enough to handle the heat fluxes and neutron loading to which it is exposed, it must be compatible with the plasma because of its large interaction area. If first wall material erodes and enters the plasma, several deleterious effects can occur. Atoms of high atomic number Z efficiently radiate energy and cause undesirable cooling of the plasma. Also, plasma impurities dilute the fuel and reduce fusion power. Consequently, the first wall material should be resistant to erosion and preferably be composed of low- Z elements. In practice, the sputtering yields for fusion-relevant plasmas are highest for low- to medium- Z materials; therefore, either low- Z or high- Z materials offer a compromise solution for overall least deleterious impact on plasma performance. Resistance to retention of significant amounts of tritium is another important requirement for the first wall.

Carbon and refractory metals such as molybdenum have been used as first wall materials. As discussed in Sect. 3.1.2.1, graphite first walls that are not actively cooled can bloom at high temperature, limiting the power handling capability of the device (Ramsey et al. 1990). High- Z metal walls may increase the Z_{eff} of the core plasma if the plasma edge temperature exceeds the sputtering threshold. The ITER first wall will be made of beryllium ($Z = 4$) and exposed to a heat flux of 0.5 MW/m² during normal operation and a neutron loading of 0.2–0.7 MW/m² (depending on the position of the wall relative to the plasma). During off-normal events such as disruptions, the energy flux to the first wall may reach 9–18 MJ/m² for periods of 1 to 1.5 ms. Edge-localized modes (ELMs) in the ITER plasma are expected to deposit 0.14–0.19 MJ/m² over short intervals (0.4 ms) at rates near 5 Hz. Plasma disruptions known as Marfes may also occur in ITER, resulting in radiant heat fluxes to the first wall of 1.4 MW/m² over 10-s periods. As the planning and design for ITER progress, the mitigation of ELMs is a topic of intense research, and it is unclear whether ELM-related stresses will be completely eliminated or just reduced in amplitude.

Limiter and divertor PFCs. Limiters and divertors provide pumping slots to remove energetic species after they have been neutralized. They are exposed to deuterium, tritium, and α particles, as well as neutrons and X-rays from the plasma. Charged particles escaping confinement can be accelerated by the plasma sheath on limiter and divertor targets, resulting in impact energies of hundreds of electron-volts. In machines with higher power density, active cooling of the first wall, limiter, and divertor targets is required. Surface temperatures on beryllium-armored PFCs are typically 200–300°C. CFCs can operate at up to 600°C before sublimation becomes a concern; refractory armor such as molybdenum or tungsten can operate at temperatures up to near 1000°C before recrystallization occurs. Divertors typically use high-melting-point materials

such as carbon, CFCs, or refractory metals to handle the high heat loads at the vertical targets. During off-normal events such as plasma disruptions, the PFC armor may experience extreme temperatures resulting in surface melting. Only the strongbacks and the PFC mounts are designed to withstand the higher forces and torques generated by plasma disruptions.

Currently, the only means of preserving the integrity of the PFC armor during plasma disruptions is to mitigate the disruption by altering its temporal behavior through gas injection or introduction of a “killer pellet” into the plasma. There are no materials or engineering solutions that allow PFCs to endure more than a very few unmitigated disruptions. For a discussion of disruption scenarios and their mitigation, see Sugihara et al. 2007.

Electric propulsion PFCs. Using electric or magnetic fields to accelerate ionized propellant, exit velocities of >30 km/s may be achieved with advanced electric propulsion devices, compared with 4 km/s for the most efficient chemical thrusters (Frisbee, VanLandigham, and Brophy 1996). Ion thrusters for propulsion systems generate thrust by ionizing a gas (typically xenon) and accelerating the ions electrostatically through a set of multi-aperture optics. The electron emitter is a hollow cathode with a porous tungsten insert. Hall thrusters, another form of electric propulsion, use an annular anode configuration, in which xenon is ionized in the anode channel and accelerated out of the thruster by an imposed electric field. The anode is fabricated from a ceramic material such as boron nitride.

While typical discharge voltages are kept fairly low (25 eV), ions with energies of up to 90 eV immediately downstream of the cathode have been measured and may cause considerable erosion damage. The ion extraction optics are also susceptible to erosion due to energetic neutrals created by charge-exchange processes in the thruster beam. Depending on the design of the optics, these particles typically have energies of 150–450 eV. Near-failure of the cathode assembly and grids has been observed in a long-term test (Sengupta, Brophy, and Goodfellow 2003).

3.1.2.3 Technology needs and challenges for materials in extreme plasma environments

Broadly speaking, an improved understanding of PMIs is needed. In particular, investigations of sputtering and erosion at high incident fluxes and in complex materials would provide needed information, as would studies of the formation of layers created by redeposition of sputtered particles and characterization of their properties. The behavior and compatibility of mixed material systems formed by plasma redeposition from diverse PFCs also require further study.

In addition, research to improve the performance of materials in extreme plasma environments could address the following:

- Coatings for PFCs and in situ deposition techniques for repair or replenishment of these coatings.
- Development of liquid metal PFCs, which could be replenished and remove high heat loads without neutron damage. This would entail studies of chemical reaction kinetics and the wetting and capillary behavior of liquid metal systems.
- Joining of dissimilar materials, including functionally graded layering and the development of compliant layers.

- Improved processing methods for fabrication of fully dense refractory materials that exhibit no outgassing behavior.
- Development of hybrid nondestructive evaluation and monitoring diagnostics, including integrated sensors that can monitor the health of components (hydrogen content, mechanical damage, erosion, etc.).

For advanced magnetic fusion systems, two PFCs present particular challenges: the first wall and the blanket. For a commercial power reactor, and even for the DEMO device expected to immediately follow ITER, the damage that would be done to a first wall made of stainless steel would be >300–500 displacements per atom (dpa) over a 30-year life. This is far beyond the capability of austenitic steels, which show significant swelling above 30 dpa. Materials that have longer lifetimes, or that experience less damage for a given neutron fluence, will be needed. Promising candidates include low-activation ferritic steels and SiC composites that can withstand doses of >150 dpa without swelling. A detailed discussion of radiation effects and displaced atom damage is presented in Sect. 3.1.3.

Future magnetic fusion reactors are expected to be equipped with a blanket, located between the vessel wall and the TF coils. The blanket has two roles: breeding tritium and converting both the surface heat fluxes on the first wall and the 14-MeV neutrons into high-grade heat for subsequent use in the power conversion system. Thus it is the design nexus for the three overarching goals for a fusion power system—electric power production, sustainable tritium breeding, and safety. Blanket systems are expected to use either a lithium-based fluid or solid to breed tritium at a sustainable rate (~1.1 tritium atoms per 14-MeV neutron). The blanket system must also shield the magnet coils from radiation (i.e., neutrons and X-rays) to prevent radiation-induced degradation of magnet materials and serve as the first line of containment against an accidental release of the radioactive components of the plasma. The plasma-facing wall of the tritium breeding blanket comprises the structural boundary at the physical edge of the fusion plasma. In addition to withstanding high radiation fields and magnetic fields, it must operate in an environment characterized by very high vacuum, energetic ion fluxes that “leak” radially out of the plasma during operation, and high thermal loads. It also may come into contact with the tritium blanket coolant, currently envisioned as a molten Li-based metallic alloy or salt. Barrier coatings for blanket structural materials will be needed to inhibit the thermally driven diffusion of tritium and helium, while surviving the extreme blanket environment.

Because ICF is at an earlier stage than magnetic fusion, materials environments for ICF power production systems are somewhat less well characterized and optimized. It is clear, however, that achieving ion-driven or Z-pinch-driven fusion power systems will involve advancing the frontiers of materials performance in pulsed electronic systems operating at extremely high power. The ICF chamber environment will involve intense bursts of 14-MeV neutrons, X-rays, and γ radiation. In electricity-generating systems based on laser fusion, these bursts would occur at tens of hertz; in the electrical discharge-based Z-pinch concept, they would occur at 0.1 Hz.

A crucial materials issue is the lifetime of the final optical components of the laser system. The materials in the final optics must accommodate the most intense laser-energy flux/fluence within the laser system and must also, by definition, have a direct line of sight to the fusion targets. The

line-of-sight requirement implies the exposure of the optical materials to the extremely harsh ionizing radiation created by the fusing target.

The development of sputter-resistant PFCs is also a key aspect for electric propulsion systems. Accurate assessment of damage accumulation from sputtering requires detailed knowledge of the plasma bombardment conditions and sputtering yields. Because of the difficulties associated with obtaining sputtering measurements below 100 eV, few experimental data relevant to cathode sputtering have been acquired. Furthermore, sputtering of spacecraft materials that may be exposed to the thruster plume, such as Inconel or Kapton, has not been characterized extensively. The sticking coefficients for sputtered thruster materials such as molybdenum or carbon would be of great benefit to spacecraft designers wishing to assess the potential contamination to scientific instruments and solar panels during thruster operation. To allow thrusters to be scaled to smaller sizes, cathodes that provide high emission currents at low input power are also needed.

3.1.3 Technology needs for extreme displacement radiation environments

Beginning with the observation of anisotropic growth of the graphite used in the world's first nuclear reactor more than 60 years ago, the effects of radiation on materials have been an important technological concern for the success of nuclear power and are instrumental for numerous diverse applications ranging from ion implantation to micromachining. Displacement damage involves the rearrangement of the structure of a material that occurs when a host atom receives sufficient kinetic energy from an incident particle to

- displace atoms from a lattice position, creating one or more vacancy and self-interstitial atom (SIA) defects, called Frenkel pairs;
- eject, or sputter, atoms from the surface of a material;
- cause local rearrangement of elements and changes in a crystalline or amorphous material or;
- change the local composition of a material associated with atomic implantation, nuclear reactions, radioactive decay, and mixing at interfaces.

Sources of displacement damage include neutron fluxes, decay of radioactive isotopes, cosmic rays, accelerator-generated charged particle beams, ion and charge-exchange neutrals from plasma discharges, and high-energy photons. Beneficial applications of displacement damage include

- sputtering for producing vapor species for deposition and micromachining
- enhancement of surface reaction and deposition processes
- ion implantation in semiconductor and optoelectronic materials
- ion beam surface modifications
- radiation monitors and micro filters from ion tracks and color centers in gems
- magnetic flux line pinning sites in superconductors

Detrimental effects of displacement damage include

- degradation of properties and dimensional instabilities due to radiation damage and radiation-induced microstructural evolutions in metal and ceramics
- sputtering, erosion, or blistering exfoliation of materials in PFCs of fusion energy systems

- defects and compositional redistributions in semiconductor and optoelectronic materials accompanying ion implantation
- neutron and charged particle radiation damage degradation of the electronic properties of semiconductor devices

3.1.3.1 Characteristics of the nuclear radiation environment

Pertinent length and time scales range from sub-picosecond neutron collision reactions on the scale of the nucleus to the size and service lifetimes of structural components, spanning factors in excess of 10^{14} in length and 10^{22} in time (Odette et al. 2001), as schematically illustrated in Figure 6. Numerous nuclear, atomic, and solid-state physics processes are linked to complex microstructural evolutions in multiconstituent, multiphase materials through nonequilibrium thermodynamics and accelerated kinetics. The mix of microstructural features formed and the corresponding property changes depend on a wide range of material and irradiation variables, and critical outcomes often depend on small differences between large competing effects. For example, void swelling results from a small bias in vacancy vs SIA fluxes to different sinks (Brailsford and Bullough 1972).

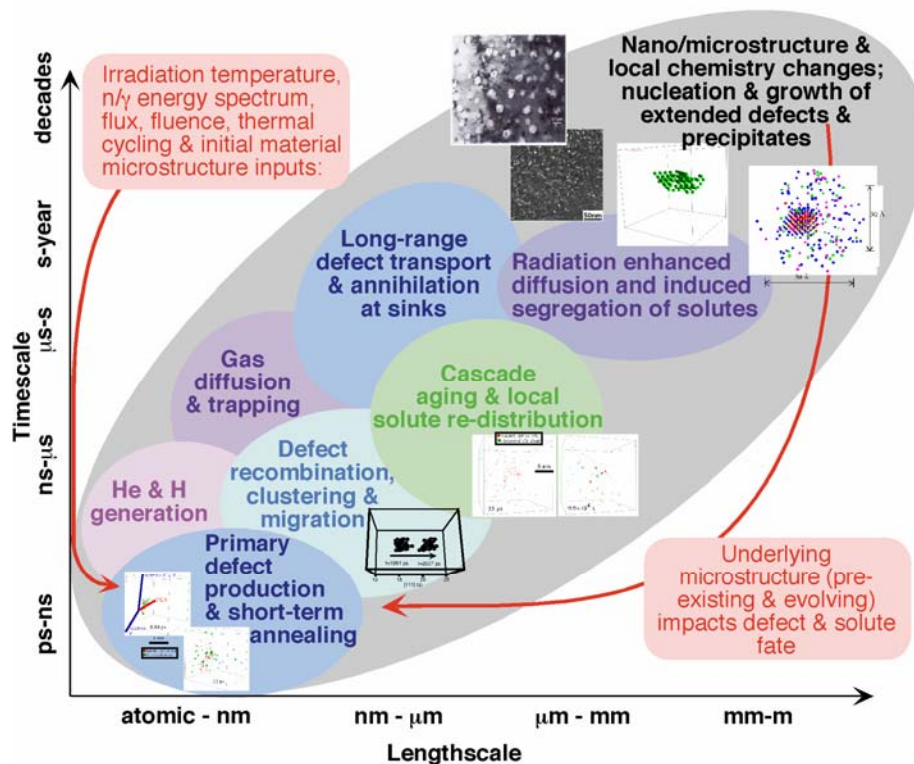


Fig. 6. Length and time scales (and inherent feedback) involved in the multiscale processes responsible for microstructural changes in irradiated materials. The processes are described in more detail in the text.

The standard radiation damage dose unit is the dpa. Computed dpa doses do not account for cascade recombination or defect reconfigurations in cascades. The dpa is essentially the total kinetic energy *dose* deposited in atomic recoils that is not lost to electrons. While the dpa has been empirically successful as a dose unit, more physical measures of damage production are

needed in multiscale–multiphysics models. This requires modeling the structure and dynamics of cascades.

Cascades: Primary defect production and evolution. Radiation damage continually initiates with the creation of energetic primary knock-on atoms by nuclear or atomic interactions with a flux of bombarding species, such as neutrons or charged particles. In the case of charged particle fluxes, the range of the incident species is governed by energy losses to electron and atomic collisions, integrated over the penetration range. The corresponding primary knock-on atoms generated by neutrons and charged particles quickly lose kinetic energy through a branching chain of atomic displacement collisions and interactions with electrons, generating a high-temperature displacement cascade containing large concentrations of vacancy and SIA defects (Brinkman 1954; Seeger 1958). If the energy density in the cascades is sufficiently high, the core region may melt and resolidify during the following cooling phase.

The formation, initial cooling, and relaxation of displacement cascades, including cluster formation and spontaneous recombination of vacancies and SIA, occurs over short times (≈ 100 ps), within regions less than ≈ 50 nm in diameter (Stoller, Odette, and Wirth 1997; Averback and Diaz de la Rubia 1998). In ceramics and semiconductors, the energy deposited to electrons can also cause damage via a process known as radiolysis or by swift heavy ion effects involving electronic energy losses above a threshold value; in addition, a variety of charge-state defects are associated with electron and displaced atom damage. Cascades near a free surface cause sputtering, which occurs at a much lower particle energy threshold than that for bulk displacements and, at the lowest energy, results in ejection of single atoms. Furthermore, the presence of a nearby surface can alter the morphology and defect production characteristics of the cascade. While the range of most displaced atoms is short in bulk crystals, cascades can also result in mixing at interfaces, as well as amorphization in some metal and ceramic compounds and semiconductors. Understanding defect production and microstructural evolution also requires the modeling of cascade overlap and long-range diffusion of defects and solutes from outside the cascade region.

Long-term microstructural evolutions. The first 100 ps in the lifetime of a displacement cascade is just the beginning of a complex and physically rich evolution. The migration of SIA and vacancy defects, solutes, and cluster complexes results in spatially and time-correlated evolution of cascade structures, or cascade aging, over a broad range of times. Aging is initially dominated by vacancy-SIA recombination and the departure of residual SIA defects from the cascade region. This is followed by a much longer period associated with the formation of mobile solute vacancy cluster complexes; in Fe-Cu alloys, these complexes evolve into relatively stable Cu-coated nanovoids. In most cases, the vacancies eventually dissolve from nascent vacancy-solute clusters and nanovoids and undergo long-range migration to sinks, leaving solute cluster remnants. The time over which cascade aging processes occurs, the details of the reaction paths, and cascade aging products are very sensitive to the temperature, local chemical environment, elastic strain, and alloy composition. At 300°C in steels, cascade aging persists up to times of $>10^8$ s.

In general, long-term microstructural evolution takes place primarily by means of coupled long-range diffusion of defects and solutes. The most important processes include the following:

- Annihilation of mobile defect species at sinks, including dislocations and grain boundaries. The sink strengths generally are different for SIA-SIA clusters and vacancies. Such sink bias can arise from strain field diffusion-drift interactions, differences in local defect annihilation processes, and one- vs three-dimensional SIA cluster diffusion.
- Clustering of insoluble He (produced by n,α reactions) to form gas bubbles that can act as nucleation sites for both voids and grain boundary creep cavities. Bubbles are stable in the sense that they grow only with the addition of gas atoms. However, a sink-bias-driven excess flux of vacancies relative to SIAs transforms bubbles that have grown beyond a critical size r^* into unstably growing voids or creep cavities.
- Void swelling and network dislocation climb, annihilation, and production from loop unfauling leading to evolved dislocation substructures, again due to bias-driven imbalances between SIA and vacancy fluxes.
- Driven non-equilibrium chemical radiation-induced segregation or desegregation due to coupling of solutes to persistent defect fluxes in fixed sinks.
- Long-range diffusional aggregation of solutes forming a wide range of equilibrium and non-equilibrium precipitate phases due to radiation-enhanced diffusion in lower temperature regimes, which are normally kinetically inaccessible under thermal aging conditions.

3.1.3.2 State of the art for nuclear fission and fusion materials

The damage production that occurs in cascades during the first 100 ps has been studied in elemental metals (copper, iron, tungsten, vanadium, etc.) for many decades. However, the physical phenomena related to cascade processes in more complex, engineering-relevant materials systems are not well understood. In addition, fundamental phenomena such as cascade formation and aging near surfaces, interfaces, and other defects remain essentially unexplored. Notably, these cascade processes are only one aspect of displacement damage evolution (i.e., the “source term”). Comprehensive understanding of radiation damage associated with large-scale, long-time microstructural evolutions and material property changes is currently insufficient.

Existing “Generation II” commercial nuclear power reactors are composed of a variety of materials that have demonstrated adequate stability under normal operating conditions. Indeed, the 103 existing U.S. nuclear power reactors (which produce more than 20% of U.S. electrical energy) have set a number of electricity generation capacity records over the past 20 years as a result of increased availability. The current U.S. fleet average availability is slightly above 90%. The key materials in existing commercial nuclear power plants include UO_2 fuel, zirconium alloy cladding that encases the fuel (one of several engineered barriers to prevent release of radioactive fission by-products to the environment), austenitic stainless steel core internal structures, and low-carbon steel for the reactor pressure vessel. These materials were largely developed during the 1960s and are currently performing near their maximum temperature and dose limits. Whereas only incremental changes are likely to be needed for continued satisfactory operation of existing and planned “Generation III” fission reactors, large-scale transformational changes are needed to develop the suite of materials for proposed “Generation IV” fission reactors that involve dramatic increases in operating temperatures and radiation exposures to reactor structural components.

Several structural materials are in the developmental stage for potential fusion energy applications, including ferritic/martensitic steels, vanadium alloys, and SiC-fiber reinforced SiC

ceramic composites (Zinkle 2005). These materials are being designed to withstand the hostile combinations of high temperatures (400–1000°C, depending on the reactor design concept), radiation damage exposures approaching 200 dpa, and a variety of chemical compatibility and thermomechanical stress issues. It is obviously an enormous engineering challenge to construct a large-scale structure several meters in height and diameter that will be exposed to steady-state plasma-facing heat fluxes of 1–10 MW/m² (comparable to rocket nozzle heat fluxes) and that must operate reliably for several years during intense exposure to high-energy neutrons and significant thermomechanical stresses. Compared with current fission reactor irradiation conditions, the anticipated fusion reactor environment is substantially more challenging because of the higher operating temperatures and damage exposure levels and the greater number of nuclear transmutation-induced reactions that can lead to undesirable alterations to the microstructure (in particular, n,α and n,p reactions that create gaseous hydrogen and helium). Whereas fission reactor irradiation generates typical transmutant helium levels in structural materials of ~0.1 appm He/dpa, 14-MeV neutrons created from D-T fusion reactions typically generate ~10 appm He/dpa.

In addition to the structural materials under development for fusion energy systems, numerous functional materials systems need to be developed to ensure reliable extraction of the deposited heat for electricity generation, adequate replenishment of tritium fuel (produced in the surrounding “blanket” region of the fusion reactor by nuclear reactions with lithium-containing materials), and radiation shielding of sensitive plasma diagnostic and control systems such as the large magnets that provide confinement of the plasma.

3.1.3.3 Technology needs and challenges for materials in nuclear radiation environments

Looking to the future, there is strong interest in improving the thermodynamic efficiency of nuclear fission power plants from their current value of ~35% by increasing the operating temperature. In parallel with increased operating temperature, there is interest in increasing fuel burnup levels in order to better use the available energy content in the fuel and reduce the amount of generated waste per generated kW_e-h. Furthermore, there is interest in recycling several of the hazardous fission by-products in the fuel in order to cause the by-products to become largely transmuted to less hazardous isotopes during extended exposure in the nuclear reactor. Because of economic considerations, these changes should not introduce a reduction in the overall plant availability. All of these desired advances require the development of improved fuel and structural materials. Whereas current nuclear power plants operate at temperatures near 300°C and experience maximum lifetime displacement damage doses to core internal structures of ~30 dpa, the structural materials in proposed Generation IV fission reactors may experience temperatures of 500–1000°C and damage levels of 30–150 dpa.

The two Generation IV fission reactor concepts currently attracting the most attention are a sodium-cooled fast reactor system that involves fuel recycling of the transuranic and other fission product elements, and a high-temperature gas-cooled reactor concept that uses a triple-containment particle fuel form substantially different from that in current commercial fission power reactors. For the sodium-cooled reactor, the key technology challenge is development of a robust fuel system that can accommodate the simultaneous challenges associated with exposure to high-temperature (up to ~600°C) sodium, intense radiation fluxes, and use of an unproven fuel containing numerous corrosive elements. For the gas-cooled reactor system, the key challenges

are development of high-temperature structural materials with adequate radiation resistance and qualification of a new fuel form.

The process used for the development of currently available nuclear reactor materials was largely based on sequential proof testing, and it was both costly and time-consuming. The time period needed to qualify a new fuel process or structural material for nuclear reactor applications has been on the order of 20 years. There is clear interest in developing an improved fundamental understanding that could substantially reduce this development time and produce high-performance materials (currently unavailable) that could operate under extreme temperature and radiation conditions. In parallel with the development of improved materials, there is strong interest in developing improved structural integrity analyses for pressure vessels and internal structures that incorporate both steady-state and thermal transient operating conditions.

