SPECIAL ISSUE

Science & Technology REVIEW

DESIGNER MATERIALS

Lawrence Livermore National Laboratory

Also in this issue:

Materials for National Security

Materials Theory and Simulation

Materials for Laser Systems

The cover image shows a three-dimensionally printed carbon fiber part created using a Livermore-developed direct ink writing process. Laboratory researchers use and refine a range of advanced manufacturing techniques and technologies to create tailor-made, high-performance materials.

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Lawrence Livermore National Laboratory

Contents

Welcome from Bob Maxwell

MATERIALS SCIENCE RESEARCH SUPPORTS NATIONAL SECURITY

MATERIALS are central to our national security missions at Lawrence Livermore, including economic competitiveness, energy and water security, and deterrence. Our staff within the Material Science Division (MSD), along with their internal and external partners, continue to make outstanding contributions to those national security missions. Our advancements in new material discovery and in our fundamental understanding of new and legacy materials impacts a broad range of scientific and programmatic applications. Our materials research finds exposure in the top international journals and at the world's top materials, physics, and chemistry conferences.

Over the last few years, MSD staff have continued their track record of making significant contributions to our programmatic stakeholders through accelerated materials development. This is exemplified by our replacement materials work for the W80-4 life-extension program, including critical energetic materials development and assessment; discovery of new damage mechanisms and mitigation strategies to limit the impact of that damage in laser optics; development of new materials for targets for high-energy-density experiments; creation of new catalytic materials; advances in understanding hydrogen storage mechanisms; development of new designer feedstock materials (inks, nanomaterials) for a wide range of additive manufacturing methods to help demonstrate new forms of unobtainium; record-setting molecular dynamics simulation of dislocations in metals, through which we discovered new deformation mechanisms; and development of new replacement options for multiple critical materials. The articles in this compilation are only the tip of the iceberg of MSD contributions to the Lab's missions and the scientific community.

The excellence that is routinely exhibited in our work is a reflection not only of the world-class and often unique facilities at LLNL (National Ignition Facility, Advanced Manufacturing Laboratory, High Explosives Application Facility, Center for Accelerator Mass Spectrometry, Forensic Science Center, etc.), but our remarkable staff and the national and international partnerships that they frequently bring to the table (including the nation's Department of Energy user facilities such as the Linac Coherent Light Source [LCLS] and the dynamic compression sector [DCS] at Advanced Photon Source).

The demand for new materials and a new understanding of materials is relentless and only expected to grow. These materials will need to be faster, cheaper, and better than existing options. They may, for instance, better withstand harsh environments, offer new functions, or save weight. They will also need to be compatible with less energy-intensive manufacturing methods that offer opportunities for tailoring both composition and architecture in 1, 2, 3 and 4 dimensions. To solve these challenges, new data and information analysis tools are needed, as are new high-yield synthesis strategies along with advanced modeling and simulation tools to advance the scope of these tools in length and time as we continue our transition from ideal to real materials.

■ Bob Maxwell is materials science division leader within the Physical and Life Sciences directorate.

PIECING TOGETHER A NUCLEAR FIREBALL

Resulting from the Sun's nuclear processes, the erupting plasma from solar flares rapidly expands and cools similarly to what occurs in a nuclear fireball. (Image courtesy of NASA/SDO.)

MATERIALS vaporized by a nuclear explosion do not simply disappear without a trace in the resulting fireball. Leftover bomb materials and fission products remain, but these interact with the surrounding environment in complicated ways, making it difficult for scientists to unravel what happened in the explosion. However, by better understanding the chemical compounds that form in the cooling fireball, researchers can more effectively uncover evidence that can help identify the nature of the bomb that produced the blast. In the event of a nightmare scenario such as the detonation of a nuclear weapon in a U.S. city by a rogue actor, such forensic capabilities would be invaluable.

The tremendous energy generated by a nuclear explosion instantly vaporizes any nearby materials. On an atomic level, electrons are stripped away from gaseous atoms to form a plasma—a mix of ions from different elements and free electrons. As it rapidly expands, the plasma quickly cools back into gases, liquids, and finally solids. During this sequence of phase transformations, the different elements segregate according to their chemical properties and fractionate (that is, separate out) as they condense into solids, forming the particles known as fallout debris. All this begins to happen within moments after the explosion, once the temperature drops below roughly 5,000 kelvins and the pressure has subsided to approximately atmospheric level.