Because a suitable high-intensity fusion reactor test stand currently is lacking, development of fusion materials must of necessity rely heavily on computational simulations in conjunction with appropriately designed fission neutron or ion irradiation validation experiments. There is therefore a strong technological need for improved understanding of the behavior of materials exposed to fusion-relevant radiation, temperatures, and stress environments.

3.1.4 Radiation environments in national security systems

Materials and electronics are exposed to extreme radiation environments in national security systems. Regimes of interest include ultrahigh total dose and high-dose-rate environments, as well as low-dose-rate environments resulting from nuclear bursts, natural and enhanced space environments, or proximity to radioactive materials. In these environments, a variety of physical mechanisms can affect materials and systems:

- particle radiation transport
- EM effects from X-rays that generate pulsed electron currents internal to the system
- electronic radiation effects from X-rays, electrons, neutrons (including neutron activation and γ rays from activated materials), and high-energy heavy ions
- radiation effects on optoelectronics, nanoelectronics, and MEMS
- mechanical shock due to rapid thermal deposition, impulses from vaporization (blow-off), and blast
- damage by reactive plasma interactions with particulates and surfaces
- polymer decomposition
- morphological changes in fissile materials

Broadening the understanding of the effects of radiation on materials will require accurate coupled simulations of these mechanisms, followed by experimental validation. New computational and experimental tools and facilities developed by NNSA will be key to these investigations.

3.1.4.1 Radiation transport

An understanding of particle radiation transport is fundamental to determining radiation effects. Methods are needed to evaluate the transport of neutrons, γ rays, electrons, and ions. In addition,

transport calculations must be performed to provide information on dose and dose enhancement, charge deposition, and electron emission currents.

3.1.4.2 Electromagnetics

Nuclear bursts give rise to a variety of EMP effects that can damage electrical components. Of particular interest for NNSA systems are the SGEMPs induced by electron currents that are internally generated within a system by the pulse of X-rays from a nuclear detonation. Simulation of SGEMPs will require advanced modeling techniques. For SGEMPs within system cavities, validated models have been developed for high-pressure (atmospheric) and low-pressure regimes, where the mean free path of electrons is significantly smaller or larger than the physical dimensions of the problem and the model approximations work reasonably well. Further development of advanced models is needed to evaluate SGEMPs within cavities at intermediate gas pressures and to assess high-voltage breakdown that occurs because of changes in conductivity induced by radiation. The latter phenomenon is becoming increasingly important as electrical components are miniaturized.

3.1.4.3 Electronics and sensors

Research is needed to predict the effect of radiation on optoelectronics, nanoelectronics, MEMS, and sensors. Complex devices will require novel approaches to monitoring and diagnostics.

3.1.4.4 Material effects: Electronic excitations

Molecular ions and radicals produced in irradiated gases and in plasmas undergo many chemical reactions both in the gas phase and on surfaces. In this manner, new materials can form as particulates and as surface films. The entire chain of events and reactions, from the generation of the molecular ions or radicals to the formation and growth of surface deposits, requires innovative approaches to address the various time and length scales.

The passage of high-energy ions through matter creates an ion track and an intense shower of secondary electrons. Subsequent charge recombination and dissipation of deposited energy can result in material ejection and in structural changes within the ion track. Large macroscopic deformation can be induced in amorphous materials that are exposed to penetrating beams of heavy ions. These radiation effects are collective phenomena of the exposed material driven temporarily into extreme states of non-equilibrium. New approaches must be developed to describe such extreme states of matter.

3.1.4.5 Material effects: Polymers and fissile materials

A combination of theory and experiment is needed to study material responses to various scenarios that lead to the decomposition of polymer and fissile components. This combined approach should focus on development of an expanded understanding of rate-controlling processes for different radiation exposures; mathematical models of processes to address the shortcomings of standard chemical kinetics analysis methods; decomposition kinetics and gas generation models and equations of state; an improved understanding of fundamental decomposition chemistry, along with *ab initio* quantum chemistry calculations of transition states; and methods for testing new hypothetical models.

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3.2 CHEMICALLY REACTIVE ENVIRONMENTS

3.2.1 Introduction

Chemically reactive extremes encompass an enormous array of environmental variables under which novel materials may be fabricated or required to operate. Of principal interest are the generation, containment, and utilization of reactive fluids at extremes of temperature or pressure and the detrimental effects of such fluids on solid or semi-solid phases. Examples are

- aqueous fluids in USC fossil and nuclear power plants, hydrogen fuel cells for transportation, advanced batteries, nuclear waste processing and geological disposal, and hydrogen production via water splitting
- reactive and non-reactive gases at extreme temperatures and pressures, including gas turbines, gas-cooled nuclear reactors, solid oxide fuel cells and gaseous H₂ transmission and storage
- molten salts and non-ionic liquids as heat-transfer media in advanced nuclear reactors and thermochemical hydrogen production systems
- ionic liquids for fuel cell and battery applications
- steam, gases, and hydrocarbons produced during in situ oil shale processing and coal and biomass liquefaction and gasification

Among the many novel materials needed are

- metals that exhibit required thermal-mechanical properties while remaining sufficiently resistant to corrosion under extreme redox, pH, and embrittlement conditions and/or extreme time scales
- ceramics and cements capable of containing reactive fluids, conducting ions or electrons, and exhibiting other special properties at extremes of temperature, pressure and fluid reactivity
- polymeric membranes, coatings, and ionic liquids highly resistant to thermal and chemical degradation that either facilitate or prevent mass transfer
- non-precious-metal catalysts for fuel cells and other applications

In all applications, fabrication cost and service life are primary factors. The chemical environment may be intrinsically extreme, as it is in hydrogen production via electrolysis, where high-pH and high-ionic-strength aqueous solutions are the most efficient reaction media; or in batteries and PEMFCs in which the electrodes and other internals are exposed to highly acidic

solutions and extremely oxidizing and reducing conditions. More often, the environment is rendered chemically extreme as a result of other, application-driven, environmental variables. Chloride and fluoride salts, which are virtually inert solids, become aggressively corrosive to certain materials in the molten state required for heat-transfer applications. In electrical power plant steam generators, the overall efficiency increases with steam temperature. Therefore, operators want to operate next-generation plants under “USC conditions” ($T > 700^{\circ}\text{C}$ and $P > 30 \text{ MPa}$), in which metals that are sufficiently thermomechanically stable must also be highly corrosion resistant or effectively clad or coated with a corrosion-resistant material. Hydrogen fuel cells for vehicular transport must be capable of operation at low relative humidity and temperatures $>120^{\circ}\text{C}$ in order to maximize heat management, gas delivery, and catalyst efficiency; those conditions are show-stoppers for the currently available classes of proton-conducting membranes. In gas turbines, the exceedingly high temperatures and velocities created by the expansion of the burning fuel/oxygen mixture result in devastating corrosion and erosion of combustion chamber, flow channel, and turbine surfaces.

Elevated pressure creates unique chemical reactivity problems for hydrogen production and storage as a result of embrittlement of metals. For carbon sequestration, the corrosive nature of subsurface aqueous solutions in contact with monitoring and injection well metals and cements is directly impacted by pressurization with CO_2 , via the acid-producing reaction $\text{CO}_{2,\text{g}} + \text{H}_2\text{O}_{\text{liq}} \leftrightarrow \text{HCO}_{3,\text{aq}}^- + \text{H}_{\text{aq}}^+$. Also in this environment, the geologic repository itself can be a limiting material issue in that reservoir permeability and cap-rock integrity depend on as yet unstudied mineral transformation rates and mechanisms under highly acidic, high-carbonate conditions at elevated temperatures and pressures. The same issue applies to nuclear waste isolation. The permeability and mineralogical stability of the geologic repository—which can affect the hydrodynamics and immobilization of radionuclides by adsorption and precipitation reactions—depend on as yet unquantified reaction rates and mechanisms driven by steep thermal, radiation, and redox gradients imposed by the emplaced waste packages.

Radioactive waste isolation represents the far end of a continuum of chemical reactivity issues rendered significant largely by the time scale over which a particular material must perform. In the initial Yucca Mountain Repository design, the fundamental barrier to radionuclide release to the accessible environment was the selection of a highly corrosion-resistant metal for the outer canister walls (C-22, a Ni-Cr-Mo-W-Fe alloy). However, the generalized corrosion rate of this material is so low, and therefore so poorly quantified, that it is not possible to predict its performance over a regulatory period that is expanding from the initial 10^4 -year period to perhaps 10^5 – 10^6 years (Macfarlane and Ewing 2006). In fact, we do not have empirical data to support even the most rudimentary aspects of engineered materials performance extending beyond the 10^3 – 10^5 archeological record of preservation of metals, cements, pottery, arrowheads, and other human artifacts. This same factor of length of exposure to chemically reactive environments is an underlying theme in all materials applications, for example, metals used in fossil power plants for 5–10 years; fuel cells, engines and batteries in vehicles that should operate for at least 10–15 years; and nuclear reactor cores and primary coolant loops that must maintain integrity for 30–50 years or more. Even in the case of CO_2 injection, where a naturally occurring subsurface gas is introduced into reservoir rocks many millions of years old, the materials performance period required to ensure effective sequestration extends to thousands of years.

Much of the uncertainty related to materials performance over extended time scales in chemically reactive environments is directly related to the often Edisonian methods of new materials development. This is epitomized by the development of metal alloys that exhibit superior thermal-mechanical and joining properties and resistance to oxidation/corrosion/cracking/creep. Typically new alloys are formulated on the basis of previous experience with similar alloys, rather than predictive models of the physical and chemical characteristics produced by the type and concentration of each alloy component. For materials that must perform over time scales longer than recorded history, this is not a useful approach. Fundamental research over a 20- to 30-year time period—incorporating breakthroughs in characterization, computational and theoretical developments—that leads to a predictive capability for materials fabrication and performance would enormously impact materials development for unique applications.

3.2.2 Development of Corrosion-Resistant Metal Alloys

3.2.2.1 Corrosion by aqueous solutions

Fossil steam generators. The majority of current fossil steam generator systems in the United States are single-reheat, pulverized-coal-fired Rankine units with an efficiency of approximately 3.4. The main steam conditions are 538°C and 16.6 MPa, and typical utility boilers are designed to produce 350–500 MW. Supercritical single-reheat boilers with steam pressures of 24.1 MPa and the same steam temperature are also constructed. The pulverized coal is pneumatically injected through large nozzles in the walls of a large square or rectangular cross-section vessel, of the order of 15 m in cross section and 50 m in height. The vessel is formed of tubes, usually vertical, some 50 mm in diameter, separated by webs of 5-mm or so. Water enters the tubes at the bottom of the wall and is heated by the combustion within the vessel. The water begins to boil about one-third of the way up the tube; at the top of the vessel, the tubes are manifolded into a steam drum. The remaining water is separated from the steam and is re-injected into the bottom of the wall tubes. The steam is further superheated and eventually passes to a high-pressure turbine, which drives the generator. The steam cools as it passes through the turbine and, in most units, is returned to the boiler, reheated, and then transferred to a second turbine. At the exit to this turbine, the steam has started to condense. The steam/water mixture then enters a condenser, and the water at the exit of the condenser is returned to the bottom of the boiler.

Chemical-related problems occur in both the fire side of the components, which sees the combustion environment, and the steam side, which sees the fairly pure water or steam. Problems on the fireside in the past have included

- water wall corrosion, associated with the deposition of iron sulfides present as an impurity in the coal
- superheater corrosion, associated with the deposition of molten alkali sulfates, again principally from impurities in the coal
- low-temperature corrosion in the exhaust system, associated with the condensation of water containing sulfuric and sulfurous acids

On the steam/water side, an oxide layer forms, the composition and structure of which depend on the alloy composition. However, the cooler parts of the system are generally low-alloy steels,

and the oxide is typically magnetite, Fe_3O_4 . Significant problems can arise from the spallation of this oxide, which may have two adverse effects:

- collection of the spalled material in the bottom of tube bends, leading to blockage, overheating, and rupture
- transport of the oxide through the system to the main steam valves and the steam turbine, resulting in erosion damage

In addition to these materials issues, other problems arise from downstream effects in the exhaust. Over the last 40 years, there have been efforts to reduce the emission of harmful contaminants from these units; initially the major effort was directed at the control of oxides of sulfur (SO_x) by flue gas desulfurization. The principal product of combustion of the sulfur in the boiler is SO_2 , which in the presence of excess oxygen oxidizes to SO_3 . The exhaust combustion gas is high in water vapor, and eventually the temperature will fall below the dewpoint; sulfuric acid will then condense and be deposited with calcium salts on the walls and floors of the flue. A further problem is the presence of chlorine as HCl in the exhaust. Many of the potential alloys are sensitive to HCl: Type 316L stainless steel can be used only with low-chlorine coals; higher-chlorine coals require alloys such as C-276. Nitrogen oxides (NO_x) are also significant flue gas contaminants, and noncatalytic reduction methods require extreme operating conditions that can result in corrosive materials problems.

A reduction of up to 25% in tons of CO_2 produced per kilowatt hour of electricity can be achieved in USC plants operating at $T > 700^\circ\text{C}$ and $P > 30 \text{ MPa}$, since efficiency is directly related to primary steam temperature. The best example is the supercritical boiler built at the Eddystone plant of the Philadelphia Electric Company in which steam conditions were 649°C , 34.4 MPa. When it was installed, the efficiency was 0.41, a >20% improvement over conventional plants; but no other units of this type were built, although a number of supercritical boilers have been installed.

Worldwide efforts are now focused on materials for USC steam generation and utilization (Viswanathan et al. 2005; LeComte-Beckers et al. 2006), resulting in numerous high-strength alloys for heavy section piping, tubing, water walls, and steam turbine rotors. Minimizing thermal fatigue and maximizing thermal creep strength are major issues for heavy-section components; research is focused on 9–12%Cr ferritic steels, the optimization of C-Nb-Mo-V content, and substitution of tungsten for molybdenum. For enhanced oxidation resistance at steam temperatures $>620^\circ\text{C}$, 12% Cr alloys with cobalt and additional tungsten are being investigated. Nickel-based alloys and austenitic steels offer advantages over ferritic steels for higher-temperature operation, particularly for tube metal applications. Another route to achieving the needed corrosion and fracture resistance with stronger alloys is cladding or weld-overlaying with high-Cr alloys and other highly resistant materials. A large area of fundamental research lies in the atomic-scale nature of bonding in welds, at cladding interfaces, and along grain boundaries as a function of temperature, pressure, and chemical environment, including attack by SO_x and NO_x compounds.

A different set of targets for Rankine systems relates to the need to handle fuels of different types. These include

- biomass, including agricultural waste and wood byproducts

- industrial and domestic solid wastes
- lower-grade fossil fuels, including lower rank coals, peat, and residual tars

Obviously, the chemistry demands for materials of construction are considerable; the variability of the fuel chemistry and physical characteristics are of particular concern. While all of these technologies have been studied for many years, the new demands imposed by environmental concerns, and questions about fuel availability, have increased the need for advanced research. The combustion techniques of most interest are fluidized-bed combustion and variations in incineration methods.

Advanced nuclear reactor systems. In current pressurized water reactors (PWRs) and boiling water reactors (BWRs), the primary aqueous coolant serves the dual functions of (1) moderating the neutron flux in the core (LiOH and boric acid are added as a “chemical shim,” with the pH and total boron content adjusted as the fuel characteristics change with time) and (2) transferring heat to a secondary water/steam system similar to that found in fossil steam generators. Because of the highly radioactive nature of the primary coolant, reactor internals and heat exchanger tubing use high-Ni-Cr alloys, wherein a chromium oxide surface coating serves as the corrosion inhibitor. There is a strong desire to increase the efficiencies and operational lifetimes of existing and new BWRs and PWRs because doing so would be economically advantageous and would curb undesirable emissions. Also, in PWRs, raising the operating temperature has increased power output. However, this has given rise to problems associated with unpredictable neutron flux and fuel consumption characteristics (axial offset anomalies), boiling within corrosion product or “crud” deposits, and boron “hideout.” The sorption/desorption characteristics of the ZrO_2 film that forms on Zircaloy fuel cladding, as well those of as high-NiO crud deposited on fuel surfaces, are poorly known under these operating conditions. In nuclear reactors for naval and other small applications in close proximity to human activities, a major concern is transport of activated cobalt and other radionuclides, often derived from corroding gaskets and other core-external components, into the heat exchanger area. This can be the limiting factor in the life cycles of such power plants. Thus improvements in the chemistry and fabrication of a variety of materials will facilitate the expansion of nuclear electrical power generation in the interim period as next-generation plants with non-aqueous primary coolants begin to be licensed and deployed.

Nuclear waste isolation. All current worldwide designs for permanent nuclear waste disposal involve final emplacement of waste-containing metal canisters in deep underground repositories. In these environments, the canisters inevitably come in contact with liquid water, whether in the below-water-table (saturated zone) designs envisioned in most countries, or in the U.S. Yucca Mountain facility that will be in the unsaturated zone above the extremely deep water table in an arid region (MacFarlane and Ewing 2006). In saturated-zone systems under reducing or at least anoxic conditions, copper is emerging as the preferred outer liner, for which there are empirical performance data spanning many millions and even billions of years from naturally-occurring native copper deposits. Many such repository designs also include a backfill material to serve as an additional barrier to radionuclide release by permeability occlusion, as well as radionuclide adsorption or precipitation.

The current Yucca Mountain Repository design does not include a backfill barrier; rather, canisters with a highly corrosion-resistant outer shell will be placed under titanium canopies (to

serve as drip shields and deflectors of falling rock) within open cylindrical drifts. A significant concern in this system (which is open to the ambient atmosphere via numerous fractures in the mountain) is the formation of high-chloride deliquescent brines (in the system Na-K-Ca-Cl-NO₃-SO₄) from salt-laden dust on canister surfaces after final closure, when the relative humidity in the emplacement drifts is expected to rise to 100%. Dripping of liquid formation water onto drip shields and canister surfaces is also possible during the post-closure cooling-off period. Because the canisters will be hotter than their surroundings for many thousands of years, these processes will inevitably lead to brine concentration in any liquid water contacting the canister surfaces. The primary concern associated with such aggressive brines is the development of localized pitting and crevice corrosion of C-22, a high Ni-Cr-Mo-W alloy. Much current research (sponsored by the Yucca Mountain Project and more recently the Office of Civilian Radioactive Waste Management, Science and Technology Program) has focused on localized corrosion characteristics of titanium, C-22, and various analog metals with faster corrosion rates that are more practical for laboratory investigations spanning months to years. Much additional research will be required in order to develop confidence in C-22 and future alloy compositions for performance projections over million-year time spans.

Future waste streams may be drastically altered from the current commercial nuclear power plant spent fuel, which consists of Zircaloy-clad UO₂ fuel pellets containing 3–5 wt % fission products. Indeed, if nuclear energy is to replace fossil fuels for a much larger percentage of worldwide electrical energy production, changing from the current fuel is a necessity, since the once-through fuel cycle would quickly consume all of the world's high-grade uranium ores without reprocessing of spent fuel. As discussed in the recent DOE workshop report on basic research needs for advanced nuclear energy systems (July 31–August 3, 2006, http://www.sc.doe.gov/bes/reports/files/ANES_rpt.pdf), the final waste may be very different in internal chemistry, radiation and heat flux vs time, and packaging for geological disposal. This will spark a major new effort to develop suitable alloys, cements, and other materials for very long-term storage under geochemical conditions.

CO₂ sequestration. In order for CO₂ sequestration to become a viable mechanism for permitting the continued use of fossil fuels without adverse effects on climate, truly enormous volumes of high-pressure gaseous or liquid CO₂ must be reliably contained within deep underground reservoirs such as spent oil and gas fields and deep saline aquifers. Since injection is expected to span many decades, and monitoring wells will be needed for operation over tens to hundreds of years, new alloys are needed that are stable against acid attack at modest temperatures (50–100°C) in the presence of abundant H₂S, carbonates, sulfates, and other corrosive components. For setting and plugging injection and monitoring wells, new cements are desired that are self-healing after fracturing and highly resistant to attack by highly saline, acidic brines. Given the enormous scale of this endeavor, an emerging issue is the effect of emplaced materials on subsurface water quality and microbial communities. Alloys containing nickel, chromium, and other highly toxic metals may be prohibited.

3.2.2.2. Corrosion by gases under extreme temperatures

A number of high-temperature commercial processes produce complex gaseous environments that can be highly aggressive from the standpoint of surface degradation of structural components. These processes are typically multi-oxidant and include oil refining, coal

gasification, fossil-fuel conversion, and gas turbine operation. New fossil power plant designs incorporating oxygen-fired combustion produce a concentrated CO₂ output stream desirable for capture and sequestration, but the severe oxidative corrosion and high combustion temperatures associated with a pure-oxygen feed pose major materials challenges. Multi-oxidant process environments are often non-equilibrium and can involve both gaseous and deposit-induced attack. In the case of metallic alloys and coatings, the formation and maintenance of a thermally grown oxide scale or a thermal barrier coating (TBC) is required for surface protection. Only in very specific environments, such as those containing a high level of H₂ or CO, is the oxygen partial pressure, pO₂, insufficiently high for the oxide to be thermodynamically stable in a multi-oxidant environment. Thus it is primarily the formation kinetics of the oxide scale and its resistance to chemical and mechanical instabilities that dictate surface protection. As a consequence, most high-temperature alloys are designed for oxidation resistance, and the requisite slow-growing oxide usually is either Cr₂O₃ or Al₂O₃ (cf. Yamamoto et al. 2007). Total alloy content and specific alloying additions often play important roles in determining the resistance of a given alloy to secondary types of surface reactions.

Oxidation–sulfidation. The high-temperature degradation of metallic alloys and coatings in oxidizing-sulfidizing environments has been reviewed by Gesmundo et al. (1989), Stringer (1990), and Gleeson (2004), among others. Important factors associated with oxidation-sulfidation include

- gas pressure, temperature, and time at temperature
- gas composition (whether sulfur is present primarily as H₂S or SO₂, and presence of additional species such as HCl, CO, H₂O, or a combination of these)
- downtime or dewpoint corrosion
- temperature differential between the component surface and the surrounding gas
- component geometry

At issue with these factors is whether the alloy or coating surface reacts to form a sulfide. Although the mechanism of sulfidation is fundamentally similar to that of oxidation, the two processes differ both in complexity and in rate of attack because of a larger number of stable sulfides and low-melting-point eutectics formed in many of the metal/sulfide systems.

Oxidation–hot corrosion. Hot corrosion is an accelerated degradation process that involves deposition of corrosive salts (e.g., sulfates) from the surrounding environment (e.g., process gas) onto the surface of hot components, followed by destruction of the thermally grown oxide scale by a liquid fluxing mechanism. The formation and subsequent deposition of a salt depend on trace metal species (e.g., sodium, potassium, lead, zinc compounds) in the gas streams and other reactive gas species (e.g., SO₂, SO₃, HCl). The rates of corrosion depend, among other factors, on the rate of deposit formation, deposit composition, temperature, and process environment. The temperature range over which hot corrosion is apt to be the principal mode of surface degradation is about 650–950°C. Coatings exist that protect against hot corrosion; however, there are currently no coatings or alloys that provide adequate protection in both hot corrosion and oxidation regimes. This is indicated in Fig. 7, which compares cross-sectional images of a β-NiAl coating after (a) oxidation and (b) Na₂SO₄-induced hot corrosion at 900°C for 100 h. The oxidized coating shows no noticeable degradation, whereas the hot corroded coating is completely attacked, forming internal particles of sulfide and oxide together with microcracks.

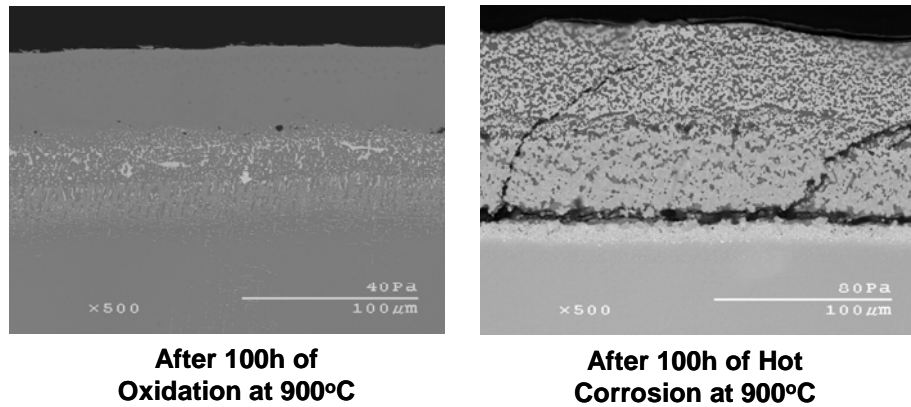


Fig. 7. Degradation incurred by a β -NiAl coating after 100 h of exposure at 900°C under (a) oxidizing and (b) Na_2SO_4 -induced hot corroding conditions.

Resistance to hot corrosion depends on the extent of the protection provided by the oxide scale, which can prolong the initiation stage and inhibit the propagation stage. The initiation stage ends when salt or sulfur penetrates protective scale by forming sulfide particles beneath the scale. The mechanism by which a secondary oxidant penetrates the oxide scale is not clear. The duration over which the scale provides protection against hot corrosion is influenced by factors including alloy composition, composition and thickness of the oxide scale, gas composition, salt composition and its physical state, salt deposition flux, temperature, thermal cycles, erosion, specimen geometry, and thickness of the salt deposit.

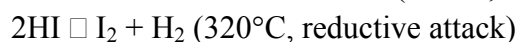
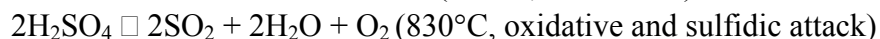
Gas turbines. For electrical power generation using fossil fuels, a major alternative to the Rankine cycle is the Brayton cycle, often used in combustion turbines. In the combustion turbine, air is ingested using a turbine and compressed; the fuel is then injected into a combustion chamber with the compressed air. The hot combustion gas then enters another turbine. The first stage or stages of this cycle drive the compressor. The rest of the energy then generates electricity (for example), using a gas turbine to drive the generator. For many years, natural gas was the fuel used; the advantage over the Rankine cycle is that the whole system could be started and stopped very quickly. From the point of view of the electric utility, power generated this way could be used to satisfy peak demands. The maximum temperature, which is experienced by the first stage of the turbine used to drive the compressor, can be very high. However, the power turbine which is driven by the exhaust, experiences a lower entry temperature, and the effectiveness of the power turbine drops very quickly. As a result, a Brayton cycle is seldom much more efficient than a Rankine cycle. The temperature of the exhaust, which is at a relatively low pressure, is quite high; thus it is possible to recover the energy from it using a Rankine cycle machine. This approach is called a combined cycle, and it may be much more efficient than a Brayton cycle alone.

Within the last few years, DOE has supported research by turbine manufacturers to develop systems such as the combined cycle and, in particular, to develop very large combustion turbines with very high peak temperatures. These temperatures have been achieved by the introduction of advanced materials originally developed for aircraft engines, along with sophisticated component cooling schemes. Hot section materials include directionally solidified nickel-base superalloy single crystals (up to 30kg in mass) with advanced thermal barrier coatings (TBCs). The exhaust

gas heat recovery steam generator system is basically similar to a conventional boiler and generally drives a separate generator. The overall efficiency of these combined cycle systems has reached an impressive 60%, and a number of electric utility installations are under way. One of the most exciting technologies at the moment is coal gasification, because it combines the benefits of a combined cycle and a low-cost fuel. The system is called an integrated gasification combined cycle (IGCC). One of the major attractions of the system is that one of its exhaust stream can have a very high concentration of CO₂, which offers the possibility of being able to sequester the CO₂. This requires that the gasifier be oxygen blown. In conventional oxygen-blown gasifier systems, it has been demonstrated that virtually complete removal of SO_x, NO_x, chlorine, and particulates, can easily be achieved. While it still has to be demonstrated, it is believed that removal of mercury should also be possible. Four large-scale demonstration units have been running for several years at Wabash River, Tampa Electric Company, Buggenum (in Holland), and ELCOGAS (Puertollano, Spain). It has been shown that integration of the plant and the air separation unit should be avoided. The general success of these plants is encouraging, and improvements in all the key components may be achievable (Vaswanathan et al. 2005):

- Air separation units: ion transfer membranes or other new membranes
- Gasification: feed systems, refractories, injectors
- Gas cooling: higher metal temperatures
- Gas cleaning: sulfur, nitrogen, and trace elements—new sorbents
- Separation of gas species: membranes for CO₂ and H₂
- Gas turbine advances: high-temperature materials, coatings
- Advanced cycles: humid air turbine, O₂/CO₂, hybrids
- Fuel cell cycles: lower-cost materials, manifolds

Thermochemical hydrogen production. Generation of hydrogen for transportation fuel using heat from solar, nuclear, gas turbine, or SOFC sources involves the operation of thermochemical cycles at extremely high temperatures. Many such cycles, which become energetically favorable at moderate temperatures, involve highly corrosive solutions, for example, the sulfur-iodine cycle:



Both I₂ and SO₂ can be recovered; thus this and other such cycles simply facilitate the splitting of water into separate H₂ and O₂ streams. The latter could be used for oxygen-fired combustion systems, while the former could be combusted, stored, or transported. For this type of system to become practical for large-scale hydrogen production, new alloys must be identified that can withstand these extremely corrosive conditions over long periods of time.

3.2.3 Organic and Polymeric Materials

3.2.3.1 Ionic liquids

During the past decade, the chemistry of low-melting-point molten salts, referred to as ionic liquids (ILs), has expanded exponentially. Examples of published and patented applications

include fuel and solar cell designs, materials for electronics, solvents and catalysts for organic synthesis, separations and purifications, heterogeneous and homogeneous catalysis, polymer synthesis, metals refining, lubricants, and biopolymer processing. A number of stable organic cations such as ammonium, phosphonium, pyridinium, and imidazolium salts are low-melting and have been known for quite some time. The emergence of imidazolium room temperature ILs (RTILs) based on their chloroaluminate derivatives and the hydrolytically stable BF_4^- and TfO^- derivatives (Wilkes and Zaworotko 1992) initiated an era of active and interdisciplinary research, which is still in progress. The liquid range of the emim-based ILs depends on their counteranion and can extend to surprising low temperatures (Fig. 8a). 1-Methyl-3-pentylimidazolium tetrafluoroborate is a liquid to -88°C (Fig. 8b). For a given organic cation, structural symmetry leads to a higher melting point. For instance, the dimethylimidazolium salt ($C_n = 1$) has a much higher melting point (103°C) than either its imidazolium ($C_n = 0$, melting point = 52°C) or 1-ethyl-3-methylimidazolium (emim; $C_n = 2$, melting point = 6°C) counterparts (Fig. 8b). Along with low melting points, ILs also have very low vapor pressures at high temperature. As organic solvents, they have extraordinary liquid ranges ($> 200^\circ$). They are also nonflammable.

(a)	X =	Cl^-	PF_6^-	NO_3^-	BF_4^-	AlCl_4^-	TfO^-	Tf_2N^-	CF_3CO_2^-
	emim-X	83	62	38	15	7	-9	-12	-14

$\text{TfO}^- = \text{CF}_3\text{SO}_3^-$, $\text{Tf}_2\text{N}^- = (\text{CF}_3\text{SO}_2)_2\text{N}^-$

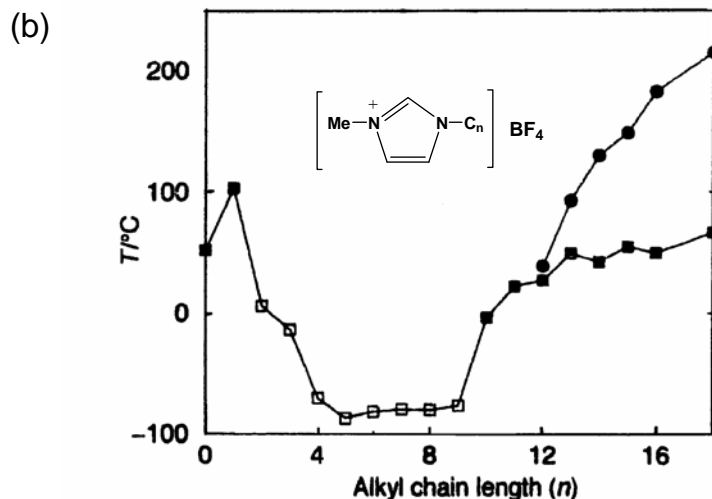


Fig. 8. Phase diagram of $[\text{C}_n\text{mim}][\text{BF}_4]$ (a). Melting points (■), glass (□) and clearing (●) transitions measured by DSC (b).

A wide “electrochemical window” (i.e., range of stability), is an important asset for solvent-free electrolyte applications such as capacitors, actuators, batteries, fuel cells, and solar cells. Conductivity is also important. The conductivities of most ILs range from 10^0 to 10^1 mS/cm and, not surprisingly, the conductivity and viscosity of ILs are inversely related. In Fig. 9, a Walden plot of over two dozen alkylimidazole ILs illustrates the inverse correlation of viscosity and conductivity for these electrolytes.

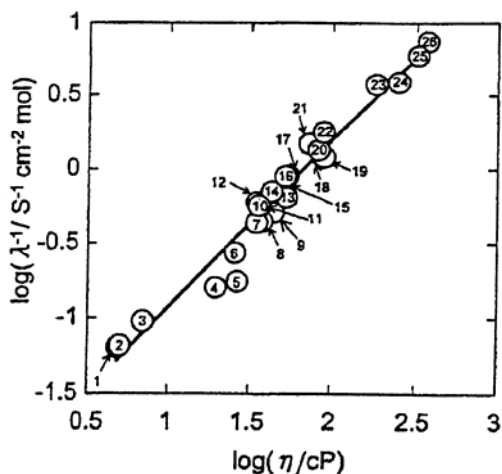


Fig. 9. Walden plot of alkylimidazole ILs.

Table 4 compares the properties of [emim][BF₄] as an electric double layer capacitor (EDLC) relative to aq. sulfuric and electrolyte/solvent standards. Numerous patents and disclosures by Panasonic suggest that a [emim][BF₄]-containing EDLC for automotive applications will soon be commercialized. Supercapacitors are already being used in the Toyota Prius. If ILs establish a role in the supercapacitor market, their impact on transportation energy technology could grow to be significant.

ILs may also establish a role as electrolytes in PVs and fuel cell applications. Grätzel has recently compared dye-sensitized solar cell designs (capable of >11% efficiency) employing either RTILs or organic solvent-containing electrolytes. The low vapor pressure of ILs is a major advantage over organic solvents for long-life devices. For fuel cells, the class of ILs known as protic ILs (PILs) is important for producing electrolytes that have enhanced proton conductivity. It is also possible to plasticize polymers with ILs and thus produce polymer gels or conductive polymer matrices that are solid-state proton conductors. The design of ILs or PILs that facilitate proton conduction and enhance electrode processes beyond the performance of water-based systems may improve fuel cell efficiency.

Table 4. Physical properties of ILs and electrolytes in EDLC cells

Electrolyte	Conductivity (mS/cm)	Viscosity (cP)	Capacitance (F/cm ³)	Resistance (Ω)
35 wt% H ₂ SO ₄	848	2.5	23.2	4.6
[emim][HF]2.3F	100	4.9	11.1	6.6
[emim][BF ₄]	13	43	6.8	19.8
1M [Et ₃ MeN][BF ₄]/PC	13	3.5	8.1	11.8

PC = propylene carbonate

The use of ILs for the treatment and refining of the byproducts of nuclear fission, in particular for the reprocessing of valuable actinides from mixtures of other fission products, appears promising. The low volatility and flammability of ILs provides obvious benefits with regard to the safety and containment of contaminated materials. Likewise, radiation studies have shown that imidazolium ILs are relatively stable to α , β and γ -radiation when compared with the tri-n-butylphosphate/odorless kerosene mixture used in the PUREX process. Extraction of uranium, plutonium, and americium by alkyl-imidazolium systems and the electrodeposition of metallic uranium has been demonstrated. Progress is also being made on ILs that are appropriate to electrodeposit plutonium.

3.2.3.2. Proton-exchange membranes

Novel proton exchange membranes (PEMs), which serve in H₂/O₂ and direct methanol fuel cells as proton conductors as well as electrical insulators and barriers to fuel/oxidant mixing, are

critically needed for advanced fuel cells that operate efficiently and reliably at -40 to $>130^{\circ}\text{C}$ and relative humidities between 0 and 100% (Eikerling et al. 2006; Kreuer et al. 2004). The chemical/thermal/mechanical stability and proton conductivity of PEMs and the power output of assembled fuel cells have been the target of basic and applied studies for decades. Nafion®, the industry standard PEM, is a statistical copolymer of tetrafluoroethylene and tetrafluoroethylene substituted with pendant perfluoroether chains terminated with sulfonic acid groups. This material is highly polydispersed, its molecular weight is not known, and placement of the sulfonic acid groups along the backbone is not readily controlled. Although statistical copolymers usually do not form multiphase morphologies, in the case of Nafion the very high incompatibility between the two types of units does result in a nanometer-sized phase-separated morphology. Over 500 papers per year for the past 10 years have focused on Nafion, yet the functional structure of this material remains uncertain (Mauritz and Moore 2004; Gebel and Diat 2005). Nafion proton-conducting membranes are expensive and suffer severe decreases in proton conduction and durability during sustained operation at $>80^{\circ}\text{C}$ and $<100\%$ relative humidity. It has become clear that, particularly for transportation applications, hydrogen/oxygen PEMFCs must be capable of (1) cold starts at extremely low temperatures and (2) sustained operation at temperatures of up to at least 120°C in order to facilitate heat management, minimize degradation of the anode catalyst by CO and other fuel contaminants, and enhance cathodic reaction rates, a limiting factor in power output. Furthermore, operation at relative humidities $\leq 25\%$ are essential in order to (1) permit operation at or near atmospheric pressure; (2) prevent blocking of gas inlet channels, diffusion layers and electrodes by condensed water; and (3) facilitate efficient removal of the water produced at the cathode. Despite many advances in polymer membrane R&D, with the goal of developing less expensive membranes with improved high-temperature/low-relative-humidity performance, no new material has emerged that is completely satisfactory (cf. Kreuer et al. 2004; Harrison et al. 2005).

In recent years, a number of researchers have recognized that the addition of inorganic nanoparticles (oxides and other compounds of Al, Mo, P, Si, Ti, W, Zr, etc.) to Nafion membranes (and to a lesser extent other polymer membranes) can dramatically improve proton conduction, water uptake and retention, and membrane tensile strength, while reducing polymer decomposition and deleterious fuel, oxygen, and water transport across the membrane (Alberti and Casciola 2003).

These observations suggest that optimization of the effect of inorganic additives might result in further enhancements in high-temperature/low-relative-humidity performance and might also enhance the high-temperature/low-relative-humidity performance of less expensive alternative polymers to meet the performance and durability targets specified by the DOE Office of Energy Efficiency and Renewable Energy. A number of studies also indicate that inorganic additives enhance polymer strength and durability, permitting fabrication of thinner membranes and resulting in cost savings that scale directly with membrane thickness. Finally, increased proton conductivity, membrane resistance, catalyst efficiency, and reduced fuel/oxygen crossover directly impact power output per kilogram of fuel consumed, providing several additional vectors for cost savings.

The performance of such materials is dictated by their nanoscale structure; thus the rational design of advanced membranes requires control and understanding of morphology and interfacial

interactions at the nanoscale. To overcome technical barriers to the development of superior alternative ion-conducting membranes for fuel cells and other applications—including batteries, desalination, dialysis, etc.—the relationship among chemistry, structure and function must be understood on more than a phenomenological level.

3.2.3.3. Membranes for CO₂ capture

With support from DOE/FE (Klara and Srivastava 2002), Los Alamos National Laboratory is developing a high-temperature polybenzimidazole film supported on sintered metal that exhibits excellent chemical resistance, a high glass transition temperature (450°C), and good mechanical strength. This membrane can be made highly selective for CO₂ removal and is suitable for operation at flue gas conditions in existing fossil power plants. Since membranes can be synthesized from inexpensive feedstocks and can provide high surface area and high selectivity for chemical separations, this is a ripe area of research, particularly applied to CO₂ capture for subsequent underground injection.

3.2.4 Advanced ceramics

3.2.4.1 Solid oxide fuel cells

SOFCs can be made very environmentally friendly, compared with other sources of electrical power, and can be large sources of decentralized power. Their fuel versatility, reversible electrode reactions, low internal resistance, high tolerance to typical catalyst poisons, and high-quality waste heat for downstream applications make them particularly attractive (Adler 2004). In an SOFC (Fig. 10), fuel and oxidant (air or oxygen) are introduced directly into porous and electrically conductive ceramic or cermet anodes and cathodes, respectively. At the cathode, O₂ accepts electrons from the external circuit to form O²⁻ ions, which diffuse through a gas-

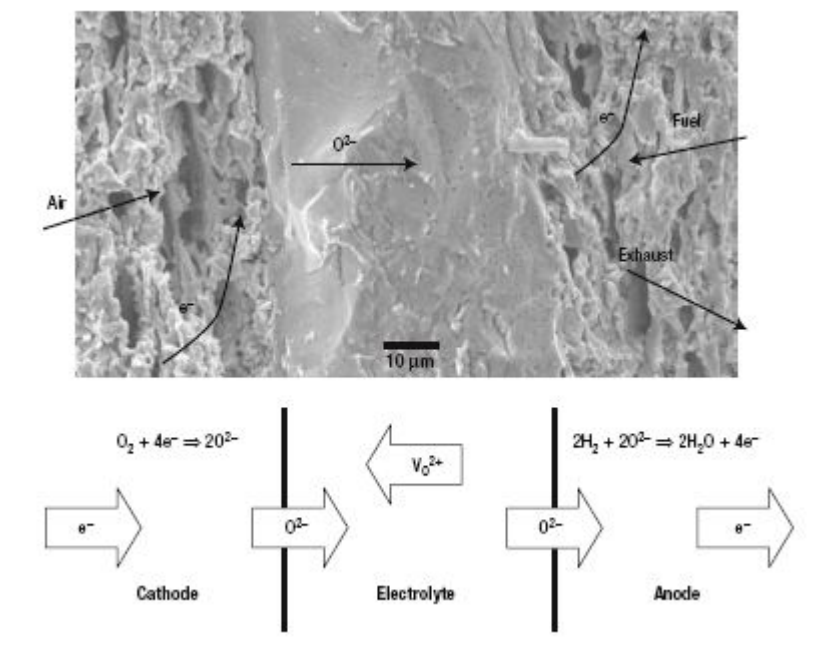


Fig. 10. Cross-section of actual and schematic SOFC. (Source: Atkinson et al. 2004.)

impermeable and electrically insulating “solid electrolyte,” such as Y-stabilized cubic zirconia. At the anode, fuel molecules (H_2 or a variety of hydrocarbon fuels) react with O^{2-} , releasing electrons and H_2O , CO_2 , and other combustion products. The electrons produced at the anode are transmitted either to the external circuit or to the next SOFC in the stack via an interconnect that also serves to separate the fuel and oxidant gas streams. The interconnect can be a suitably corrosion-resistant and inexpensive metal, such as ferritic steel, in “low-temperature” SOFCs (600–900°C), but it must be replaced by an electrically-conductive but gas-impermeable ceramic (such as Sr-doped $LaMnO_3$) for operation at temperatures exceeding 1000°C. The high operating temperature permits the use of much cheaper catalysts, such as nickel, than in PEMFCs, which are also much less subject to poisoning and other forms of thermal and chemical degradation. Reviews by Kharton et al. (2004), Adler (2004), Atkinson et al. (2004), and Steele and Heinzel (2001) demonstrate that virtually every material used in SOFCs can be improved to enhance the economics and applications of SOFC for both stationary and mobile electrical power generation. Perhaps the greatest promise for the future, however, is in combined systems where the additional energy in the extremely high-temperature exhaust can be extracted in a gas turbine and/or steam generator system. Efficiencies of >80% can be achieved in such applications.

3.2.4.2. Ceramic materials for CO_2 capture

Carbon can be removed from fuel either before or after combustion for sequestration as CO_2 (Klara and Srivastava 2002). An innovative water-gas shift reactor is being developed by Media and Process Technology, Inc., and the University of Southern California with support from DOE/FE. This system contains ceramic tubes that incorporate a magnesium silicate membrane permeable to CO_2 and are filled with a catalyst. As fuel from a coal gasifier passes through the reactor, the reaction $CO + H_2O \rightleftharpoons CO_2 + H_2$ produces a hydrogen-rich fuel stream and a pure CO_2 stream for various uses, including sequestration with or without enhanced oil recovery. The hydrogen can then be sent to a fuel cell or combustion turbine. Additional research sponsored by FE includes separation of CO_2 from hot gas streams using Na_2CO_3 , zeolite and carbon sorbents, and CO_2 -permeable membranes composed of Cu-Pd, zeolite, silica, and electro-ceramic.

3.2.5 Material needs for the U.S. oil and gas industry

The oil and gas industry continues to be the likely supplier for much heating and electrical generation fuel and nearly all transportation fuel for decades into the future. Enormous reserves of heavy hydrocarbons in tar sands and oil shales represent an extremely large additional energy resource if the economics can be improved by, among other things, advances in materials for application over wide ranges of temperature and pressure. The conditions extend from seafloor, pack ice, and permafrost environments to the 700–800°C conditions of in situ hydrocarbon extraction from oil shales. The increasing levels of industrialization among growing economies in the developing nations and the unabated demand for energy in the developed world continue to limit the availabilities of critical materials such as finished alloys, steels, CRAs, high-performance plastics/polymers, and other materials used in the oil and gas industry. The sustained high energy prices caused by strong demand for energy continue to be a strong stimulus to increase the availability of oil and gas as energy supplies for the world. Increased supplies of oil and gas will be supported with increased flexibility in choices and lower costs for materials used to fabricate the equipment used in the exploration, production, and processing of oil and gas. Methods of supporting the evolving oil and gas industry include

- increasing diversity of the sources and producers of critical materials
- enhancing technologies for assessing and evaluating the corrosion behaviors and mechanical properties of materials for alternate applications
- Enhancing information management capabilities for comparing materials properties and behaviors and projecting materials responses into novel conditions

As in the fossil power plant systems discussed earlier, many applications in the oil and gas industry require new materials with chemical resistance or increased resistance to corrosion caused by sea water or high-H₂S, high-CO₂, high-Cl⁻, and low-pH fluids and hydrogen entry into steels and titanium alloys. Lower-cost and more available alternatives are needed to current CRAs rich in nickel, chromium and molybdenum, the availability of which is increasingly limited as worldwide demand for them increases and nickel prices continue to rise. Research on austenitic alloys that include manganese to minimize the use of nickel in CRAs might benefit from evaluation of the historic 200 series stainless steels for application in the oil and gas industry. (These were “national emergency” steels developed in the first half of the 1900s, when nickel supplies were limited because of war.) Potential cost savings of a third can be found in comparison of 347 SS to 204, even though their mechanical properties and corrosion resistances are similar. Titanium and aluminum alloys may be attractive substitutes for applications that require CRAs; however, needed advances include improved hydriding resistance (to reduce the risk created by cathodic protection of nearby steel structures), methods of welding/brazing/joining titanium alloys to titanium alloys and other alloy types suitable for service in sea water or other corrosive environments, and high strength-to-weight ratios.