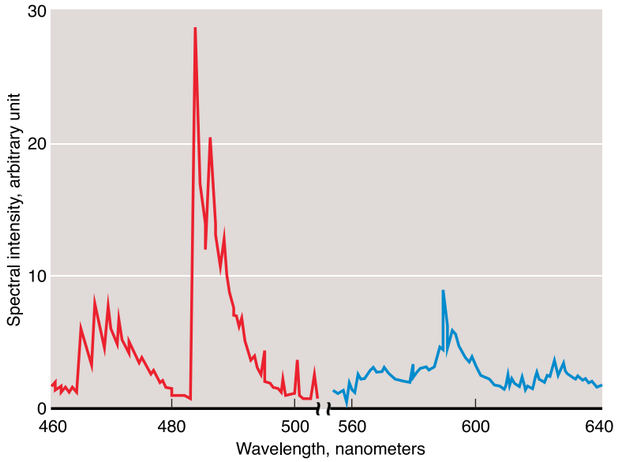
The ability to disentangle the effects of this fractionation process is essential for accurately piecing together a nuclear fireball. To study this complex fractionation process, researchers at Lawrence Livermore and collaborators from Stanford University and the University of Illinois at Urbana-Champaign (UIUC) have developed two different methods of physically simulating the plasma conditions in nuclear fireballs: pulsed laser ablation and the plasma flow reactor method. Research with the latter method is headed by Livermore radiochemist Tim Rose. "An advantage of having both methods running in parallel is that we cover two timescales, which differ by three orders of magnitude," says Rose. "Pulsed laser ablation heats and cools very rapidly, in microseconds. However, events in a plasma flow reactor happen over tens of milliseconds, even as slowly as a tenth of a second."

Plasma Flow Reactor Experiments

Starting as a project funded by the Laboratory Directed Research and Development Program, work with the plasma flow reactor method initially focused on one element at a time, looking at how each reacts with oxygen. Iron was examined early on as an element commonly found in debris and one that follows a straightforward pathway when forming chemical compounds.

A plasma flow reactor is an open-ended quartz tube, 1 meter in length and 4 centimeters in diameter, with a radiofrequency induction coil at one end. The coil forms a plasma torch that heats a constant inward flow of inert argon into a plasma. Dissolved in a nitrate solution, iron is atomized and injected into the plasma torch, the hottest part of the reactor. Livermore postdoctoral researcher Batikan Koroglu explains, "The end-to-end temperature profile along the tube is well constrained, steeply decreasing from 5,000 to 1,000 kelvins. The reactor operates in steady state, so that the setup is like a nuclear fireball frozen at a moment in time." After physically mixing with the stream of plasma, the iron ionizes, then cools while flowing down the reactor tube and begins to react with oxygen to form individual molecules of iron oxide (FeO). These molecules condense into a liquid, which finally solidifies into FeO particles.

By probing various positions along the tube in situ, optical emission spectroscopy reveals where the FeO chemically forms. This information in turn indicates at what temperature the reaction occurs. Inserted into the cooler end of the tube, a sample collector captures particles at different positions, thereby sampling different temperatures. Captured particles are analyzed using electron microscopy to uncover their morphology and microstructure. After iron, the researchers separately studied aluminum and uranium, also common constituents of nuclear debris. Once these individual metals had been looked at, combinations of metals were then evaluated.



In experiments simulating conditions in a nuclear fireball, equal amounts of iron and aluminum were injected into a plasma flow reactor. The patterns of emission spectra, like separate sets of fingerprints, reveal the presence of both aluminum oxide (red) and iron oxide (blue) in gas at 1,740 kelvins that cooled from plasma.

Rose adds, “The oxide particles of uranium look different than those of aluminum, which look different than those of iron. Experimenting with multiple metals together results in even more complexity. For instance, an aluminum oxide particle that formed early in the process may have iron oxide particles sticking to it, indicating that the aluminum oxide condensed first.” Investigating the interrelation between metals provides more clues that researchers hope will lead to a better understanding of chemical fractionation inside a fireball.

Plasma by Pulsed Laser Ablation

Livermore physicist Harry Radousky, who leads the pulsed laser ablation work at Livermore, states, “Laser ablation is much different than the plasma flow reactor method in that it is not steady state. Instead, the method involves creating a plume of plasma that changes very rapidly in temperature and density. In addition, we can carefully control the surrounding atmosphere that interacts with the plasma.” Radousky, chemist David Weisz, and physicist Jonathan Crowhurst run the experimental aspects of this research at Lawrence Livermore while collaborators at UIUC conduct the kinetics modeling.

The team recently studied strontium and zirconium, both of which are fission products created after a nuclear detonation. As with the metals studied with the plasma flow reactor, strontium and zirconium undergo the same change in state—from plasma to gas, gas to liquid, and finally liquid to solid. To compare the dynamic behavior of these elements as they condense, the researchers use strontium zirconate ($SrZrO_3$), an oxide with a uniform distribution of strontium and zirconium throughout its lattice. A crystal of $SrZrO_3$ is mounted inside the reactor’s sealed sample chamber. A beam is fired from a neodymium-doped yttrium–aluminum–garnet laser, entering the chamber and breaking down the crystal’s surface layers into ions, which erupt as a plume of plasma initially at a temperature of approximately 10,000 kelvins.

Optical emission spectroscopy is again used to analyze the chemicals that form as the plasma cools. Filters reveal the spatial distribution of strontium oxide (SrO) and zirconium oxide (ZrO) as the plasma evolves over time. Researchers found that ZrO—a precursor to ZrO_2—formed sooner than SrO in the vapor, which was consistent with their thermodynamic properties. In short, the stable and highly refractory oxide ZrO_2 can exist as a solid at higher temperatures, and may condense earlier, than SrO. Weisz adds, “We then took the experiments one step further and demonstrated that the earliest ZrO formed from reaction with oxygen released by the $SrZrO_3$ crystal, whereas later ZrO formed by reaction with gas in the surrounding environment.” These reactions were verified by conducting ablation with the sample chamber filled with oxygen-18, a rare but stable oxygen isotope. Because $SrZrO_3$ is naturally rich in the more common isotope of oxygen (oxygen-16), the isotopic shift exhibited by oxygen-18 in the ZrO was easy to detect in its emission spectrum.

This oxygen-scavenging behavior yields insight into how early-forming oxides could reduce the amount of oxygen available for other types of compounds to form as the plasma cools. Laser ablation experiments were conducted with uranium, one of the key elements used in fission nuclear weapons. Again, two oxygen isotopes were used in the experiments to confirm the resulting uranium oxide’s stoichiometry (the numerical relationship of elements and compounds as reactants and products in a chemical reaction). As with the plasma flow reactor work, further understanding also leads to experiments of greater complexity.

Where the Forensics Lead

In an idealized nuclear airburst occurring high above the ground, the resulting fireball interacts only with air and bomb materials, resulting in debris consisting of relatively known and homogenous materials. However, the fireball from a detonation near, at, or below the surface will consume materials from the ground. Some of these materials will vaporize while others—especially in the fireball’s late stages—will remain solid. Rose says, “A debris sample picked up from the ground after detonation will represent not the initial composition of the fireball but rather what condensed out of the fireball at certain points in its evolution.”

As they better understand how individual debris components fractionate, the researchers have added more components to their experimental mixtures. This growing complexity better represents real-world scenarios and makes their experiments and the results increasingly accurate. In the future, researchers aim to study more components mixed together in a plasma, including silica and other carrier materials that might enter the fireball from the ground and remain solid. Eventually, this work will lead to a comprehensive understanding of the basic science behind chemical fractionation that is needed to create predictive models. Validated by both modern experimental data and historic empirical data, such models would prove invaluable not only to nuclear forensics investigators but also to those monitoring the consequences of a nuclear explosion.

“These models will allow us to examine matrices that are not necessarily represented in our test history,” explains Rose. “We could simulate an urbanlike matrix and see how the condensation patterns are affected, including whether the results match our predictions. This understanding of fractionation and debris formation would be extremely helpful if we ever have to collect debris after an unthinkable event.”

—Dan Linehan

Key Words: chemical fractionation, electron spectroscopy, fireball, fission, forensics, fusion, nuclear explosion, Laboratory Directed Research and Development Program, optical emission spectroscopy, oxide, plasma, plasma flow reactor, pulsed laser ablation, uranium.