Advanced composites and polymers are needed for a wide range of applications in corrosive environments, especially in high-temperature or physically challenging settings:

- well completions, tubulars, gathering lines, wellheads, and hydraulic control lines
- coatings that serve as corrosion monitors (e.g., coatings that exhibit changes in optical or electronic properties prior to failure under corroding conditions).
- foam insulation for reducing energy consumption in fired equipment such as refineries, chemical and gas plants, incinerators and process heaters
- large-diameter composite piping (up to 10 in.) for service up to 150°C and 7 MPa

3.2.6 Sensor technologies

Every aspect of energy conversion depends on sensors, and almost every kind of signal domain is represented. Accurate, reliable sensors for high-temperature and/or corrosive environments would offer multiple benefits for many applications: avoiding damage to heat-transfer surfaces, combustion control for individual burners in utility boilers (not possible at present), reducing noxious emissions, and structural health monitoring of critical components, to name a few. By way of illustration, three examples of the more obvious needs for improved measurements are summarized in this section.

Sensors for combustion processes. For control purposes, it would be beneficial to measure the composition of combustion gases in real time, for instance, in the furnace section of coal-fired boilers where temperatures are typically 1300–1650°C. In principle, sensors based on fiber optics might make the requisite measurements, except that fiber function is limited by two temperature-

dependent effects: (1) the dopants in conventional silica fibers diffuse rapidly enough to adversely affect signal attenuation and wave-guiding properties; and (2) the silica softens. Since crystalline sapphire has reasonable optical properties (although not as good as those of silica fiber), melts above 2000°C, and resists corrosion, investigations have aimed at developing fiber-optic sensors capable of operating above 1500°C (Claus et al. 1995). Schemes involving sapphire-fiber-based Fabry-Perot interferometers, fiber-Bragg gratings, and intensity-based sensors have met with little success because the coatings and claddings that enable sensors to function cannot survive long enough in the high-temperature combustion bases.

An important challenge for high-temperature sensing is managing emissions from fossil fuel combustion. To control NO_x, ammonia (NH₃) or urea (NH₂-CO-NH₂) is injected into the combustion gas to react with the NO_x and produce molecular nitrogen and water. At the same time, post-combustion NO_x reduction must avoid significant NH₃ in the exhaust, both to comply with emission regulations and to prevent fouling of downstream components. A feedback control system is needed, but reliable, real-time NO_x or NH₃ sensors have not been available. The use of radiative emissions from single molecular transitions (that are well separated from emissions from other constituents in the flow) has been explored for measuring nitric acid (NO) levels. Feedback-stabilized, scanning Fabry-Perot interferometers were linked with thermoelectrically cooled wavelength detectors; cavity lengths were digitally controlled for wavelength scanning. One detector monitored NO upstream of the injection plane and a second monitored NH₃ downstream to determine in real time the quantity of NH₃ or urea to be injected. The prototype system, however, was cumbersome and costly.

pH measurement. Corrosion of steam-plant materials is strongly influenced by the pH of the circulating water. Since the physiochemical properties of water are highly sensitive to temperature, there is a strong incentive to develop online pH sensors that can be used at system temperatures (360–400°C) rather than rely on analytical extrapolations from grab samples cooled to ambient temperature (the current practice). However, attempts to develop online sensors for pH at elevated temperatures confront two problems: degradation of the sensor materials by hot water, and the sensitivity of measured values to the impurities introduced by even slight dissolution of the sensor in the high-purity water characteristic of cooling loops. Attempts to develop sensors for high-temperature water have centered on immobilizing pH-sensitive organic dyes at the ends of optical fibers. If dyes with two absorption peaks are used, pH can be determined from the ratio of the peaks. pH changes associated with additions of 1 ppm morpholine have been measured reproducibly, during long immersions only to about 50°C, with azo-based indicators. A multilayer coating (Ti-Pt-Au), 250 nm thick, on sapphire fibers with a copper phthalocyanine chromophore extended the temperature capability only to 150°C. An alternative approach is the use of highly corrosion-resistant Pt/H₂ electrodes and/or stabilized cubic zirconia pH sensors, either in the process stream or in an external loop that permits electrode calibration prior to measurement of the working fluid. Lvov and Palmer (2004) summarize a variety of high-temperature pH and electrochemical measurement and monitoring approaches attractive for application in a broad range of energy applications.

Analysis of gases in transformer oil. Substation transformers are large, oil-filled structures that are critical to electrical grid system reliability. The cost of a failure, or an outage to repair a unit, can exceed the original cost of the transformer within five days if the cost of replacement power

from a less-efficient station is included. Thermal or electrical stresses in transformers can cause faults in the form of hot spots, partial discharge (corona), and, ultimately, arcing. Such faults produce gaseous breakdown products that dissolve in the oil. By measuring the concentration of fault gases in the oil, incipient faults can be detected and identified before they escalate into forced outages. Typically, nine gases are analyzed for fault identification: hydrogen, oxygen, nitrogen, methane, carbon monoxide, carbon dioxide, ethylene, ethane, and acetylene. Analysis is usually by gas chromatography of a sample extracted from the transformer and, more recently, photoacoustic spectroscopy. These measurements are cumbersome, not acquired in real time, and expensive. Monitoring with fiber optics has been frustrated because transformer oil is an extreme environment: the oil penetrates the fiber jackets and is absorbed by the polymer cladding.

Basic research on sensor materials. The needs outlined in the foregoing discussion have a common theme: Conventional methods for real-time measurements of chemical species in aggressive fluids are not good enough. New approaches are required. A promising direction is the alteration of electrical properties that ensues when analyte molecules are adsorbed on the surface of a sensor material. For example, various nanometer-sized semiconducting oxides have shown sensitivity to NO_x and NH_3 (Shimizu and Egashira 1999); doping these oxides with noble metals increases the sensitivity (Hoel et al. 2004). WO_3 seems to be the most versatile of this class. Similarly, carbon nanotubes exhibit up to five-fold changes in conductance when exposed to ppm concentrations of NO_2 or NH_3 (Cantalini et al. 2004; Kong et al. 2000). This does not necessarily imply that the cited sensor materials would be suitable for extreme combustion environments, but only that molecular adsorption is a possible route to solving the problem.

Measuring the pH of high-purity hot water is an equally difficult problem. Successful pH sensors have been made from boron-doped silicon nanowires functionalized with oxygen and amine (Cui et al. 2001). However, silicon-based sensors are not stable in high-temperature water. It may be possible, though, to adapt this approach to materials that are stable in high-temperature water. Iridium oxide-coated iridium wire is shown to respond Nernstianly to changes in solution pH and, when coupled with a reliable high-temperature reference electrode, might enable routine pH monitoring in the near-critical region of water (Li et al. 2007). Nanocrystalline diamond thin films are a good example. Largely as a consequence of the special nature of grain boundaries in diamond (Kebinski et al. 1998), the higher proportion of grain boundaries in nanocrystalline diamond confer greater stability, higher strength, and better electrochemical properties than can be achieved with either polycrystalline or single-crystal diamond. Advances in the thin-film deposition and the doping of diamond to obtain n-type conductivity (Härtl et al. 2004 and references therein) suggest that methods be explored for creating functional groups on the surface of nanocrystalline diamond that protonate/deprotonate with sufficient sensitivity to chemically “gate” its surface electrical properties.

At this time, sensor discovery and development is largely empirical; there is only a limited basis for rational design. Basic research into transduction mechanisms, such as the effects of molecular adsorption/surface functionalization on electrical properties, would foster codifying results, mapping what is or is not possible for each material class, and relating the observed effects to first principles. There is no reason why sensor materials should not achieve equivalence to the current status of structural alloys, for which computation and modeling guide design.

3.2.7 References

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3.3 THERMOMECHANICAL EXTREMES

3.3.1 Power generation systems

3.3.1.1 Status and technology drivers

The availability of suitable materials with high strength at elevated temperatures is critical to the further development of power generation systems with improved efficiency and lower emissions relative to power output. This applies to units operating with either the Rankine or the Brayton cycle or combinations of the two. Revolutionary advances in high-temperature materials directly translate to revolutionary improvements in efficiency. An example of this is the introduction of nickel-based single crystals into natural-gas-fueled combined-cycle systems, increasing plant efficiency to 60%. In the last 20 years, research efforts have produced significant incremental improvements in the performance of metallic systems, including steels and nickel-based alloys.

The current situation is illustrated in Table 5. Although the potential alloy design space is still not fully explored, there have been no revolutionary monolithic material systems discovered that could displace nickel and/or steel systems, despite significant expenditures in programs worldwide. Eutectic materials, intermetallics, rapidly solidified materials, monolithic ceramics, and various composite materials with exceptional high-temperature properties have been developed. However, these materials have often lacked the set of balanced thermal and mechanical properties possessed by nickel and steel and therefore have not been adopted. Although there have been some efforts to modify designs to mitigate shortcomings such as low ductility, this approach is generally viewed as too risky. TBCs represent an alternate approach to increasing temperature capability for internally cooled components. Such multilayered systems exploit the low conductivity of zirconia-based ceramics in combination with the strength and toughness of the superalloy substrate. Future progress may well arise from innovative use of disparate materials systems, as multilayers or with more sophisticated three-dimensional assemblies.

Table 5. Temperature capabilities of alloy systems for engineering applications

Material	Max service temperature, T	Melting point, T_m, °C	T/T_m
Ni-Base Alloys	1100	≤1375	0.80
Austenitic Steel	700	≤1420	0.49
Ferritic Steel	600	≤1510	0.40
Titanium Alloys	700	≤1530	0.46

Revolutionary improvements in the performance of nickel-based superalloys and steel are not likely because of fundamental thermodynamic and kinetic barriers. Thus higher-melting-point systems have been investigated for their potential to increase operating temperatures; recent increments in power output from gas turbine engines, for example, owe as much to improvements in coatings and cooling technology as to increased capabilities of the core alloys. Indeed, one view is that work to improve coatings represents a more productive use of development funds than further alloy improvement.

In evaluating alloy systems, it is critical to recognize that the outstanding performance of the nickel-based alloys is based on a unique property of the intermetallic Ni_3Al phase, which strengthens these materials. The strength of this phase increases with increasing temperature and gives the high-strength capability at up to 90% of the incipient melting point, which is a characteristic of the superalloys. So far, no other alloy system with the same characteristic has been identified.

On several occasions in the last 30 years or so, a number of efforts have been made to exploit the refractory metals (Cr, Nb, Mo, and W) as engineering alloys. Multiphase Mo-based and Nb-based systems with good creep properties above 1200°C have been identified. However, alloys have not yet been introduced into application because of the poor ductility and toughness of the alloys produced and/or the sensitivity to environmental attack at high temperatures. Tungsten has the added disadvantage of high density, and this is a serious limitation for its application to rotating parts. Some work continues in this area, particularly in the characterization of $MoSi_2$ -type alloys, but with little indication of an encouraging outcome. Maximum service temperatures are estimated for current systems in Table 6.

Table 6. Melting temperatures of refractory metals

Metal	Melting point °C	Max service temperature (assuming $T/T_m = 0.60$)
Chromium	1857	1114
Niobium	2468	1481
Molybdenum	2610	1566
Tungsten	3410	2046

Intermetallics have similarly received significant attention over the past two decades. The systems of greatest interest for turbine applications were typically the class of aluminides, which form protective oxide scales. Base systems subjected to extensive alloying studies include NiAl, TiAl, Ni₃Al, Ti₃Al, Ti₂AlNb, Fe₃Al and FeAl. Among these, TiAl is the most promising and is likely to be introduced into aircraft engine applications shortly. However, this system will have a temperature limit of less than 800°C. Ni₃Al is more effective as a constituent phase of superalloys than as a monolithic alloy. NiAl suffers from limited ductility, but development efforts in this system have subsequently paid off in the development of new bond coat interlayers for TBC systems.

Similarly, there have been several attempts to develop “engineering ceramics” for power plant applications, but the poor ductility and toughness of these materials has remained a stumbling block in efforts to use monolithic ceramics in load-bearing applications at high temperatures. On the other hand, the application of thin coatings of ceramics on the surfaces of turbine blades for thermal insulation has been an essential feature of the operation of cooled blades at the high turbine entry temperatures now used in gas turbines for both air- and land-based applications. There has been some success in the development of ceramic composites, and these (SiC-SiC) have been demonstrated as potential materials for combustors in small land-based gas turbines. However, the service temperature is somewhat lower than originally envisaged because of high-temperature surface degradation. Figure 11 summarizes the historical development and anticipated near-term trends for conventional metals, superalloys, coatings, monolithic ceramics, and ceramic matrix composites (CMCs).

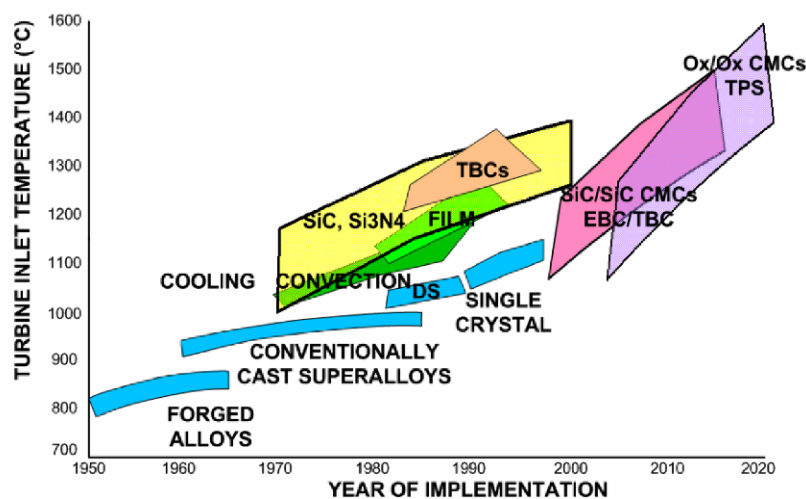


Fig. 11. Historical trends and future trends of materials for gas turbine application (from van Roode). DS = directionally solidified.

As the power generation industry faces a future of higher-efficiency requirements to reduce pollution levels, there are few good materials options for meeting the targets that are likely to be set. For the foreseeable future, power plants burning fossil fuels will remain the mainstay of the U.S. power generation business. However, to meet the demands for zero emissions, these units will be operated in such a way that the carbon produced in the combustion process can be captured and stored. Minimizing the output of CO₂ per unit of power output will require operation at higher efficiencies than those currently typical of the industry. Thus higher operating temperatures will be necessary, and this will make heavy demands on materials, especially since costs also must be contained.

With this background, the key technology drivers will be

- reduced environmental impact
- increased efficiency
- competitive costs
- high availability
- cyclic capability
- extended intervals between outages

Also, if the price of natural gas remains high (it generally tracks the price of oil), coal will remain the dominant energy source for plants of this type. On this basis, the two major power-generation technologies will be USC steam (Rankine cycle) and IGCC (Rankine and Brayton cycles). Each is expected to secure a major segment of the generation industry worldwide in the next two decades. Competing technologies may emerge and become commercially viable, but for large-scale, thermal power generation, materials limitations and requirements are likely to be similar to those for USC and IGCC, as discussed in the following paragraphs.

3.3.1.2 Materials limitations: USC steam plant

In a USC steam power plant, the performance of the critical components in both the boiler and the steam turbine is limited by materials capabilities. Figure 12 is a plot of creep-rupture stress as a function of temperature, by materials class. Using the discriminator of 100,000-h rupture strength at 100 MPa (to allow the use of relatively thin-walled tubes and pipes, so minimizing thermal fatigue issues), the temperature limits of the current alloy classes become ~620°C for ferritic steels, ~690°C for austenitic stainless steels, ~720°C for primarily solid solution-strengthened nickel-based alloys, and >720°C for age-hardenable nickel-based alloys. Economic factors call for maximizing the use of the relatively inexpensive ferritic steels, with austenitic steels and nickel-based alloys used only where absolutely necessary.

For the boiler in a USC steam plant, the two areas with the most demanding materials issues are the water walls and thick section parts such as steam headers and main steam piping. In each case, the steels currently used are inadequate in terms of both strength and environmental resistance for the higher temperatures envisaged for the future. Water walls are currently fabricated from low-alloy steels, and maximum metal temperature is limited to about 550°C. In some boiler designs, this is a limiting factor and will control the overall performance of the power plant. A water wall must

- have strength and environmental resistance to about 700°C
- be field-weldable with no post-welding heat treatment (this rules out higher alloyed ferritics)

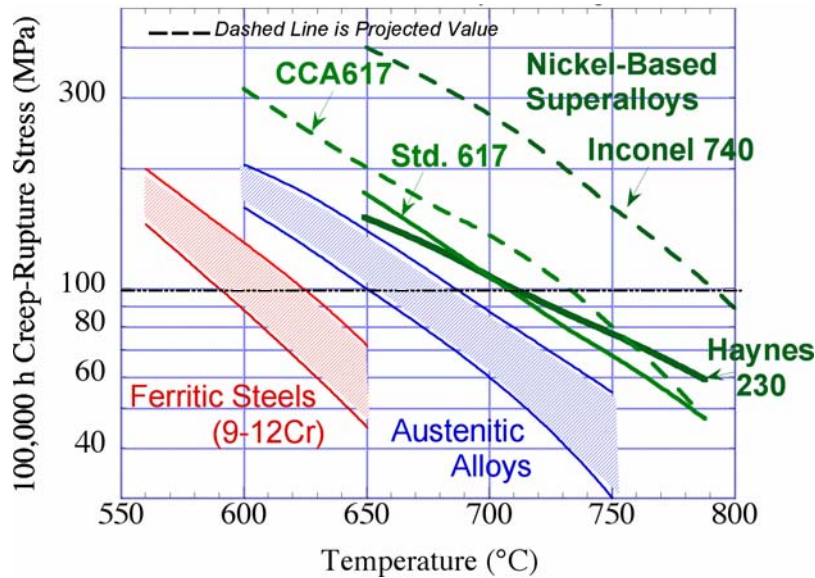


Fig. 12. Stress for rupture in 100,000 h as a function of temperature, by materials class (after Shingledecker)..

- be insensitive to stress corrosion cracking (this rules out austenitic steels)
- be relatively inexpensive (this rules out nickel-based alloys and superalloys)

If no solution can be found to these materials limitations, future steam temperatures will be limited to the levels that low-alloy steels can withstand, and plant efficiencies will be relatively low.

Thick section parts—the superheater and reheater headers and the steam pipe that carries the main steam to the turbines—are exposed to the highest temperatures in the boiler, but they are not subjected to heat transfer. The key requirements in these cases are

- strength to about 800°C (to allow the use of thin-walled vessels to minimize thermal fatigue problems) and environmental resistance to the same operating temperature
- good fatigue resistance for cyclic operation (this rules out austenitic steels)
- relatively low cost (this rules out nickel-based alloys and superalloys)

Efforts to improve today's high-alloy steels continue, but in the best case, temperatures will be limited to $\approx 620^\circ\text{C}$. The environmental resistance of these steels in steam tends to limit their temperature of operation, and there are no obvious routes for improvement that are compatible with the compositional restrictions set by strengthening considerations. Improved understanding of the oxidation mechanism(s) in steam (i.e., effects of hydrogen on transport in oxide scales) may lead to new concepts for alloy design. Consequently, this application may justify an effort to produce a lower-cost nickel-based alloy with good high-temperature strength (up to about 800°C). There is no experience with using an alloy strengthened by the high-temperature strengthening γ' (Ni_3Al) phase, and its characteristic mode of degradation in Rankine cycle units. An approach involving specifically tailored chemistry and microstructure might yield a rewarding outcome in both areas. It is worth noting that alloy development efforts that have targeted other applications, i.e., aircraft engines, do not necessarily result in alloys optimal for the operating environment of power generation systems.

The critical components in both high-pressure and intermediate-pressure steam turbines are limited to about 620°C by current materials properties. The components involved, particularly the rotor and casing, typically are very large and are made from ferritic steels. Figure 13 illustrates a typical steam turbine rotor and blades. In planning for steam temperatures of 700°C for increased efficiency, a compromise solution for a higher-temperature rotor is being explored, involving welding sections of a nickel-based superalloy into the hottest part of the turbines. As a result, the temperature requirements can be met and costs minimized; durability issues have yet to be addressed.

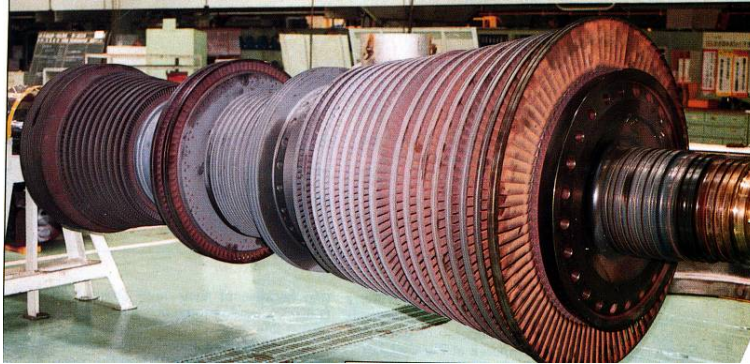


Fig. 13. Typical steam turbine rotor and blades made of ferritic steel 12CrMoVNb, after 14kh at 593°C.

The key materials requirements for turbine components such as rotors and blades include

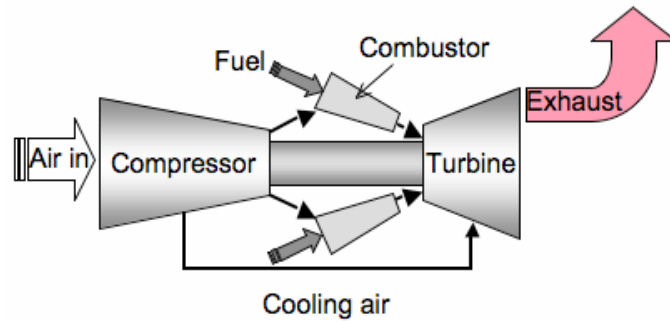
- resistance to fatigue and creep
- ease of welding and fabrication

The steam turbine casings represent a particular problem, since these large structures are currently made from castings to minimize costs. Casings for use in higher-temperature steam will need to use nickel-based alloys (austenitic steels are considered to be prone to thermal fatigue problems), but there is little experience of cast nickel-based alloys having the requisite strength at the temperatures required. As mentioned earlier, precipitation-strengthened nickel-based alloys appear to be needed to attain the 760°C/35 MPa USC steam plant goal, and it is difficult to imagine how such large components with widely varying section sizes could be practically heat-treated to produce controlled modification of the as-cast microstructures.

As before, efforts continue to improve these properties in both the highly alloyed steels and the superalloy materials to enable the use of higher temperatures, but further improvements will be necessary to meet the continued requirement for increased efficiency.