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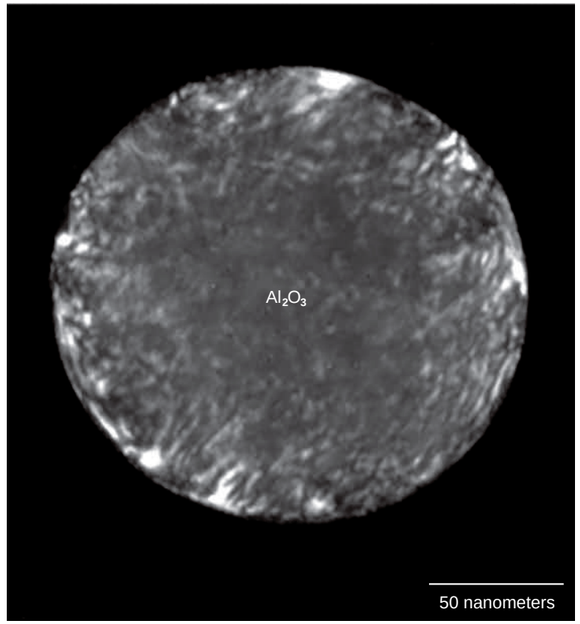
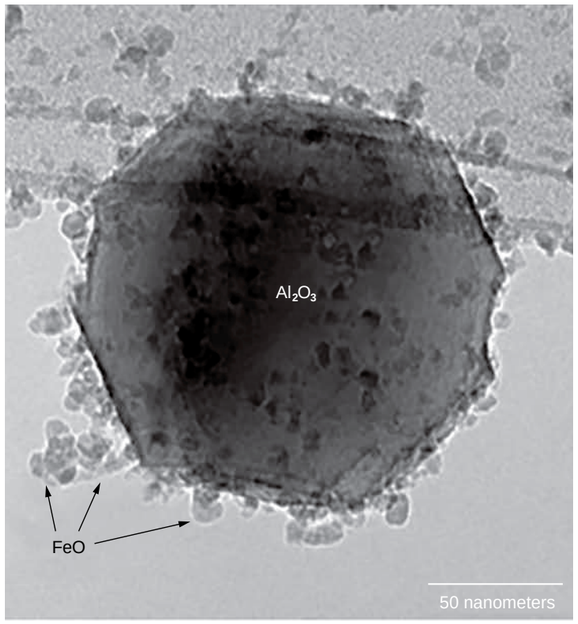
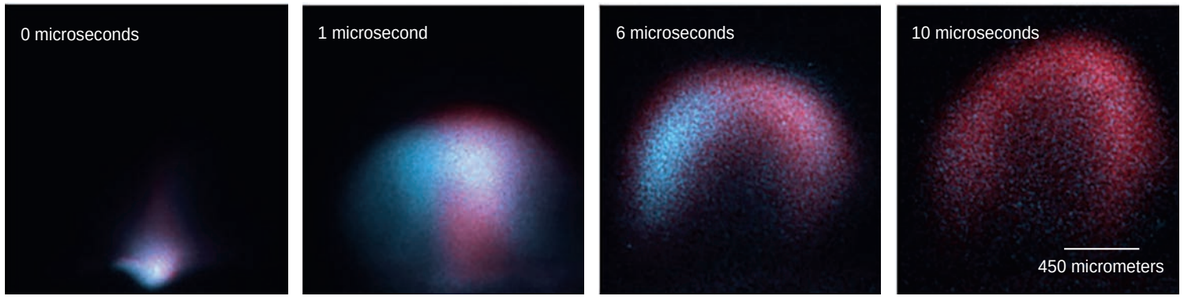




(left) Collected at a location of 16 centimeters downstream from the radio-frequency coil of a plasma flow reactor, the aluminum oxide (Al_2O_3) particle shown in this transmission electron microscope image is a perfectly spherical, single-crystal condensate. (right) A similar image shows the results of an experiment conducted with both iron and aluminum together. The large Al_2O_3 particle, which condensed early in the cooling process, is surrounded by small traces of more volatile iron oxide particles (FeO), which condensed later.