3.3.1.3 Materials limitations: Gas turbines

Figure 14 is a schematic diagram of a turbofan engine and the approximate operating environments of the various parts. Typically, the combustor and the turbine have the most aggressive environments. The development of the modern turbine engine closely tracks the development of advanced materials. The major corrosive gases from clean aircraft fuels are



Component	Typical operating conditions			Critical problems
	Temperature (°C)	Stress (MPa)	Life (h)	
Combustors	850–1100	20–35	4000	Thermal fatigue, oxidation
Disks	400–650	420–1050	15000	Low-cycle fatigue
Vanes	950–1100	35–70	5000	Thermal fatigue, oxidation, hot corrosion
Blades	900–1050	140–210	5000	Creep strength, stability, oxidation, hot corrosion, thermal fatigue

Fig. 14. Schematic diagram of a gas turbine engine illustrating approximate operating conditions and critical problems (after Jacobson).

oxygen and water vapor. However, in the case of dirtier fuels, such as diesel oil and coal-derived gases, other corrosive agents, such as sulfur oxides, may be important.

All of the components subjected to the highest temperatures in a gas turbine are fabricated from superalloys. Given that these materials already operate at an exceptionally high fraction of their melting temperature, development of new alloys with substantially higher-temperature capability is unlikely to yield large gains. Thus further progress with gas turbine technology will be heavily dependent on new materials with higher-temperature capabilities. Development of the gas turbine is not likely to cease entirely, as engineering refinements and improvements in coatings (particularly TBCs) and cooling systems will give incremental improvements in performance, and developments are possible in ceramics. However, with the materials currently available, turbine performance will plateau.

The implications are particularly significant for engines used in IGCC applications, since there is a strong demand for higher levels of efficiency than those currently available with rotor inlet temperatures of around 1300°C. However, in order to achieve efficiencies of (say) 60%, rotor inlet temperatures will have to be significantly increased, presumably by oxy-firing, to levels beyond those that could be sustained by components manufactured from superalloys and using currently available cooling systems and coatings.

Thus further development of gas turbine-based power systems will be stalled unless

- there are continued improvements in coatings, including ceramic thermal barriers
- a major breakthrough occurs in the development of an alloy system to replace the nickel-based superalloys with a temperature capability of up to (say) 2000°C.

The availability of computational tools such as the phenomenological CALPHAD approach, and the development of greatly improved computational thermochemical analytical tools, will provide an improved basis for a scientific approach to alloy design, rather than the trial-and-error methods frequently used in the past. However, it is important to note that the databases will be reliable only when all constituent ternary systems have been assessed to a high degree of

accuracy. Kinetic databases that contain information about diffusion in multicomponent systems are even more sparse. Thus there is a continuing need for experimental measurement of quantities such as phase boundaries and diffusion profiles to verify first-principles calculations and to compare measurements with computed properties.

Critical requirements for improved coatings are as follows:

- bond coatings with improved oxidation and corrosion resistance and greater thermochemical stability so that interdiffusion with the substrate will be reduced, TBC adherence improved, and component lifetime increased
- ceramic TBCs with reduced thermal conductivity and improved stability and toughness, to serve as more efficient insulators, and with compositions tailored to resist environmental degradation leading to failure

Work to develop improved coatings is being carried out, primarily by the manufacturers and coatings suppliers. However, a fresh approach based on scientific fundamentals would lead to greater innovation and increase the prospects of success in a difficult technical area.

New alloy systems need to be evaluated to determine whether any has the potential to succeed the current nickel-based alloys. Critical requirements will be

- high-temperature strength to $\sim 2000^{\circ}\text{C}$
- good toughness and ductility from room temperature to 2000°C
- oxidation resistance comparable to that of NiCrAl alloys
- compatibility with existing coatings systems

Oxide dispersion strengthening (ODS) is the ultimate expression of precipitation strengthening, and such alloys have been shown to have temperature capabilities equivalent to $T/T_m \approx 0.90$ (from Table 6). ODS alloys are processed via a powder-metallurgical route, and so the incorporation of intricate cooling channels is less straightforward than in alloys made by casting. However, the “core and skin” type of design could provide a route for component manufacture. A further advantage of MCrAl-type ODS alloys is that their compositions are more easily tailored to incorporate inherent resistance to oxidation, so they may be more compatible with TBCs.

Alloys based on the Pt-group metals such as iridium, which has a melting temperature of 2410°C , have been produced and evaluated in Japan and show some promise. Given the prohibitive cost of these systems, their application within coating systems is the most likely path for leveraging their interesting properties.

Because of the limitations on increasing the temperature capabilities of superalloys, new materials are needed, particularly for the hot sections of gas turbines. These materials will require superior high-temperature durability, light weight, and independence from strategic elements (Co, Ni, Cr, etc.). Monolithic ceramics, CMCs, and ceramic coatings are the candidates that have received the most attention. These materials continue to hold promise for certain applications, such as combustor liners. However, continuous fiber-reinforced ceramics provide increased toughness, but current technologies involve easily oxidized phases (C or BN) for the

fibers or fiber coatings. Development of tough ceramics will continue to be a critical area of research.

Despite extensive programs on ceramic materials conducted between 1970 and 1995, the true requirements for ceramics for the sustained long-term performance expected from commercial gas turbine equipment were typically not addressed. More recently, the limitations of ceramic gas turbine designs and materials have become evident, particularly the deleterious effect of water vapor. Based on two long-term materials property requirements, creep rupture strength and water vapor degradation, current monolithic ceramics and CMCs have temperature/stress capabilities that are generally insufficient for the demanding applications envisioned.

Future requirements (through 2020) include the following.

1. For small gas turbines, silicon-based monolithic ceramics with 1400–1500°C temperature capability for 30,000 h of life are required. It is expected that such properties cannot be achieved by current Si_3N_4 materials without the use of oxide-based coatings for environmental protection (EBCs) or surface treatment technologies. Such surfaces must be highly resistant to water vapor attack and to impact from foreign objects, and their coefficients of thermal expansion must be an acceptable match to that of Si_3N_4 . A near-term goal is to improve the K_{1C} of Si-based monolithics to $15 \text{ MPa}\cdot\text{m}^{0.5}$, with a long-term goal of $20 \text{ MPa}\cdot\text{m}^{0.5}$. Monolithic-composite hybrid materials may offer a direction.
2. For larger components (turbine airfoils, combustor liners, scrolls), CMCs will be prime candidates. A temperature capability of 1600°C or greater will be needed, which has implications for high-temperature fibers, matrices and interfaces, coatings, and/or effective cooling technologies. SiC/SiC materials will require EBCs that are also effective thermal barriers (TBCs). These EBC/TBC hybrids will need a capability of 1500°C in the near term and 1600–1700°C in the long term.
3. The SiC/SiC and oxide/oxide CMCs should be developed to attain increased proportional-limit strength and yield strength of 300–400 MPa so that they can be used for rotating components. Interlaminar tensile strengths need to be well beyond the current limit of 30 MPa.
4. Support technologies are also needed, including nondestructive evaluation for in-process as well as diagnostic uses (both for as-received and in-service component inspection). Life-prediction methodologies that encompass all relevant modes of degradation must be developed, and their use should be integrated with component health monitoring.

However, given the poor damage tolerance and environmental stability of these ceramic systems, the ultimate solutions are more likely to derive from innovative hybrid metallic/intermetallic/ceramic systems, by analogy with TBC systems.

Some novel combustion schemes proposed to minimize pollutant production involve fuel-rich combustion and the use of hydrogen or hydrogen-rich fuels. A more thorough understanding of hydrogen effects on materials will be required to ensure that interactions with the various classes of materials are taken into account during component design and during service operation. Thus more interaction between materials scientists and combustion scientists is important. Also, the high temperatures associated with these combustion processes will impose severe demands on

critical components, thereby exacerbating the materials challenge and providing a basis for a more innovative approach.

3.3.2 National security systems

The extreme conditions of interest to NNSA include regimes of high pressure and temperature, high strain and strain rates, and extreme radiation environments. Materials responses, and the ability to predict the properties of materials under these conditions, involve areas that overlap traditional scientific disciplines.

Damage and failure processes for polycrystalline metals encompass a complex sequence of physical events occurring at different length scales. These processes are influenced by loading state, microstructure, and boundary conditions. Ductile and brittle behaviors are both of interest. Atomic-level scale investigations serve as the basis for elucidation of the physical processes leading to failure, and there is a strong practical need to develop continuum-level tools capable of predicting the phenomena in question at the engineering scale.

The situation can be even more complex under dynamic loading conditions, since many materials exhibit structural phase transformations. A transformation in crystal structure is also a stochastic process that may transition between crystallographic structures, which can change the response of the material from ductile to brittle, or vice versa. Some structures may be prone to exhibit one type of behavior over another. Moreover, crystal structures can exhibit transitions between ductile and brittle behaviors, depending upon loading and strain rate, which may or may not be related to a phase transformation.

Modern mechanical strength models for metals explicitly include the relationship between stress and the resulting strain during elastic and stable plastic deformation. However, at some strain, metals will transition from uniform or homogeneous deformation to heterogeneous or localized unstable behavior. The level of strain and the location of the instability are largely stochastic.

There is an overall need for experimentally validated models that capture the fundamental relationships connecting the variables of stress, strain rate, strain, and temperature to specific bulk material responses such as yield strength, strain-hardening, texture evolution, evolution of global damage, subsequent heterogeneous damage such as strain localization and cracking, and finally material failure. Some specific issues are discussed in the following sections.

3.3.2.1 Structural phase transformations

The development of accurate, robust, efficient treatments of structural phase transformation is central to the establishment of scientific capabilities to predict the materials response. Basic research challenges encompass advanced experimental capabilities and diagnostics for real-time, in situ observations of structural phase transitions (including melt and solidification) of materials under static and dynamic high-pressure and high-temperature conditions. Next-generation physics-based models and simulation capabilities are needed to investigate p/T-driven structural phase transformations, including kinetic effects across phase boundaries. Scientific needs include knowledge of kinetic effects occurring during structural phase transformations and a comprehensive understanding of the physical and chemical processes dominating the dynamic response of materials under shock (and shockless) compression.

3.3.2.2 Equation of state and warm dense matter

The equation of state establishes fundamental relationships among thermodynamic variables (e.g., stress, density, temperature) and provides closure of the hydrodynamic equations that explicitly ensure conservation of mass, energy, and momentum. *Warm dense matter* refers to states of matter that are plasma-like but that are too dense and/or too cold to be adequately treated by standard plasma physics approaches. Consequently, this warm dense matter regime (roughly spanning the energy range between $k_B T_m$ and $k_B T_F$) defines states of matter between solids and plasmas. The prediction of the properties of warm dense states of matter is particularly challenging, because many competing processes are active, while none dominate. The basic research needs are for advanced experimental capabilities and diagnostics to create and interrogate the thermodynamic states of materials over a wide range of extreme pressure and temperature. Theoretically and computationally, advances in finite-temperature ab initio electronic structure methods beyond mean-field theories are needed to predict the thermodynamic properties of warm states of matter. The scientific gaps include the ability to create high-p/T states of matter in large volumes (e.g., within a laser-heated diamond-anvil cell apparatus) necessary for certain classes of probes (e.g., neutron); theoretical approaches to describe the thermodynamic properties of warm dense states of matter; etc.

3.3.2.3 Elasticity

Simulation tools and experimental capabilities are needed to predict the elastic properties reliably at elevated temperatures and pressures and to formulate fundamental approaches that account for the presence of defects, damage, multi-phases, and multi-components that lead to modifications of the elastic response from that corresponding to perfect material. There are scientific gaps in understanding the deviations of the elastic properties of alloys and compounds from ideal behavior, and in the prediction of behavior under extreme conditions. In many cases, there is no physical mechanism for extrapolating data obtained under experimentally accessible conditions (e.g., quasi-static compression) to behavior under extreme conditions (e.g., as produced in high-explosive-driven shock). Bridging this scientific gap is a key challenge for understanding and predicting materials performance under extreme conditions.

3.3.2.4 Plasticity

The foremost scientific challenge in predicting the plastic response of materials is in the development of multilength-scale simulation tools and experimental capabilities to predict the plastic flow of materials under conditions of high temperature, pressure, strain, and strain rates. Other scientific opportunities include, but are not limited to, the investigation of

- post-failure material response and subsequent behavior
- failure under long-term aging and aggressive environments
- failure mechanisms spanning long time scales
- material failure in micro- and nano-systems

3.3.3 Further reading

Materials issues in gas turbines

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3.4 MAGNETIC AND ELECTRIC FIELDS

In this section, high magnetic field and electric field extreme environments are addressed broadly and discussed in relation to advanced energy systems.

3.4.1 The magnetic (B and H) and coupled electric interaction (E × B, J × B) extreme environments

3.4.1.1 Introduction

Fundamental science breakthroughs are being facilitated by high magnetic field studies in a broad spectrum of research disciplines such as condensed matter physics, materials, biology, and medicine. Current science-based high magnetic field research topics and opportunities in these disciplines are itemized in Table 7. Fundamental studies on these topics are frequently published in journals such as *Science* and *Nature*.

The development of new materials that fuel technology increasingly hinges on improved understanding of emergent properties in condensed matter. High magnetic (*B*) fields are an important tool in this context. High-*B* field conditions are needed both to interrogate materials and to access novel phases of matter. Just as extremely high pressures (~100 GPa) may increase the dimensionality of the periodic table by changing valence, high magnetic fields coupled with high temperatures (subsequently referred to as “*BT*”) may increase the dimensionality of equilibrium phase diagrams through thermodynamic and other effects. The *BT* free energies compare well with many energies of interaction such as energies of mixing, ordering, and formation as well as energies associated with stacking faults, twinning, short range order, vacancy site preference, antisite defects, diffusional barriers, and elastic constants. The increased degree of freedom as a result of the presence of high magnetic fields allows additional phases to coexist in equilibrium for a given composition and temperature. In this way novel microstructures and transformation sequences, unachievable through other means, are feasible

Table 7. Current science-based high magnetic field research topics and opportunities^a

High T_c superconducting cuprates ^b	Bose condensed magnons	Nanomagnetics in biotechnology
Soliton lattices in superconductors	Charge-stripe order	Magnetically induced change of gene expression
Spin-Peierls compounds	Spin-liquid phases in frustrated magnets	Cell and virus structure manipulation
Charge density waves	Self-assembled electronic devices	Protein crystal growth
Magnetoresistive manganates	Magnetic field assisted crystal growth	Diamagnetic organized molecular assemblies
Colossal magnetoresistance (paramagnetic and charge-ordered insulators)	Strongly correlated electron phenomenon in f-electron materials	Magnetic alignment and crystallization behavior of polymers
Metamagnetic quantum criticality heavy fermions	Magneto-chemical systems	Semiconductor crystal growth
Field-induced antiferroquadrupole	Feeble magnet systems	Electrophoresis of DNA

order		
Quantum Hall effect	Superconducting tape processing	Oriented biomaterials
Organic metals	Magnetic texturing	Nanostructured materials processing
Magnetic nanodots and nanoparticles	Carbon materials synthesis	Nano-mechanical property enhancement
Molecular magnets	Carbon nanotube composites	Multiferroic compounds

^aCompiled from presentations at “Probing Matter at High Magnetic Fields with X-rays and Neutrons Workshop,” National High Magnetic Field Laboratory, Florida State University, Tallahassee, Florida, May 10–12, 2005.

^bHigh T_c = high transition temperature.

through *BT* processing. This combination of extreme environments affects phase stability, phase solubilities, diffusion barriers, dislocation cores (magnetoplasticity), stacking fault energies, phonons, and magnons. Therefore, nucleation and growth rates, transformation kinetics, and microstructure product phases and variants are impacted during solidification and solid-state phase transformations. Contributing factors include differences in magnetic moment between parent and product phases, magnetocrystalline anisotropy, shape magnetic anisotropy (e.g., in nanofilms), induced magnetic anisotropy, and magnetostriction effects. The *BT* extreme environment provides a disruptive technology for making significant major scientific and technological advances in developing the next generation of novel structural and functional materials for broad energy applications. Improvements in performance can be manifested in mechanical and/or physical properties as well as in the development of nanocrystalline or textured microstructures or reaction paths made easier through the catalytic chemical effect of the extreme *BT* environment.

3.4.1.2 State of the art

As early as 1929, the literature provided evidence that the application of a high magnetic field during quenching of a ferrous alloy from an elevated temperature resulted in higher hardness than when a magnetic field was not used. Additional research in the 1960s extended these results and found that high pulsed magnetic fields, despite their short duration times, could yield comparable results to static magnetic fields. Although most initial research has focused on ferromagnetic transition elements, *BT* environments have been documented to impact many other material systems (paramagnetic and diamagnetic) over the last decade, as highlighted below.

As stated in Sect. 3.4.1.1, extreme *BT* environments can change the dimensionality of phase diagrams, as there are no longer just two thermodynamic variables, temperature and composition (at ambient pressure), but three including magnetic field. The additional dimension of magnetic field opens a rich diversity of new phases and physical phenomena that promise new materials functionality. The growing emphasis on high-*B* field research facilities around the world enables studying the influence of static magnetic fields of up to 45 T and pulsed magnetic fields approaching 100 T on very small specimens.

An example of the phase equilibria shift achieved with the *BT* environment is shown in Fig. 15, where a 30-T magnetic field has shifted transformation temperatures on the order of 100 K (nominally 3 K/T) and increased the solute solubility of Fe-C alloys. The magnetic contribution to the free energy of the ferromagnetic α phase was calculated to be ~ 378 J/m or 12.6 J/m/T. However, results are not yet consistent, as the impact of magnetic fields on shifting transformation temperatures of Fe-based systems has been reported as being as low as 1 K/T and

as high as 3 K/T. The reason for these inconsistencies is still a major research issue. Modeling approaches to predict the shift in phase equilibria using either Weiss molecular theory or local spin density functional theory [LSD, a local approximation to the formally exact density functional theory (DFT)] are needed to clarify these earlier experiments.

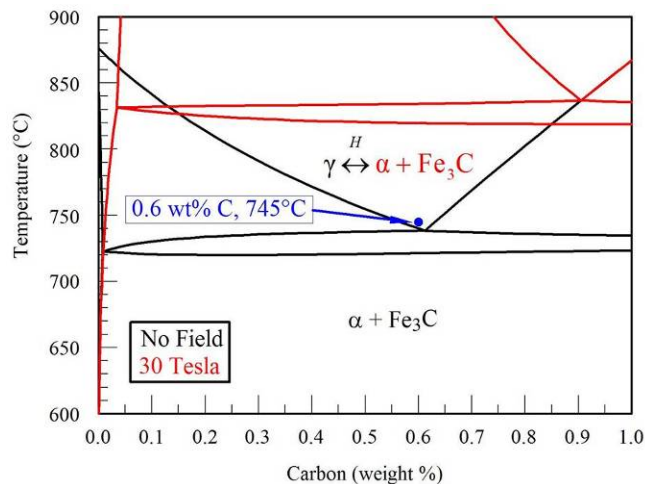


Fig. 15. Influence of a 30-T magnetic field on the calculated phase equilibria for a pseudo-binary Fe-C alloy. (Source: G. M. Ludtka, ORNL, unpublished research)

For brevity, various summary statements will be made to highlight the varied impacts that extreme *BT* environments can have on microstructure and performance. Phase transformation kinetics in ferromagnetic systems are accelerated significantly upon cooling under the influence of a high magnetic field; therefore, *BT* processing holds the potential to be a major energy saving technology for many industrial process efficiency applications mentioned in Sect. 2. The evolution of nanocrystalline spacing in microstructures has been shown to be viable as a result of enhanced nucleation during phase transformation; therefore, higher-strength and higher-toughness alloys are achievable. Microtwinning (via magnetoplasticity) in a 1032 steel alloy was induced in microstructures that normally do not twin, resulting in more homogeneous and copious precipitate formation during subsequent aging with a 21% increase in strength and no loss of ductility. A new National Science Foundation (NSF)/DOE program to develop the third generation of advanced high-strength steels may be able to capitalize on these findings, as twinning-induced-plasticity (TWIP) steels are a potential candidate but have not been economical at this time because of high alloy content requirements that might be offset through *BT* processing.

In recent research (Ludtka et al. 2005) a 29-T magnetic field applied at 500°C on a Fe-15 at. % nickel alloy was shown to increase the solid solubility of nickel by 22% in the ferrite (α) phase and 42% in the austenite (γ) phase while changing the volume fraction ratios of α to γ from 70:30 to 85:15. These changes in phase equilibria that remain stable at ambient temperatures cannot be achieved by any other means. In this same reference, the “equilibrium” volume fraction of α phase in AISI 1045 steel was increased from 40 to 65% under a comparable magnetic field. Future high-strength structural materials for magnetic fusion systems may include ferritic steels; such steels with novel and superior properties may result from high magnetic field processing research. The ramifications of these research findings are relevant to the needs of other energy

application areas because high magnetic field processing opens up a new processing methodology to develop the next generation of advanced structural and functional materials. The ability to dramatically increase interstitial and substitutional solute content in candidate alloy systems with an applied magnetic field and then to dramatically destabilize these alloys (at elevated temperature) by turning off the field means that superior solid solution and precipitation-hardened alloys are possible. The implications are that significant increases in strength and creep resistance at elevated temperature are viable. Additionally, enhanced corrosion-resistant alloy families may be made possible through high magnetic field processing.

Similar interesting results have been observed in non-ferrous alloy families. Magnesium alloys showed a 15% increase in strength after aging in a *BT* environment. Deformed aluminum alloys exhibited enhanced recovery and earlier initiation of primary recrystallization. A NiAl-Cr(Mo)-Hf alloy had a 75% increase in bending strength accompanied by transition in fracture mode from brittle to ductile as a result of different phase equilibria. This finding opens up a processing methodology to improve performance in materials that classically have behaved in a brittle fashion because of grain boundary segregation or embrittling grain boundary films. Therefore, the extreme *BT* environment provides a new technology to engineer grain boundaries and their crucial influence on final performance.

A high- T_c (high-temperature) superconductor, $YBa_2Cu_3O_7$, was bulk-textured by solidification in a 7-T magnetic field. Similarly, during solidification in a 12-T field, the primary Al_3Fe phase in an Al-Fe alloy was texture-aligned in a homogeneous distribution as a result of crystal magnetic anisotropy. The ramifications of these texture studies for energy transmission line applications may be significant. If the appropriate texture can be developed in the ferrous alloy cable so as to align the high elastic modulus direction (depending on crystallographic orientation, E varies from 131 GPa to 283 GPa) in the axis of the wire, a conservative 15% improvement in wire stiffness would be viable. This would allow the use of either thinner cables or increased distances between the supporting transmission wire towers, reducing cost appreciably.

Of particular interest has been the use of extreme *BT* environments to make diamond from carbon precursor materials under *ambient* pressure conditions. Normally, extremely high-pressure and high-temperature environments have been required to create diamond, with the high-pressure requirement being a limiting condition. Additionally, in other material systems, high magnetic fields have been shown to increase the free energy of grain boundaries, and so grain coarsening has been observed in several materials. These results may have significant ramifications for developing diamond for wide-bandgap semiconductor applications in next-generation power electronics. Diamond has not been successfully employed because it is extremely difficult to fabricate and because of the presence of grain boundaries and other defect structures that reduce the lifetime and mobilities of carriers. High magnetic field processing may mitigate these issues. A side issue is that relatively low magnetic fields have been shown to slow diamond decomposition when it is used for grinding and abrasion purposes (local high-temperature and high-pressure environment at the contact point) while enhancing metal removal.

Other potential material systems that may benefit from a similar approach are boron compounds, halogen oxides, and carbon nanotubes. Therefore, high magnetic field thermal processing may be

a new catalytic chemical processing approach for current processes requiring high pressures in conjunction with high temperature.

Extreme *BT* environments have been shown to result in magnetic field orientation of diamagnetic liquid crystalline epoxy thermosets, yielding almost three-fold increases in elastic tensile modulus in the direction of the applied magnetic field. In addition, moderate success has been demonstrated in aligning carbon nanotubes in polymers during curing. Therefore, the use of high magnetic field processing to yield high-performance polymeric materials with superior performance for structural and functional applications is a very promising technology.

When discussing high-temperature, high-*B* environments, the potential interaction of the method used to heat a test sample in the *BT* environment must be considered, as with induction heating methods. When induction heating is applied in a high magnetic field environment, the induction heating coil is typically configured in such a way that a high-intensity ultrasonic treatment occurs naturally that can dramatically impact liquid and solid state processes. The resulting configuration is that of a highly effective non-contact EM acoustical transducer (EMAT). This approach is unique because the magnetic field strength of the high-field magnet can greatly exceed that used in a typical EMAT device. As a consequence, the synergistic interaction of a high surface current density (induced via induction heating) with the steady-state high magnetic field results in an especially effective method for creating a high-energy-density acoustic environment. The exceptionally high energy efficiency of the resulting EM transducer is due to the use of high magnetic field, which greatly reduces the current needed to achieve the same acoustic pressure. The beneficial effects of this approach have been demonstrated for solidification experiments on an aluminum alloy, in which improved chemical homogeneity was achieved. The EMAT is shown schematically in Fig. 16.

The EMAT technology has the potential to develop advanced composite materials by enabling the uniform ultrasonic dispersion of nanoparticles in candidate alloys. Increases in strength of 100% have been achieved in an aluminum alloy using ultrasonic dispersion methods (Han, Ludtka, and Zhai 2007). Alternately, this EMAT discussion indicates that materials exposed to $J \times B$ (and possibly $E \times B$) environments, as they would be in fusion reactors, may be subject to ultrasonic fatigue issues not normally considered by design engineers.

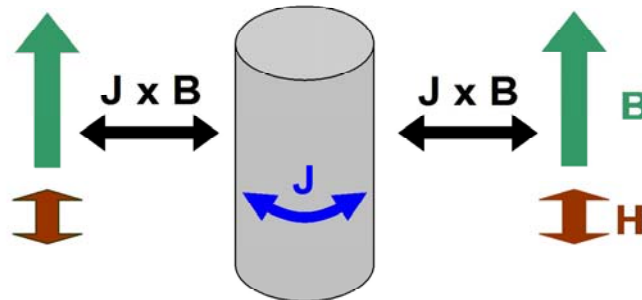


Fig. 16. Induction heating in a high-field magnet, showing the applied H-field of the induction coil, the induced surface current in the sample (*J*), the static field of the magnet (*B*), and the resulting $J \times B$ force. The H-field of the induction heating coil is insignificant ($\mu\text{H} \ll B$) by

comparison with the static B-field of the high-field magnet.

Finally, microwave processing is normally not viewed as an environment where both E and B issues coexist. The application of microwave energy to process various kinds of materials has been demonstrated to be a highly efficient, economical, and effective process. It is now certain to be an innovative technology with great commercial potential and many attractive advantages from the climate change perspective. In the area of materials sintering and synthesis using microwave energy, remarkable enhancements in materials diffusion and reaction kinetics have been reported by many researchers all over the world. While almost all earlier work was conducted in multimode microwave systems in which the electric and magnetic fields cannot be separated, recent dramatic results (Roy et al. 2002a; Roy et al. 2002b; Peelamedu et al. 2004; Roy et al. 2005) obtained by the separation of electric and magnetic fields in a single-mode cavity (at 2.45 GHz) have confounded the scientific community working in this area. These recent studies are now providing new insights in understanding the mechanisms of microwave-matter interactions in terms of the electric and magnetic components of the microwave radiation.

3.4.2 Potential extreme high magnetic field processing: Environmental ramifications for advanced energy systems

3.4.2.1 Introduction

As discussed above, high magnetic field processing has potential for use in developing next-generation structural materials with superior combinations of strength and creep resistance at elevated temperature. Such materials are needed for virtually all of the advanced energy systems identified in Sect. 2.

In addition, high magnetic field environments in superconducting magnets and systems involving high magnetic field superconducting magnets, such as magnetic fusion power plants, must be considered in terms of microstructural instability and degradation of performance. Just as high magnetic fields can be used to tailor microstructures, sometimes they can evolve microstructures not amenable to the needs of the final application. An example is the current use of 301 stainless steel for the reinforcement material of the 100-T long pulse magnet. Typically the 300-series stainless steels are considered austenitic and paramagnetic (therefore having limited interaction force with the applied magnetic field). However, when this alloy is exposed to a large magnetic field pulse, the ferritic/martensitic phase equilibria will be dramatically thermodynamically enhanced over that of the austenite phase and the large volume expansion phase transformation to martensite (ferromagnetic, with a large force response to an applied field) will be favored to form. Coupled with the influence of cryogenic temperatures that cause austenite to convert to martensite in some ferrous alloy systems (because of the thermal nature of the transformation), this can produce the negative result shown in Fig. 17, where martensite formation has occurred and grain boundary cracking is rampant. Poor mechanical response and short life are anticipated in this condition. Therefore, it is crucial to consider the presence of high magnetic fields and the cryogenic environment of superconducting magnets when selecting materials normally considered acceptable for most applications under ambient (no field or cryogenic temperature) conditions.

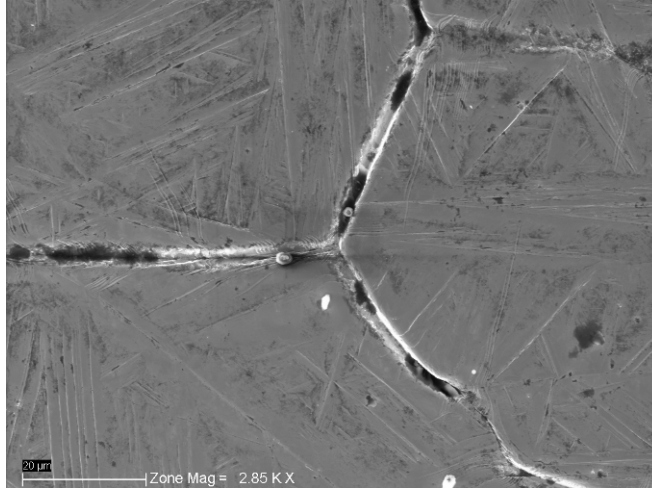


Fig. 17. Scanning electron microscopy micrograph of grain boundary cracks in 301SS upon quenching from room temperature to 4.2 K in liquid helium post-annealing at 1100°C. (Source: S. Downey, Florida State University, unpublished research, used by permission.)

3.4.2.2 Technical and cost barriers

Fundamental understanding of the influence of extreme *BT* environments on material behavior and state is lacking as a result of the inability to perform real-time, in-situ characterization experiments so that ab-initio modeling predictions can be compared with microstructural data obtained while specimens are under the extreme *BT* environment. This limitation was addressed at an National High Magnetic Field Laboratory Workshop on Probing Matter at High Magnetic Fields with X-Rays and Neutrons, held May 10–12, 2005, in Tallahassee, FL (co-chairs: Frank Klose, Alex Lacerda, George Srajer). At this meeting, the need to develop extremely high field magnet facilities at the Spallation Neutron Source and Advanced Photonic Source was addressed. Hybrid magnet systems >30 T are being designed (via a joint NSF/DOE program) for installation at these facilities within the next 5 years or so.

For significant scientific advances to be made in the *BT* processing environment, the ability to predict material response is essential to direct this research effectively. The current capabilities of ab-initio LSD modeling have been shown to be very robust, but they cannot completely capture the effects of the extreme *BT* environment, particularly in the vicinity of the Curie temperature and for highly correlated electron materials. Major advances are needed to go beyond LSD. Researchers are developing several relativistic approaches.² The solution of this problem is critical for photovoltaics, batteries, nuclear fuels, oxide precipitation-hardened steels, and light-emitting diodes. High magnetic and electric fields need a generalization of DFT to density-current functional theory and time-dependent DFT. Magnetic and ferroelectric problems also need to include macroscopic (domains walls) effects to provide multiscale coupling of electronic-level and higher-level models. Therefore, ab-initio modeling in conjunction with well-defined and well-instrumented experiments is crucial to capitalize on this novel materials processing extreme environment. In addition, modeling behavior in reasonable-size atomic clusters requires significant computational capabilities and will need to rely heavily on future

²D. Nicholson, M. Stocks, T. Schulthess, T. Maier, and X. Zhang, private communication.

petascale computing capabilities being envisioned for the open scientific community. A focused effort on modeling kinetics is also needed because the changes in local environments encountered during diffusion of one species in another are extreme compared with the difference between the specific crystal structure environments. The magnetic moments may change radically during diffusion and may therefore be influenced greatly by the presence of a magnetic field. For example, in the process of diffusion of iron between neighboring iron atoms, the moments will be reduced and the exchange interaction between the iron atoms may switch from ferromagnetic to antiferromagnetic.

The ability to evaluate and implement extreme *BT* environments for processing will rely heavily on the capability to reduce the cost of superconducting magnets while increasing their maximum magnetic field capabilities and uniform field strength bore size and length. Currently, most high-B field superconducting magnets are made in the solenoid configuration, which is ideal for producing bar and rod product forms of enhanced structural materials with superior strength and creep resistance. However, many energy applications for structural uses may require magnetically processed materials in a sheet or plate configuration, so innovative high-B field parallel plate superconducting magnets will need to be designed and fabricated. As is the case for all successful implementations of new structural materials, joining methods will need to be developed and evaluated for magnetically processed materials. Such methods may involve friction stir welding or conventional welding processes with high magnetic field capability superimposed so the welded zone will retain its magnetic processing enhanced properties after welding.

The introduction of high-temperature superconductors without the need for cryogenic coolers is also essential to make systems cost-effective. Virtually all working (rather than demonstration) superconducting magnets up to this time have been made of NbTi or Nb₃Sn. As the recent COHMAG (Committee on Opportunities in High Magnetic Field Science) report emphasized, this may be about to change (COHMAG 2005). The highest field working magnets so far are the persistent mode nuclear magnetic resonance (NMR) magnets operating at proton resonance frequencies of 900–950 MHz, which correspond to fields of ~22 T. Niobium-base magnets are not likely to be capable of much more development, meaning that the demand for higher fields must be satisfied by hybrid superconducting-normal magnets or new superconducting material technologies. The potential domain of materials like MgB₂, Bi-2212, Bi-2223, and YBCO greatly exceeds that of NbTi and Nb₃Sn. The path forward to many new application challenges—either unprecedented fields for NMR (e.g., the COHMAG grand challenge of a 1.3-GHz/30-T NMR coil) or the 50-T fields required for a muon collider, or even fields of a few Tesla at 77K—is now open with the new high-temperature superconducting materials that have been discovered in the last 20 years.

The fundamental mechanisms responsible for the different behaviors of various families of materials in the electric and magnetic components of microwave radiation are not well understood. Therefore, ab-initio modeling of these interactions in conjunction with well-defined and instrumented experiments is crucial to capitalize on this novel materials processing extreme environment.

3.4.3 Materials for high electric field and high-power applications

3.4.3.1 Introduction

Electric fields, as either a processing tool or a component environmental factor, impact material microstructure evolution and stability, performance, and potential failure. Fundamentally, an electric potential applied to an electrical conductor leads to current flow in the conductor and induces a magnetic field. The electric currents can affect phase transformation kinetics and phase stability by accelerating the dissolution of unstable phases or retarding the formation of precipitates by impacting vacancy mobilities and concentrations. Sufficiently strong electric fields can untwist helices in cholesteric liquid crystal films into the more perpendicular homeotropic nematic configuration. High electric fields were shown to enhance the antiferroelectric (AFE) to ferroelectric (FE) phase transformation in certain lead zirconate titanate compounds by raising the FE-to-AFE phase transformation temperature. Phase separation in glasses could be either enhanced or inhibited, depending on the relative dielectric constants of the matrix and precipitating phases; this suggests that microstructures for glasses and ceramics may be tailored *or damaged* by exposure to high electric fields.

A novel electric field–assisted reaction sintering technique was shown to dramatically accelerate synthesis and consolidation of ceramic compounds. Reactions that normally took hours to days to complete were accomplished in fractions of an hour with enhanced homogeneity. This suggests that electric fields can promote chemical reactivity that may lead to accelerated degradation in a component under a sustained electric field condition. The extreme electric field environment, therefore, has major implications for the microstructures and performance of a broad spectrum of material families, from conductors to dielectrics (insulators) to liquid crystal materials, glasses, and ceramic compounds. Many of these are relevant to the needs of advanced energy systems. Therefore, the following discussion highlights the state of the art for the electric field environment and defines some of the critical research needs to understand the impact on materials from processing, performance, and environmental survivability perspectives.

The performance and cost of electric power equipment have always been limited by materials, mainly in the area of the material's ability to tolerate heat, voltage, and mechanical stress. Given the need to transfer larger amounts of power each year through existing corridors and electrical equipment within the delivery infrastructure, improvement in materials performance will provide benefits throughout the electricity grid. Electrical equipment encounters relatively large electric and magnetic fields (~2 T). Transmission conductors typically operate at a maximum voltage of 765 kV at around 1000 A. Failure of electrical equipment can result in inadequate protection from lightning strikes and surges. Peak discharge currents in each lightning stroke vary from several thousand amperes to 200,000 A or more. Current rises to these values in only a few millionths of a second (microseconds), and the major part of each stroke usually lasts much less than a thousandth of a second. According to the National Lightning Safety Institute, lightning protection systems provide only limited protection. Key areas for materials research include dielectric materials for transmission equipment, fault protection systems, and power electronics. Each of these areas is highlighted in the following sections.

3.4.3.2 Dielectric materials under extreme environments

Dielectrics (electrical insulating materials) are an integral part of the T&D grid from overhead lines to transformers, cables, and switchgear in substations [1] and are expected to perform under

demanding conditions, including high temperatures (transformer applications), pressures (compressed gas insulating cable), cryogenic temperatures (high-temperature superconducting applications), and mechanical stresses and thermal gradients. New materials with high dielectric strength when performing under extreme conditions with high reliability and longevity need to be developed.

Dielectric materials may be in the form of gas, liquid, and solid, depending on the high-voltage device, the voltage class, and the particular application. In general, two or more forms of dielectric material must be used for practical design considerations. Thus in either air-insulated, compressed gas-insulated, or oil-insulated systems, there are interfaces with solid insulation spacers that prove to be dielectrically weak points. The most critical area is the triple junction where two dielectric materials and the conductor come into contact. New materials, whether they are solid, liquid or gas, will have to be tested individually and in combination with other materials to assess their ability to hold off high voltage, their compatibility, and their potential for a long working life.

Dielectric strengths of solid materials are not well understood despite more than 100 years of research and testing. This is largely because the failure mechanism has more to do with the imperfections, impurities, cracks, inclusions, trapped charges, and internal voids than with the pure material. Therefore, dielectric materials are chosen for an application based more on the secondary requirements (such as mechanical and thermal) than on dielectric strength. Other dielectric properties, such as permittivity and dielectric losses, are more predictable than strength; these are materials properties that can be tailored to the application. Generally, when substances are added to a dielectric to effect an improvement in nonelectrical properties, the dielectric strength suffers. The recent development of nanocomposite dielectric materials offers the possibility of increasing the dielectric strength as well as enhancing the material's nonelectrical properties. Such materials offer the potential for tailoring new dielectric materials for demanding applications.

A good source of data on electrical, mechanical, and thermal properties of dielectric materials is the *Handbook of Electrical and Electronic Insulating Materials* (Shugg 1995). In it, a wide range of materials encompassing diverse applications are described, along with their physical and electrical properties. Among the solid materials are thermoplastics (polymers), thermosetting molding compounds, glasses, extrusion and embedding materials, and insulating coatings and impregnants. Liquids (oils) and gases are also listed. Within the class of thermoplastic materials, 18 polymers are listed, having dielectric strengths that range from 380 V/mil (14 kV/mm) for polycarbonate to 600 V/mil (24 kV/mm) for polypropylene. These strengths are not particularly high (only about 5–10 times the strength of air and generally declining with increasing thickness). These dielectric strengths are for an insulator thickness of 125 mil (3.2 mm). For a thickness on the order of 1 mil, the same materials can have a dielectric strength an order of magnitude higher. Thus improvement in dielectric strength permits either operation at higher voltage and electric fields or decreased insulation thickness, reducing the size and footprint of electric power equipment. The dielectric strengths are often given for dc breakdown or 60 Hz and do not provide information on the effect of frequency, which can range from power frequency (60 Hz) to fast-rising pulses in the case of lightning, switching, or other fast electrical surges. Materials behave differently under these conditions as a result of the manner in which molecules and charges move in the electric field and with respect to changing electric fields.

These considerations apply to both the bulk materials and to discharges that occur on surfaces. Requirements for specific applications are given below.

Transformer insulation materials. It is remarkable that new insulation systems based on plastics and synthetic fluids have not been able to displace cellulose materials—i.e., paper, transformer board, (laminated) wood—and mineral oil as the predominating insulation system for most power transformers. This is primarily because of the high reliability, long lifetime, and comparatively low price of the oil-cellulose system. Only under more demanding environmental conditions (e.g., fire hazard, contamination of the ground water supply in residential and highly populated areas) has the combination of oil/polymer films and SF₆ gas been introduced as an alternative.

In addition, the dry transformer insulation systems used in smaller indoor applications are limited by the breakdown characteristics of air. Dry components, while allowing for higher-temperature operation, do not offset the added spacing needed for voltage standoff, and excessively large and high-loss designs are the norm. Development of cost-effective epoxy insulation systems that also enable more effective heat transfer is needed. Gas-insulated transformers have been built that use SF₆ as the insulating gas. They offer a smaller footprint and higher-temperature and higher-voltage operation. Research that enhances SF₆ operability or replaces the gas would be very cost-effective.

Transformer dielectrics. Transformer insulation generally consists of enameled conductors with paper tape and barriers immersed in mineral oil. Use of improved insulation (i.e., insulation with higher dielectric strength) means that transformers can be reduced in size, leading to smaller footprint and lower cost. Areas of materials research for improving transformer performance and reliability include improved stress control, additives to liquids for improved performance, streamer-flashover studies for long gaps, and multifactor aging studies.

High-voltage equipment insulators and standoffs. High-voltage insulators are an integral part of all high-voltage devices used in today's transmission and distribution grid, including transformers, overhead transmission lines, cables, switchgear (including circuit breakers), and motors/generators. Used in the form of bushings or standoffs, they must have high dielectric strength and high mechanical strength, be resistant to partial discharge, retain performance at elevated temperature, and have a 30-year life expectancy. For high dielectric strength and long electrical life, bushing materials must not only have high intrinsic strength but also be able to be made free of voids or other imperfections, which lead to partial discharge and eventually to dielectric failure.

Although ceramics are widely used in high-voltage devices, alternatives that are lighter in weight, inexpensive, and mechanically stronger are desirable. So far, nonceramic substitutes have not performed as well, suffering mechanical failures in the field. New materials—including polymers, epoxies, and composites—are sought that can replace the ceramics used at present. Many new materials have the potential for providing better and longer-lasting high-voltage insulation, but data on their electrical characteristics are presently sparse. For any proposed substitute, electric field strength data (for both puncture and flashover) are needed over a range of temperature, pressure, humidity, and pollutant buildup. Electrical field strength data should include 60-Hz ac breakdown and impulse voltage breakdown (often referred to BIL) for both lightning impulse and switching surge impulse waveforms. Detection of partial discharges,

which affect the expected life of the insulation, is needed, as well as a diagnostic of incipient failure. Partial discharge is often due to the presence of internal voids in solid insulators. Diagnosis of solid insulation by partial discharge detection is made more difficult by the statistical time lag effect, which results in variation of partial discharge inception voltages. Improvements in partial discharge analyses are needed, such as the use of X-ray-induced partial discharge initiation to produce reproducible signals at reproducible field strengths.

Improvements in other electrical properties, such as permittivity and dissipation factor, are also needed. In the case of permittivity, it is important to match the permittivity of the material to that of other materials (such as SF₆ gas, transformer oil, paper, or other materials in contact with bushings or standoffs) to avoid mismatched permittivities leading to electric field intensification, which in turn leads to electrical insulation failure. Dissipation factors need to be measured to determine that ac losses can be kept as low as possible.

3.4.3.3 Technical barriers and research needs

Theory of breakdown. In contrast to gases, for which dielectric breakdown is fairly well understood, breakdown in solids (and liquids) is poorly understood to the extent that predictions of the breakdown strength of solids cannot be made solely on a molecular basis. Manufacturing issues cannot be easily assessed in breakdown theory owing to the lack of understanding of the various mechanisms that may be operational for the particular material. Therefore, improved analytical and computational methods are needed in order to provide predictive value to the development of new dielectric materials and to increase understanding of how existing materials age and fail under high electric fields.

New materials: nanodielectric composite materials. The area of nanodielectrics has emerged in the past 5 years, offering the potential for designing dielectrics with improved properties, including the dielectric strength. Challenges include control of dispersion of particles and improved theoretical understanding of how and why particles influence the breakdown process. Self-assembly techniques offer the possibility of both solving dispersion issues and modifying the host material to improve its dielectric and physical properties.

Magnetic fields. The movement of charged particles is influenced by magnetic fields and can have an influence on breakdown in gases, whereas for solids the influence may not be very important. However, for EM fields, a dielectric material may be influenced, as in the case of EM fields from lasers and EM pulses from nuclear detonations. These are extreme conditions that may occur under unusual circumstances and are not considered here. Under normal use in the power grid, these factors are anticipated to be small or nonexistent.

Diagnostics. Improved diagnostics are needed in order to assess the electrical condition of a dielectric material when electrical field stresses are present. Typically, partial discharge and polarization techniques are employed to assess the presence of voids, defects, and space charge in dielectric materials. Improvements in these techniques, and the development of new techniques that provide improved visualization of the internal structure of solid materials, are needed to provide better prediction of aging and time to failure and to aid in the development of new materials.

3.4.4 Materials under high power surge environments

3.4.4.1 Overview

Each cloud-to-ground lightning flash involves energy of the order of 10^9 J. This is approximately equal to the energy required to operate five 100-W light bulbs continuously for one month. The estimated range of the lightning energy delivered to the strike point is from 10^6 to 10^7 J, which is only 10^{-2} – 10^{-3} of the total energy. A direct lightning strike on unprotected equipment can cause immediate damage and trigger a ripple effect throughout the power delivery system. Similarly, electrical energy flowing in the grid can produce surges in the same magnitude caused by line or equipment failure. These line surges (often characterized as transients), if not directed safely, can have disastrous effects.

Presently, faults in an electrical grid are detected by protective relaying and cleared by operation of circuit breakers or fuses. Protective relaying and fuses both operate by detecting abnormal levels of current flow. In the future, it will be desirable also to evaluate the signature of the current to determine the presence of an arcing fault, high-resistance ground fault, and other fault types that are difficult to detect currently. In addition, it is important that in the future fault protection act much faster, static switches operate much more quickly than circuit breakers, and fault currents be cleared much more quickly. This improvement will result in greatly reduced equipment damage due to faults and shortened voltage sag events during fault clearing. In addition to protective relaying, utilities incorporate protective systems around sensitive equipment.