A plume created by pulsed laser ablation erupts from a strontium zirconate crystal over a timeframe of 10 microseconds. The formation of zirconium oxide (blue) dominates the emission spectra early on, followed by the formation of strontium oxide (red).

DETONATION SCIENCE BLASTS INTO A NEW FRONTIER

HIGH-EXPLOSIVE (HE) detonation events unfold in a few millionths of a second. A high-voltage current vaporizes a thin metal foil within a specialized detonator, which throws a tiny plastic flyer—traveling around 2 kilometers per second—into an explosive. The impact shock initiates a detonation whose front propagates supersonically through the material as the explosive rapidly decomposes. After the energy release and associated chemical reactions conclude, many HEs leave behind excess carbon that condenses into solid soot.

At Lawrence Livermore, a key aspect of stockpile stewardship includes fine-tuning and experimentally observing HE detonation processes and developing computer models to predict the behavior of different HEs. Over the last several decades, HE detonation science has progressed toward higher resolution experimental and modeling capabilities that explore initiation processes, the precise chemical reactions involved and how quickly they occur, and the specific temperatures and pressures attained.

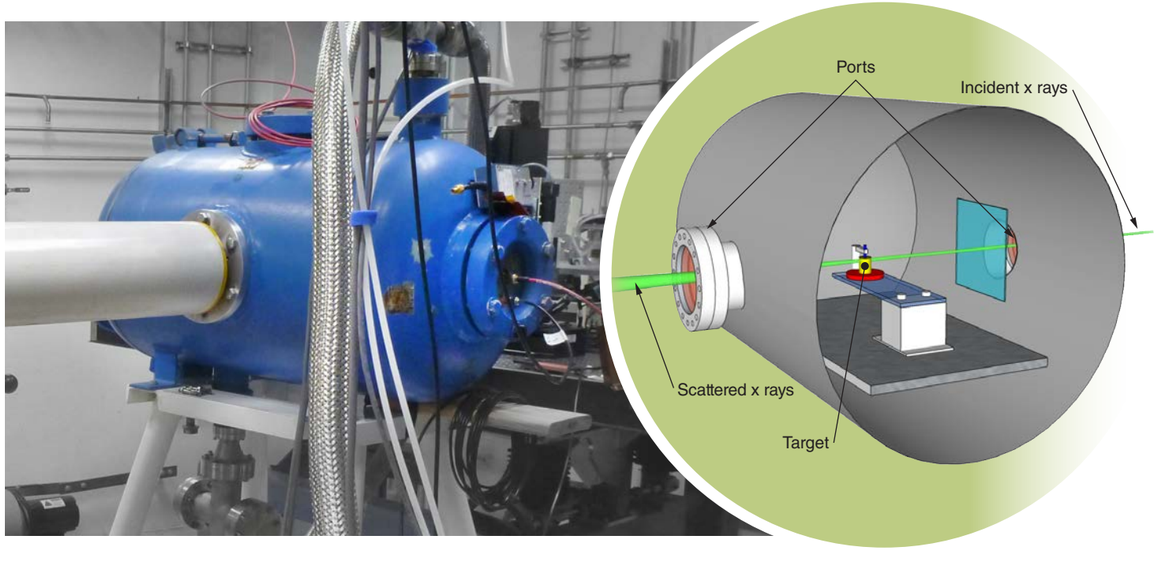
Livermore researchers (from left) Ralph Hodgin, Lisa Lauderbach, and Michael Bagge-Hansen prepare a high-explosive (HE) target at Livermore's High Explosives Applications Facility. (Photo by Randy Wong.)

Accurate computer modeling of a detonation depends on understanding how quickly the carbon condensates, or allotropes (such as graphite and diamond), form within HE detonation soot. Previous research into this process has focused on validating microsecond phenomena. However, recent computer simulations have modeled the formation of carbon condensates at nanosecond timescales—an uncharted territory experimentally.

To validate the model predictions, a Livermore team led by physicist Trevor Willey has been investigating detonation processes using the intense, pulsed x rays at Argonne National Laboratory's Advanced Photon Source (APS) in Lemont, Illinois. "Detonation experiments produce so much visible light, and solid explosives are generally opaque. Therefore, determining what is happening—for example, optically—is difficult," explains Willey. "X rays help us penetrate deeply into the detonation with wavelengths conducive to observing nanoscale phenomena."