Of great importance in energy storage and energy transmission is a class of materials that can absorb a huge amount of energy from a lightning strike or a line surge. They ensure that the electrical energy can be delivered safely and related facilities can be protected from the most extreme surge conditions. The state-of-the-art material is the metal-oxide varistor based on zinc oxide. This is a grain-boundary-controlled device, in which the Schottky barriers have a breakdown voltage of about 3 V per grain boundary. By making ceramic blocks with various thicknesses (controlling breakdown voltage) and diameters (controlling total current), the ZnO-based material has been used for shunt devices to protect critical equipment and facilities (Fig. 18.).

3.4.4.2 Technical barriers and research needs

Protection provided by surge arresters requires high reliability (Fig. 19.). The arresters are low in cost compared with the equipment that they are protecting. When the arresters fail to protect the high-cost equipment, the economic impact of the failure is often very high. The main technical barriers of the lightning/surge arresters are as follows:

- Uniformity of materials is hard to control and monitor during processing. Since arrester current handling capability is largely dependent on grain size, it remains a challenge to make large ceramic block with uniform grain size. It takes just one small defect to cause current concentration in one block, which can result in failure of the entire assembly (usually a stack of more than 10 blocks).

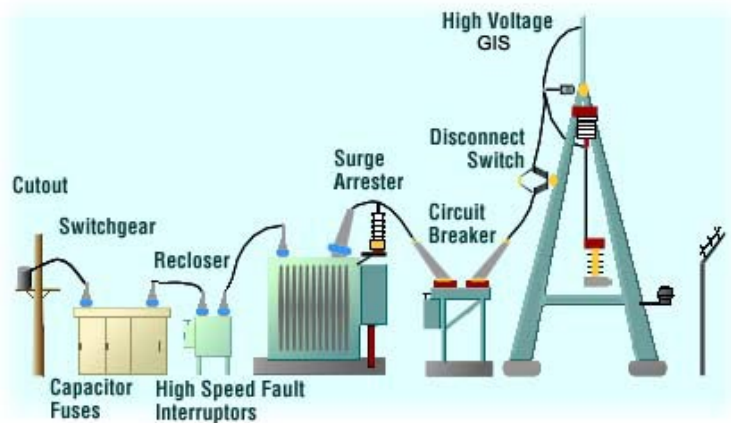


Fig. 18. A typical substation with surge arresters to protect critical equipment such as the transformer.

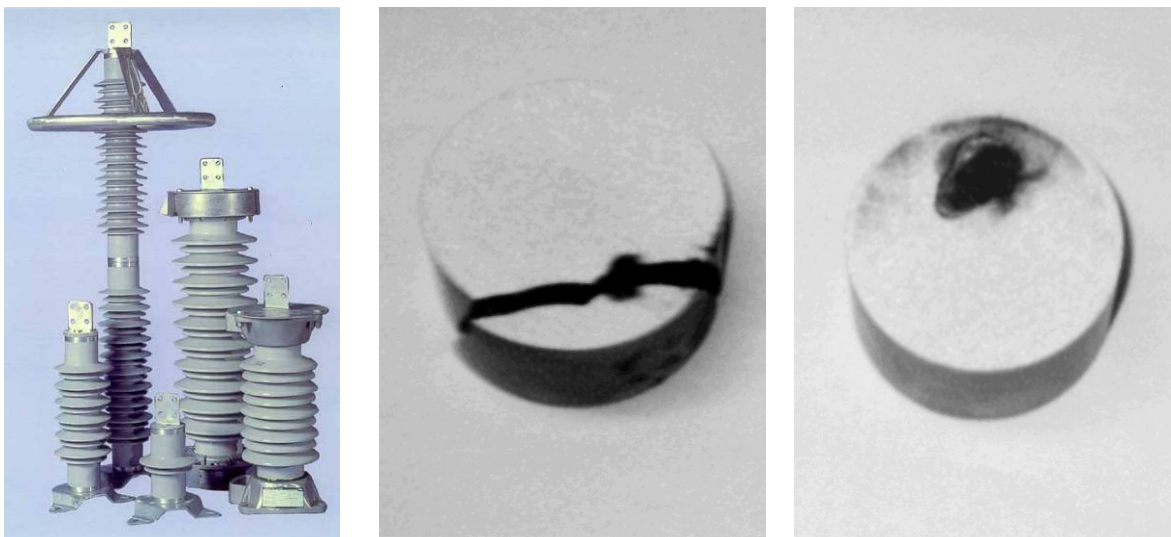


Fig. 19. ZnO surge arresters; cracking and puncture failure due to current concentration.

- Overprotection due to uncertainty regarding material quality requires excess materials and multiple assemblies in parallel. This is the main reason for selecting protection of equipment instead of 100% protection. Improved materials may require smaller devices and lower material cost.
- The industry could benefit from better ceramic processing technology, improved energy handling capability of the materials, and a cost-effective way to screen every block to prevent potential failure.
- Smart materials or devices embedded in or attached to the assembly are needed to record the surge history and indicate damage to the assembly. Some arresters get damaged or heavily degraded after a severe surge. Although the equipment is protected from the previous strike, it becomes vulnerable to subsequent strikes if not replaced in time. This is especially important for devices placed in remote, unstaffed locations.

3.4.5 Semiconducting materials under high-power environments

As power electronics play a more and more important role in the utilization of electric power, the requirements for these materials will also be increased. Material selection and performance will play a key role for advancing power system technologies. Important issues for power electronics include

- **Voltage blocking.** Increasing the voltage blocking capability is a primary limitation of existing materials.
- **Thermal control.** Advanced cooling methods need to be considered in order to reduce the footprint of power electronics systems.
- **Efficiency.** Efficiency needs to be as high as possible in order to save energy, lower cooling requirements, and improve device performance.
- **Control.** Advanced hardware and control strategies are needed to take full advantage of power electronics.

3.4.5.1 Technical barriers of silicon semiconductor technology

With the most advanced and mature technology for power electronics devices, silicon power devices can be processed with practically no material defects. However, it is difficult for silicon technology to meet the demand for some high-power utility applications as a result of limitations in its intrinsic material properties.

Voltage blocking capability. The primary limitation, voltage blocking capacity, is due to silicon's relatively narrow bandgap (1.1 eV). This bandgap leads to a low intrinsic breakdown electric field, which is approximately 5×10^5 V/cm in undoped material and even smaller in doped material. Correspondingly, the voltage blocking capacity of silicon devices is less than 6.5 kV. For high-voltage applications (>6.5 kV), stacking packaged devices in series is required (such as the series stacking of thyristors that is commonly seen in high-voltage inverters of high-voltage dc stations). Series stacking of devices is expensive from a packaging standpoint, and it requires complicated triggering to maintain voltage-sharing between devices in the stack. Hence there is a strong incentive to develop devices having greater voltage blocking capacity in the same or a smaller device package.

Thermal conductivity, temperature limits and switching frequency. The normal operational temperature limit of silicon devices is less than 150°C , and a significant thermal management effort is required to maintain the junction temperature of these devices below that limit. Low thermal conductivity limits and high switching losses impact the operational temperature of silicon devices. The switching frequency of these devices is also limited because of the heat generated by switching losses in the devices. Typically, silicon devices have a switching limit of less than 20 kHz for power levels in the range of a few tens of kilowatts and are highly susceptible to harsh environments, such as high ambient temperatures and intense radiation. Since recent advances have driven silicon power electronic devices to approach the material limits, the margin for switching speed to improve is small. However, higher-frequency operation is preferred because converters with higher switching frequencies allow smaller filtering requirements, less audible noise, smaller passive components, and exact control for high performance.

3.4.5.2 Research needs: New materials for power electronic devices

It is clear that the demands on power electronics will continue to increase; the use of alternative materials for power electronics is inevitable. Since the limits of silicon-based power devices can be attributed to the narrow bandgap of silicon, wide-bandgap materials are good candidates for next-generation power electronic devices. Of the contenders, silicon carbide (SiC), gallium nitride (GaN), and diamond are emerging as the front runners. SiC is used for power devices because of its high thermal conductivity; it is also used as a substrate for other semiconductor materials. GaN-based electronic devices are the leading candidates for achieving ultrahigh-frequency, high-power amplifiers. However, problems associated with this material make it difficult to build high-voltage devices, as discussed below. Some scientists and technology researchers are attempting to make diamond-based power electronic devices because of the unique thermal, mechanical, electrical, and chemical properties of diamonds. Diamond is intrinsically suited for high-speed, high-power, high-temperature applications. It is viewed as the ultimate semiconductor, but it presents significant material process challenges that must be overcome before commercial devices are made with it. Some physical characteristics are listed for the most popular wide-bandgap materials and silicon in Table 8.

Table 8. Physical characteristics of silicon and the main wide-bandgap semiconductors

Property	Target	Si	GaAs	6H-SiC	4H-SiC	GaN	Diamond
Bandgap E_g , (eV)	↑	1.12	1.43	3.03	3.26	3.45	5.45
Dielectric constant, ϵ_r	↑	11.9	13.1	9.66	10.1	9	5.5
Electric breakdown field, E_c (kV/cm)	↑	300	455	2500	2200	2000	10000
Electron mobility, μ_n (cm ² /V·s)	↑	1500	8500	500	1000	1250	2200
Hole mobility, μ_p (cm ² /V·s)	↑	600	400	101	115	850	850
Thermal conductivity, λ (W/cm·K)	↑	1.5	0.46	4.9	4.9	1.3	22
Saturated electron drift velocity, v_{sat} ($\times 10^7$ cm/s)	↑	1	1	2	2	2.2	2.7

Silicon carbide

SiC power devices can work in harsh environments where silicon power devices cannot function. SiC power devices, with their close-to-ideal characteristics, offer great performance improvements. Some of the advantages are as follows.

- SiC unipolar devices are thinner, and they have lower on-resistances.
- For a given conduction loss, SiC-based power devices have higher breakdown voltages because of their higher electric breakdown field. SiC power devices, as mentioned earlier, have higher voltages, reducing or maybe eliminating the need for series connection of devices and voltage balancing circuits.
- SiC has a higher thermal conductivity and can operate at high temperatures.
- SiC-based bipolar devices have excellent reverse recovery characteristics.
- With low switching losses, because of their smaller size and lower parasitic capacitance, SiC-based devices can operate at higher frequencies.

Although silicon semiconductor technology is highly developed, the fabrication of SiC semiconductors is not a one-to-one duplication of silicon semiconductors; and the implementation of SiC semiconductors is not chip-to-chip replacement of silicon

semiconductors. New device structures, processing technology, and electric circuits are required in order to take advantage of SiC semiconductors. Therefore, a series of issues need to be solved before SiC devices gain widespread use in power electronics applications.

Fabrication of defect-free wafers. Although micropipe density has substantially improved, there are still opportunities to improve the size of the SiC wafer. Additionally, large area yields are limited by other defects in the epitaxy, such as closed-core threading dislocations and basal plane dislocations. “Generation III” substrates are being developed to reduce these defects by an order of magnitude. The best-quality commercially available wafer has a micropipe density of less than 5 cm^{-2} . This allows an active area of about 20 mm^2 . However, a micropipe density of less than 1 cm^{-2} is required to realize devices with current ratings larger than 100 A. Currently, all industrial-standard wafers are produced by an approach called physical vapor transport, which still is plagued by problems such as direction control of the gas-phase composition and control of dopant feeding that degrade the quality of SiC wafers. SiC materials and processing technology are critical factors that dominate the cost of SiC devices and influence their market prospects.

Device packaging technology. High-temperature, high-power-density packaging techniques are required to take full advantage of SiC. The currently available packaging techniques are for applications of silicon devices, which generally have a power density limit of 200 W/cm^2 and/or a use temperature of $<125^\circ\text{C}$, while an SiC device may require a power density of 1000 W/cm^2 and/or a use temperature of $\geq 250^\circ\text{C}$. Although metal packaging technology exists for these technologies, it is too expensive for commercial use. SiC and diamond are also good candidates for package materials because of the high thermal conductivity and high dielectric breakdown strength (diamond) required for the insulating layers in power semiconductor packages.

Gallium nitride

The performance of GaN power devices is similar to the performance of SiC power devices; however, GaN has several disadvantages compared with SiC.

- It does not have a native oxide, which is required for metal oxide semiconductor devices. SiC uses the same oxide as silicon, SiO_2 . For GaN, studies are under way to find a suitable oxide.
- With the present technology, GaN is difficult to grow. Therefore, pure GaN wafers are not available; instead, GaN wafers are grown on sapphire or SiC. As a consequence, GaN epitaxy grown on such wafers is far more defective than SiC epitaxy. Additional work is required to solve surface- and interface-related problems such as gate leakage and trapping effects.
- The thermal conductivity of GaN is only one-fourth that of SiC. This property is especially important in high-power, high-temperature operation because the heat generated inside the device needs to be dissipated as quickly as possible.
- High-voltage bipolar devices are not promising for GaN power devices because of GaN’s direct band structure and short carrier lifetimes. Currently, high electron mobile transistors are the technologies of choice for GaN applications. Other possible devices may be Schottky diodes. Bipolar devices will be needed if high-power devices ($>10 \text{ kV}$, $>100 \text{ A}$) are to be developed.

Diamond for general power electronics applications

Diamond shows the best theoretical performance, with several times improvement in every performance category compared with other wide-bandgap semiconductors such as SiC, gallium arsenide, and GaN. The salient features of diamond for electronics applications include

- polycrystalline diamond film
- high breakdown voltage >500V
- high current density
- high temperature tolerance
- low leakage current
- radiation tolerance

However, processing problems have not yet been solved. After several years of research, diamond SiC still has processing issues because of the high temperatures required in the process; diamond is a harder material and needs even higher temperatures for processing, and not as much research has been done on its processing yet. Chemical vapor deposition (CVD) diamond films are polycrystalline and hence contain grain boundaries, twins, stacking faults, and other defects that reduce the lifetimes and mobilities of carriers. Active devices have been demonstrated using homoepitaxially grown diamond on natural or synthetic diamond substrates but, to date, there have been no corroborated reports of heteroepitaxial growth of device-quality diamond on nondiamond substrates. This remains a major limiting factor in the development of diamond devices. Nevertheless, the effects of grain boundaries and defects upon electronic carriers in the very best polycrystalline diamond films remain to be ascertained. Clearly, this possible route to active diamond devices cannot yet be ruled out. Another outstanding problem hindering potential diamond electronics is the difficulty in producing n-type doping. The doping of diamond with various concentrations of boron allows the electrical properties of a device to be tailored. P-type doping is relatively straightforward, since the addition of a few percentage points of B₂H₆ to the CVD process gas mixture is all that is required to incorporate boron into the lattice. However, the close packing and rigidity of the diamond lattice make doping with atoms larger than carbon atoms difficult. This means that the dopants routinely used to n-dope silicon, such as phosphorus or arsenic, cannot easily be used for diamond; therefore, alternative dopants are needed.

Presently, no diamond power devices are commercially available. For many years, researchers have worked to harness the excellent properties of diamond to make faster transistors, but breakthroughs are needed to realize the promise of diamond power electronics for transmission and distribution applications.

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APPENDIX B:

**WORKSHOP ON BASIC RESEARCH NEEDS FOR MATERIALS
UNDER EXTREME ENVIRONMENTS**

**Workshop on Basic Research Needs for Materials under
Extreme Environments**

June 11–13, 2007

Salon E

Bethesda North Marriott 5701 Marinelli Road, Bethesda, Maryland 20852

<http://marriott.com/property/propertypage/WASBN>

Agendas for Plenary Sessions

Plenary Opening Session --- Monday, June 11, 2007		
Moderator:		
7:30 am - 8:30 am	Registration and Continental Breakfast	Salon E
8:30 am - 8:40 am	Welcome	Pat Dehmer, Director, Office of Basic Energy Sciences
8:40 am - 9:00 am	Introduction of Workshop Leadership and Workshop Charter	Jeff Wadsworth, Oak Ridge National Laboratory
9:00 am - 9:25 am	Energy Efficiency and Renewable Energy Perspective	Sam Baldwin, DOE/Energy Efficiency and Renewable Energy
9:25 am - 9:50 am	Fossil Energy Perspective	Robert Romanosky, DOE/Fossil Energy
9:50 am - 10:15 am	Defense Sciences Perspective	Christopher Deeney, DOE/National Nuclear Security Administration
10:15 am – 10:40 am	BREAK	
10:40 am – 11:05 am	Energetic Fluxes Extremes Science Perspective	Bob Schoenlein, Lawrence Berkeley National Laboratory
11:05 am – 11:30 am	Chemical Extremes Science Perspective	Larry Fried, Lawrence Livermore National Laboratory
11:30 am – 11:55 am	Thermomechanical Extremes Science Perspective	Neil Ashcroft, Cornell University
12:00 noon	LUNCH	Foyer Area
12:40 pm – 1:05 pm	Electromagnetic Extremes Science Perspective	Bob Laughlin, Stanford University
1:05 pm – 1:55 pm	Introduction of Panel Topics	Panel Leads: Roger Falcone, LBNL; Ian Robertson, Univ. of Illinois; John Stringer, EPRI, retired; Peter Tortorelli, ORNL; Malcolm Nicol, Univ. of Nevada; Rusty Gray, LANL; Jane Lehr, SNL; Stan Tozer, NHMFL; Tomas Diaz de la Rubia, LLNL
1:55 pm – 2:05 pm	Closing Remarks for Opening Plenary Session and Charge to Panels	Jeff Wadsworth, Oak Ridge National Laboratory
2:05 pm – 2:15 pm	BREAK	

Workshop Breakout Sessions

Monday, June 11, 2007, 2:30 PM through Wednesday, June 13, 2007, 12:00 Noon

(Detailed breakout sessions agenda and meeting room assignments will be provided separately)

Plenary Closing Session --- Wednesday, June 13, 2007

Salon E

Moderator:

1:15 pm – 1:30 pm	Opening Remarks for Workshop Report Out and Priority Research Directions Report Out	Jeff Wadsworth, Oak Ridge National Laboratory
1:30 pm – 2:00 pm	Energetic Flux Panel Priority Research Directions	Panel 1
2:00 pm – 2:30 pm	Chemical Extremes Panel Priority Research Directions	Panel 2
2:30 pm – 3:00 pm	Thermomechanical Extremes Panel Priority Research Directions	Panel 3
3:00 pm – 3:30 pm	Electromagnetic Extremes Panel Priority Research Directions	Panel 4
3:30 pm – 3:45 pm	BREAK	
3:45 pm – 4:15 pm	Cross-cutting Panel Survey and Priority Research Directions	Panel 5
4:15 pm – 4:35 pm	Workshop Conducting Remarks	Jeff Wadsworth, ORNL; George Crabtree, ANL; and Russell Hemley, Carnegie Institute of Washington
4:35 pm – 4:45 pm	Final Closing Remarks	Pat Dehmer, Director, Office of Basic Energy Sciences
4:45 pm – 6:00 pm	Reception	Salon E Foyer Area
6:00 pm	Workshop Adjourns	

Workshop Report Writing Session

Wednesday, June 13, 2007, 7:30 PM - Thursday, June 14, 2007, 3:30 PM

(Workshop Chair, Co-Chairs, Panel Leads and Core Writing Groups only)

Agenda for Energetic Fluxes Sessions:

**Co-Chairs: Roger Falcone Lawrence Berkeley Laboratory
and Ian Robertson, University of Illinois**

Monday, June 11, 2007, 2:15 p.m. – 9:00 p.m.

Panel 1A and 1B — Photons and Ions and Neutrons (Salon G)

Time	Topic	Speaker or Location
Session 1		
2:15 p.m. – 2:30 p.m.	Introductory remarks and guidance, review of agenda, general discussion of theme among all	Panel Co-Leads: Roger Falcone and Ian Robertson
Session 2		
	Scientific Issues on Materials in Extreme Fluxes <i>(In-panel presentations as discussion starters, speakers to limit themselves to no more than half of allotted time)</i>	Facilitated by Falcone and Robertson <i>(One keeps discussions on focus and on time, other works on strawman PRDs)</i>
2:30 – 2:50 p.m.	Surface-ion interactions	Eric Chason, Brown Univ.
2:50 – 3:10 p.m.		Dana Dlott, Univ. of Illinois
3:10 -3:30 p.m.	Swift heavy ion effects	Christina Trautmann, Germany
3:30 – 3:50 p.m.		Chris Jacobson, Stony Brook Univ.
3:50 – 4:10 p.m.	Fusion materials	Dennis Whyte, MIT
4:10 – 4:30 p.m.		Eric Mazur, Harvard Univ.
4:30 – 4:40 p.m.	BREAK	Upper and Lower Level Foyer Areas
4:40 -5:00 p.m.	Simulations and modeling of ion effects in solids	Simon Philpott, Univ. of Florida
5:00 - 5:20 p.m.		Jeff Bude, LLNL
5:20 – 6:00 p.m.	Separate particle and photon flux sub-panel sessions Discussion of one-sentence Priority Research Directions (PRDs)	Panel 1A – Salon G Panel 1B – Glen Echo
6:00 – 7:30 p.m.	Working Dinner	Salon D
7:30 – 8:45 p.m.	Prioritize 3-5 one-sentence PRDs	
8:45 – 9:30 p.m.	Co-leads meet to prepare for Tuesday	Falcone and Robertson (Salon E)

Tuesday, June 12, 2007: 8:00 a.m. – 9:30 p.m.

Panel 1A – Photons (Salon G) and Panel 1B — Ions and Neutrons (Glen Echo)

Time	Topic	Speaker or Location
7:30 – 8:00 a.m.	Continental Breakfast	Upper and Lower Level Foyer Areas
Session 3 (separate sessions)		
	Formulation of First-Cut PRDs	
8:00 – 10:00 a.m.	Separate particle and photon flux sub-panel sessions Draft 3–5 one-sentence and one-viewgraph PRDs for each Sub-panel	Panel 1A – Salon G Panel 1B – Glen Echo

10:00 – 10:15 a.m.	BREAK	Upper and Lower Level Foyer Areas
10:15 a.m. – 12:30 p.m.	JOINT Photons and Ions and Neutrons Sub-Panel Session -- Plenary Midpoint Session (Presentations of Draft PRDs)	Salon G
12:30 – 1:30 p.m. (1:30 – 2:00 p.m.)	Working Lunch – Mid-Point Plenary Session, Panels report on draft PRDs. (Panel leads, Chairs and DOE/BES staff caucus; panels return to their rooms to continue work)	Salon E Moderator: Michelle Buchanan Salon D
Session 4		
1:30 – 3:45 p.m.	Consideration of issues from other panels in context of extremes fluxes and refine PRDs	
3:45 – 4:00 p.m.	BREAK	Upper and Lower Level Foyer Areas
Session 5	Revision and Refinement of PRDs	
4:00 – 6:00	Revise PRDs and down-select to 3–5 PRDs for Panel 1	Salon G
6:00 – 7:30	Dinner on your own	
7:30 – 9:00	Refine PRDs	Salon G

Wednesday, June 13, 2007; 8:00 a.m. – 9:00 p.m.

Panel 1A and 1B – Photons and Ions and Neutrons (Salon G)

Time	Topic	Speaker or Location
7:30 -8:00 am	Continental Breakfast	Upper and Lower Level Foyer Areas
Session 7		
8:00 am – 12:00 noon	Draft four-viewgraph Panel Survey, one Executive Summary paragraph, one viewgraph, and a 1,000–1,500 word version of each PRD. Begin drafting 3,000–5,000 word Panel Surveys	Salon G
10:15 – 10:30 a.m.	BREAK	Upper and Lower Level Foyer Areas
12:00 – 1:00 p.m.	Working Lunch	Upper and Lower Level Foyer Areas
Session 8		
1:15 – 4:45 p.m.	Closing Plenary Session	Salon E
4:45 – 6:00 p.m.	Reception	Salon E Foyer Area
7:30 – 9:30 p.m.	Evening Writing Session if needed	

Thursday, June 14, 2007, 8:00 a.m. – 3:30 p.m.

Final Writing of Panel Report — Writers, Panel Leads, and Chairs Only

Time	Topic	Speaker or Location
8:00 am – 3:30 p.m.	Selected writers, panel chairs, and co-chairs complete writing and integration of Panel Surveys, PRDs, CCRDs, and Factual Documents into final Workshop Report	Middlebrook Room Timberlawn Room Great Falls Room

Agenda for Chemical Extremes

**Co-Chairs: John Stringer, Electric Power Research Institute (retired) and
Peter Tortorelli, Oak Ridge National Laboratory**

Monday, June 11, 2007, 2:15 p.m. – 9:00 p.m.

Panel 2 — Chemical Extremes (Salon H)

Time	Topic	Speaker or Location
Session 1		
2:15 p.m. – 2:45 p.m.	Introductory remarks and guidance, review of agenda, general discussion of theme among all	Panel Co-Leads: Stringer and Tortorelli
Session 2		
	Scientific Issues on Materials in Extremely Reactive Environments <i>(In-panel presentations as discussion starters, speakers to limit themselves to no more than half of allotted time)</i>	Facilitated by Stringer and Tortorelli <i>(One keeps discussions on focus and on time, other works on strawman PRDs)</i>
3:15 – 3:40 p.m.	Extreme aqueous environments	Hugh Issacs, BNL
3:40 – 4:00 p.m.	High-temperature electrochemistry	Serguei Lvov, Penn State
4:00 -4:20 p.m.	Geochemical environments	David Wesolowski, ORNL
4:20 – 4:45 p.m.	BREAK	Upper and Lower Level Foyer Areas
4:45 – 5:10 p.m.	High-temperature reactive gases	Brian Gleeson, Iowa State
5:10 – 5:30 p.m.	Environmental reactions of materials at extremely high temperatures	Beth Opila, NASA Glenn
5:30 – 6:00 p.m.	Other extreme reactive environments (e.g., radiation, liquid metals, erosion)	ALL (1 or 2 slides per point)
6:00 – 7:30 p.m.	Working Dinner	Salon D
7:30 – 8:45 p.m.	Other extreme reactive environments (cont'd.)	ALL (1 or 2 slides per point)
8:45 – 9:30 p.m.	Co-leads meet to prepare for Tuesday	Stringer and Tortorelli (Salon E)

Tuesday, June 12, 2007: 8:00 a.m. – 9:30 p.m.

Panel 2 — Chemical Extremes (Salon H)

Time	Topic	Speaker or Location
7:30 – 8:00 a.m.	Continental Breakfast	Upper and Lower Level Foyer Areas
Session 3		
Formulation of First-Cut PRDs		
8:00 – 9:00 a.m.	Recap of Tuesday discussions; revisit, reconsider	Salon H
9:00 – 10:00 a.m.	Drafting of rough PRDs	
10:00 – 10:15 a.m.	BREAK	Upper and Lower Level Foyer Areas
10:15 – 12:15 p.m.	Drafting of rough PRDs (cont'd.)	
12:30 – 1:30 p.m. (1:30 – 2:00 p.m.)	Working Lunch – Mid-Point Plenary Session, Panels report on draft PRDs. (Panel leads, Chairs and DOE/BES staff caucus; panels return to their rooms to continue	Salon E – Moderator: Michelle Buchanan Salon D

Time	Topic	Speaker or Location
	work)	
Session 4		
1:30 – 3:45 p.m.	Consideration of issues from other panels in context of reactive extremes and refine PRDs	Cross-panel interactions
3:45 – 4:00 p.m.	Break	Upper and Lower Level Foyer Areas
Session 5		
Revision and Refinement of PRDs		
4:00 – 6:00 p.m.	Revise PRDs and down-select to 3–5	
6:00 – 7:30 p.m.	Dinner on your own	
7:30 – 9:00 p.m.	Refine PRDs	Salon H

Wednesday, June 13, 2007; 8:00 a.m. – 9:00 p.m.

Panel 2 — Chemical Extremes (Salon H)

Time	Topic	Speaker or Location
7:30 -8:00 am	Continental Breakfast	Upper and Lower Level Foyer Areas
Session 7		
8:00 am – 12:00 noon	Draft four-viewgraph Panel Survey, one Executive Summary paragraph, one viewgraph, and a 1,000–1,500 word version of each PRD. Begin drafting 3,000–5,000 word Panel Surveys	Salon H
10:15 – 10:30 a.m.	BREAK	Upper and Lower Level Foyer Areas
12:00 – 1:00 p.m.	Working Lunch	Upper and Lower Foyer Areas
Session 8		
1:15 – 4:45 p.m.	Closing Plenary Session	Salon E
4:45 – 6:00 p.m.	Reception	Salon E Foyer Area
7:30 – 9:00 p.m.	Evening Writing Session if needed	

Thursday, June 14, 2007, 8:00 a.m. – 3:30 p.m.

Final Writing of Panel Report — Writers, Panel Leads, and Chairs Only

Time	Topic	Speaker or Location
8:00 am – 3:30 p.m.	Selected writers, panel chairs, and co-chairs complete writing and integration of Panel Surveys, PRDs, CCRDs, and Factual Documents into final Workshop Report	Middlebrook Room Timberlawn Room Great Falls Room

Agenda for Thermomechanical Extremes Sessions:

Co-Chairs: Malcolm Nicol, Univ. of Nevada and

Rusty Gray, Los Alamos National Laboratory

Monday, June 11, 2007, 2:15 p.m. – 9:00 p.m.

Panel 3A and 3B — Static and Dynamic (Salon F)

Time	Topic	Speaker or Location
Session 1		
2:15 p.m. – 2:30 p.m.	Introductory remarks and guidance, review of agenda, general discussion of theme among all	Panel Co-Leads: Malcolm Nicol and Rusty Gray
2:30 p.m. – 2:45 p.m.	Static Overview ideas #1	Christian Mailhot, LLNL
2:45 p.m. – 3:00 p.m.	Static Overview Ideas #2	Chris Tulk, ORNL
3:00 p.m. – 3:15 p.m.	Static Overview Ideas #3	Robert Averback, University of Illinois
3:15 p.m. – 3:30 p.m.	Dynamic Overview Ideas #1	Tresa Pollock, Univ. of Mich.
3:30 p.m. – 3:45 p.m.	Dynamic Overview Ideas #2	Neil Bourne, Univ. of Manchester
3:45 p.m. – 4:00 p.m.	Dynamic Overview Ideas #3	Curt Bronkhorst, LANL
4:00 p.m. – 4:15 p.m.	BREAK	Upper and Lower Level Foyer Areas
4:15 p.m. – 4:30 p.m.	Joint Static & Dynamic Preliminary Discussions on Potential Priority Research Directions (PRD's)	Salon F
Session 2		
4:30 p.m. – 6:00 p.m.	Separate Static and Dynamic Sub-Panels -- Initial Discussion of one-sentence Priority Research Directions (PRDs)	Panel 3A – Salon F Panel 3B – Forest Glen
6:00 p.m. – 7:30 p.m.	Working Dinner	Salon D
7:30 p.m. – 9:00 p.m.	Prioritize 3–5 one-sentence PRDs	
9:00 p.m. – 9:30 p.m.	Panel Chair and Sub-panel Co-chairs review PRDs	Salon E

Tuesday, June 12, 2007: 8:00 a.m. – 9:30 p.m.

Panels 3A –Static (Salon F) and Panel 3B – Dynamic (Forest Glen)

Time	Topic	Speaker or Location
7:30 – 8:00 a.m.	Continental Breakfast	Upper and Lower Level Foyer Areas
Session 3 (separate sessions)		
8:00 – 10:00 a.m.	Separate Static & Dynamic Sub-Panel Sessions --- Draft 3–5 one-sentence and one-viewgraph PRDs for each Sub-panel	Panel 3A — Salon F Panel 3B — Forest Glen
10:00 – 10:15 a.m.	BREAK	Upper and Lower Level Foyer Areas
Session 4 (Unified session)		
10:15 a.m. – 12:30 p.m.	JOINT Static & Dynamic Sub-Panel Session - Plenary Midpoint Session (Presentations of Draft PRDs)	Salon F

Time	Topic	Speaker or Location
12:30 – 1:30 p.m. (1:30 – 2:00 p.m.)	Working Lunch – Mid-Point Plenary Session, Panels report on draft PRDs. (Panel leads, Chairs and DOE/BES staff caucus; panels return to their rooms to continue work)	Salon E – Moderator: Michelle Buchanan Salon D
Session 5 (unified session)		
1:30 – 3:45 p.m.	Consideration of issues from other panels in context of thermomechanical extremes and refine PRDs	Salon F
3:30 – 3:45 p.m.	BREAK	Upper and Lower Level Foyer Areas
3:45 - 6:00 p.m.	Down-select to 3–5 PRDs for Panel 3	Salon F
Session 6 (unified sessions)		
6:00 – 7:30 p.m.	Dinner on Your Own	
7:30 – 9:30 p.m.	Refine PRDs	Salon F

Wednesday, June 13, 2007; 8:00 a.m. – 9:00 p.m.

Panel 3A and 3B — Static and Dynamic (Salon F)

Time	Topic	Speaker or Location
Session 7		
7:30 am – 8:00 am	Continental Breakfast	Upper and Lower Level Foyer Areas
8:00 am – 12:00 noon	Draft four-viewgraph Panel Survey, one Executive Summary paragraph, one viewgraph, and a 1,000–1,500 word version of each PRD. Begin drafting 3,000–5,000 word Panel Surveys	Salon F
10:15 – 10:30 a.m.	BREAK	Upper and Lower Level Foyer Areas
Session 8		
12:00 – 1:00 p.m.	Working Lunch	Upper and Lower Level Foyer Areas
1:15 – 4:45 p.m.	Closing Plenary Session	Salon E
4:45 – 6:00 p.m.	Reception	Salon E Foyer Area
6:00 p.m.	Adjourn	
7:30 – 9:30 p.m.	Evening Writing Session if needed	

Thursday, June 14, 2007, 8:00 a.m. – 3:30 p.m.

Final Writing of Panel Report — Writers, Panel Leads, and Chairs Only

Time	Topic	Speaker or Location
8:00 am – 3:30 p.m.	Selected writers, panel chairs, and co-chairs complete writing and integration of Panel Surveys, PRDs, CCRDs, and Factual Documents into final Workshop Report	Middlebrook Room Timberlawn Room Great Falls Room

Agenda for Electromagnetic Extremes Sessions:

Co-Chairs: Jane Lehr, Sandia National Laboratories and

Stan Tozer, National High Magnetic Field Laboratory, Florida State University

Monday, June 11, 2007: 2:15 p.m. – 9:00 p.m.

Panel 4A and 4B — Electric Fields and Magnetic Fields (Linden Oak)

Time	Topic	Speaker or Location
Session 1		
2:15 p.m. – 2:30 p.m.	Introductory remarks and guidance, review of agenda, general discussion of theme among all	Panel Co-Leads: Jane Lehr and Stan Tozer
2:30 p.m. – 2:45 p.m.	High Electric Field ideas #1	Steven Boggs, Univ. of Connecticut
2:45 p.m. – 3:00 p.m.	High Electric Field Ideas #2	William Nunnally, Univ. of Missouri
3:00 p.m. – 3:15 p.m.	High Electric Field Ideas #3	Krishna Rajan, Iowa State Univ.
3:15 p.m. – 3:30 p.m.	High Magnetic Field Ideas #1	Jason Cooley, LANL
3:30 p.m. – 3:45 p.m.	High Magnetic Field Ideas #2	Collin Broholm, Johns Hopkins Univ.
3:45 p.m. – 4:00 p.m.	High Magnetic Field Ideas #3	Malte Grosche, United Kingdom
4:00 p.m. – 4:15 p.m.	BREAK	Upper and Lower Level Foyer Areas
4:15 p.m. – 4:30 p.m.	Joint EM Field Preliminary Discussions on Potential Priority Research Directions (PRD's)	Linden Oak
Session 2		
4:30 p.m. – 6:00 p.m.	Separate EM Field Sub-Panels --Initial Discussion of one-sentence Priority Research Directions (PRDs)	Panel 4A – Linden Oak Panel 4B - Oakley
6:00 p.m. – 7:30 p.m.	Working Dinner	Salon D
7:30 p.m. – 9:00 p.m.	Prioritize 3–5 one-sentence PRDs	
9:00 p.m. – 9:30 p.m.	Panel Chair and Sub-panel Co-chairs review PRDs	Salon E

Tuesday, June 12, 2007: 8:00 a.m. – 9:30 p.m.

Panels 4A – Electric Fields (Linden Oak) and Panel 4B - Magnetic Fields (Oakley)

Time	Topic	Speaker or Location
7:30 a.m. – 8:00 a.m.	Continental Breakfast	Upper and Lower Level Foyer Areas
Session 3 (separate sessions)		
8:00 a.m. – 10:00 a.m.	Separate Electric & Magnetic Field Sub-Panel Sessions --- Draft 3–5 one-sentence and one-viewgraph PRDs for each Sub-panel	Panel 4A — Linden Oak Panel 4B — Oakley
10:00 a.m. – 10:15 a.m.	BREAK	Upper and Lower Level Foyer Areas
Session 4 (Unified session)		
10:15 a.m. – 12:30 p.m.	JOINT EM Field Panel Session -- Plenary Midpoint Session (Presentations of Draft PRDs)	Linden Oak

Time	Topic	Speaker or Location
12:30 – 1:30 p.m. (1:30 – 2:00 p.m.)	Working Lunch – Mid-Point Plenary Session, Panels report on draft PRDs. (Panel leads, Chairs and DOE/BES staff caucus; panels return to their rooms to continue work)	Salon E – Moderator: Michelle Buchanan Salon D
Session 5 (unified session)		
1:30 – 3:34 p.m.	Consideration of issues from other panels in context of electromagnetic extremes and refine PRDs	Linden Oak
3:30 – 3:45 p.m.	BREAK	Upper and Lower Level Foyer Areas
3:45 p.m. – 6:00 p.m.	Down-select to 3–5 PRDs for Panel 4	Linden Oak
Session 6 (unified sessions)		
6:00 p.m. -7:30 pm	Dinner on your own	
7:30 p.m. – 9:30 p.m.	Refine PRDs	Linden Oak

Wednesday, June 13, 2007; 8:00 a.m. – 9:00 p.m.

Panels 4A and 4B –Electric Fields and Magnetic Fields (Linden Oak)

Time	Topic	Speaker or Location
7:30 a.m. -8:00 am	Continental Breakfast	Upper and Lower Level Foyer Areas
Session 7		
8:00 am – 12:00 noon	Draft four-viewgraph Panel Survey, one Executive Summary paragraph, one viewgraph, and a 1,000–1,500 word version of each PRD. Begin drafting 3,000–5,000 word Panel Surveys	Linden Oak
Session 8		
10:15 a.m. – 10:30 a.m.	BREAK	Upper and Lower Level Foyer Areas
12:00 p.m. – 1:00 p.m.	Working Lunch	Upper and Lower Level Foyer Areas
1:15 p.m. – 4:45 p.m.	Closing Plenary Session	Salon E
4:45 p.m. – 6:00 p.m.	Reception	Salon E Foyer Area
7:30 p.m. – 9:30 p.m.	Evening Writing Session if needed	

Thursday, June 14, 2007, 8:00 a.m. – 3:30 p.m.

Final Writing of Panel Report — Writers, Panel Leads, and Chairs Only

Time	Topic	Speaker or Location
8:00 a.m. – 3:30 p.m.	Selected writers, panel chairs, and co-chairs complete writing and integration of Panel Surveys, PRDs, CCRDs, and Factual Documents into final Workshop Report	Middlebrook Room Timberlawn Room Great Falls Room

WORKSHOP PARTICIPANTS

Workshop Chair

Jeffrey Wadsworth, Oak Ridge National Laboratory

Workshop Co-chairs

George W. Crabtree, Argonne National Laboratory

Russell J. Hemley, Carnegie Institution of Washington

Technical Coordinator

Michelle Buchanan, Oak Ridge National Laboratory

Panel Leads

Energetic Flux Extremes

Roger Falcone, Lawrence Berkeley National Laboratory

Ian Robertson, University of Illinois at Urbana-Champaign

Chemically Reactive Extremes

John Stringer, EPRI [retired]

Pete Tortorelli, Oak Ridge National Laboratory

Thermomechanical Extremes

George T. (Rusty) Gray, Los Alamos National Laboratory

Malcolm Nicol, University of Nevada, Las Vegas

Electromagnetic Extremes

Jane Lehr, Sandia National Laboratories

Stanley W. Tozer, National High Magnetic Field Laboratory

Cross-Cutting Science

Tomás Diaz de la Rubia, Lawrence Livermore National Laboratory

Plenary Speakers

Neil Ashcroft, Cornell University

Larry Fried, Lawrence Livermore National Laboratory

Robert Laughlin, Stanford University

Robert Romanosky, National Energy Technology Laboratory

Panel 1: Energetic Flux Extremes

Jeff Atherton, Lawrence Livermore National Laboratory

Jeff Bude, Lawrence Livermore National Laboratory

Andreas Cavalleri, United Kingdom

Eric Chason, Brown University

Tom Dickenson, Washington St. Univ.

Dana Dlott, University of Illinois

Rodney Ewing, University of Michigan

James Glowina, Los Alamos National Laboratory

Costas Grigoropoulos, University of California, Berkeley

Richard Haglund, Vanderbilt University

Julie Harmon, University of South Florida

Ahmed Hassanein, Argonne National Laboratory

Chris Jacobson, Stony Brook University

Hector Lorenzana, Lawrence Livermore National Laboratory

Eric Mazur, Harvard University

Robert Odette, University of California, Santa Barbara

Michael Pellin, Argonne National Laboratory

Simon Phillpot, University of Florida

Roland Pitts, National Renewable Energy Laboratory

Robert Schoenlein, Lawrence Berkeley National Laboratory

Lance Snead, Oak Ridge National Laboratory
Joachim Stohr, SLAC
Roger Stoller, Oak Ridge National Laboratory
Christina Trautmann, GSI Gesellschaft für Schwerionenforschung mbH, Darmstadt, Germany
Bill Wampler, Sandia National Laboratory
Dennis Whyte, Massachusetts Institute of Technology
Gwyn Williams, Jefferson Laboratory
Brian Wirth, LBNL and University of California, Berkeley

Panel 2: Chemical Extremes

Larry Fried, Lawrence Livermore National Laboratory
Brian Gleeson, Iowa State University
Peggy Hou, Lawrence Berkeley National Laboratory
Hugh Isaacs, Brookhaven National Laboratory
Russ Jones, GT Engineering
Scott Lillard, Los Alamos National Laboratory
Serguei Lvov, Pennsylvania State University
Digby Macdonald, Pennsylvania State University
Greg Olson, Northwestern University
Elizabeth Opila, NASA
Gary Was, University of Michigan
David Wesolowski, Oak Ridge National Laboratory

Panel 3: Thermomechanical Extremes

Robert Averback, University of Illinois
Neil Bourne, University of Manchester
Eduardo Bringa, Lawrence Livermore National Laboratory
Curt Bronkhorst, Los Alamos National Laboratory
Michael Brown, University of Washington
Dana Dattelbaum, Los Alamos National Laboratory
Easo George, Oak Ridge National Laboratory
Kevin Hemker, Johns Hopkins University
Chi-Chang Kao, Brookhaven National Laboratory
Marcus Knudson, Sandia National Laboratories
Hector Lorenzana, Lawrence Livermore National Laboratory
Christian Mailhot, Lawrence Livermore National Laboratory
Ho-kwang (Dave) Mao, Carnegie Institution of Washington
Artem Organov, Moscow State University
Tresa Pollock, Univ. of Michigan
Sarah Stewart-Mukhopadhyay, Harvard University
John Tse, University of Saskatchewan
Chris Tulk, Oak Ridge National Laboratory
Kenneth Vecchio, Univ. of California
Julia Weertman, Northwestern University
Chris Woodward, Air Force Research Laboratory
Choong-Shik Yoo, Lawrence Livermore National Laboratory

Panel 4: Electromagnetic Extremes

Robert Anderson, Sandia National Laboratory
Steven Boggs, Steven, University of Connecticut
Collin Broholm, Johns Hopkins University
Esther Conwell, University of Rochester
Jason Cooley, Los Alamos National Laboratory
Lance Cooley, Fermi National Accelerator Laboratory
Paul Dodd, Sandia National Laboratories
Malte Grosche, United Kingdom
Joanna Groza, University of California, Davis
Donald Gubser, Naval Research Laboratory
Alex Gurevich, Florida State University
Ke Han, National High Magnetic Field Laboratory

Harold P. Hjalmarson, Sandia National Laboratories
Richard Holroyd, Brookhaven National Laboratory
Robert Laughlin, Stanford University
Gerald Ludtka, Oak Ridge National Laboratory
Chuck Mielke, Los Alamos National Laboratory
Michael Naughton, Boston College
Eugene Neau, Albuquerque Operations Office
William Nunnally, University of Missouri
Krishna Rajan, Iowa State University
Kurt Slenes, TPL Inc.
Wijun Yin, GE Global Research Center

Panel 5: Cross-cutting

William Goddard III, California Institute of Technology
Robert Hanrahan, LANL/NNSA
Christian Mailhot, Lawrence Livermore National Laboratory
Ralph Nuzzo, University of Illinois
John Sarrao, Los Alamos National Laboratory
Steven Zinkle, Oak Ridge National Laboratory

Office of Science

Adam Cohen, Office of Science
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Bonnie Gersten
Jim Horwitz
Harriet Kung
John Miller
Raul Miranda
John Vetrano
Nick Woodward
Jane Zhu

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Gerald Gears, Office of Nuclear Energy, DOE
Emily Meyer, National Materials Advisory Board
Kendra Rand, MRS Bulletin

Observers:

Craig Blue, Oak Ridge National Laboratory
Phillip Britt, Oak Ridge National Laboratory
Kim Budil, Lawrence Livermore National Laboratory
Larry Carr, Brookhaven National Laboratory
Bob Cauble, Lawrence Livermore National Laboratory
Paul Follansbee, Los Alamos National Laboratory
Natraj Iyer, Savannah River National Laboratory
Bernd Kabius, Argonne National Laboratory
Matthew Kramer, Ames Laboratory
Robert Liebermann, State University of New York, Stony Brook
Tom Lillo, Idaho National Laboratory
Tedd Lister, Idaho National Laboratory
Stu Maloy, Los Alamos National Laboratory
Wendy Mao, Los Alamos National Laboratory
James Marra, Savannah River National Laboratory
Ken Natesan, Argonne National Laboratory
George Neil, Jefferson Laboratory
Adam Schwartz, Lawrence Livermore National Laboratory
Tom Shih, Ames Laboratory
Nick Simos, Brookhaven National Laboratory
Jim Strachan, Princeton University Plasma Physics Laboratory
S. K. Sundaram, Pacific Northwest National Laboratory
Richard Wright, Idaho National Laboratory
Yanwen Zhang, Pacific Northwest National Laboratory