Livermore's multipronged approach marks the initial application of three-dimensional (3D) reconstruction algorithms to detonation systems involving an exploding foil initiator (EFI, or slapper). The effort also inaugurates the use of small-angle x-ray scattering (SAXS) for detonation experiments in the United States. Willey says, "For the first time, we can experimentally interrogate detonation phenomena on nanometer (billionths of a meter) and nanosecond (billionths of a second) scales." Initially funded by Livermore's Laboratory Directed Research and Development Program, the team's work has transitioned into small-scale detonation science experiments supporting various programmatic activities, including stockpile stewardship and defense nonproliferation.

The custom-built detonation tank developed at Livermore provides a safe, reusable venue for conducting HE experiments. (inset) During a detonation, an ultrafast pulsed x-ray beam is fired onto the target at 153.4-nanosencond intervals. The scattering patterns for individual x-ray pulses are recorded and used to ascertain information about shapes and sizes of carbon condensates.



Targets, a Tank, and Technology

Computer simulations of the performance of energetic materials rely on accurate input data related to the time-dependent shock initiation, the detonation process, its energy release, and formation kinetics of the resulting carbon condensate. The Livermore team designed small-scale detonation experiments to observe both detonator behavior and carbon condensate formation using a chemically diverse range of HEs. These experiments initially used cylindrical targets of HNS (hexanitrostilbene) and Composition B, which consists of RDX (trimethylenetrinitramine) and TNT (trinitrotoluene), fabricated at the Laboratory's High Explosives Applications Facility (HEAF). Target size varied by material, from a few hundred milligrams to a few grams, based on the minimum amount needed to maintain a self-propagating detonation.

To conduct repeated experiments, the team developed a mechanism for containing gas, soot, and other debris from the explosion. With the help of other HEAF colleagues, Lisa Lauderbach and Michael Bagge-Hansen outfitted a 120-liter steel tank with a target platform, a vacuum-handling and exhaust system, and x-ray ports, while Ralph Hodgin, Chadd May,

and others built the firing system. Meanwhile, the Dynamic Compression Sector (DCS), an intense x-ray beamline funded by the National Nuclear Security Administration and managed by Washington State University, was commissioned at APS. "The Dynamic Compression Sector provides an ideal place for dynamic shock and detonation experiments on fast timescales," says Willey, citing the facility's synchrotron radiation capabilities, which produce 50-picosecond x-ray pulses every 153.4 nanoseconds.

The researchers first conducted a series of EFI imaging experiments at APS. Subsequently, they installed their new tank at DCS, where they performed small-scale detonation experiments to better understand carbon condensate formation. The team collaborated with Los Alamos National Laboratory and National Security Technologies, LLC, who had been performing similar x-ray imaging tests. A four-camera array developed by Los Alamos was used to capture individual snapshots of x-ray pulses during the experiments.

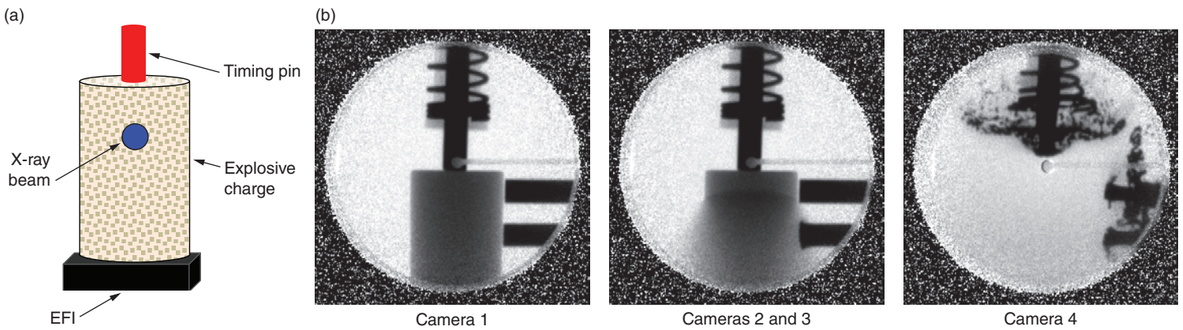
Game-Changing Results

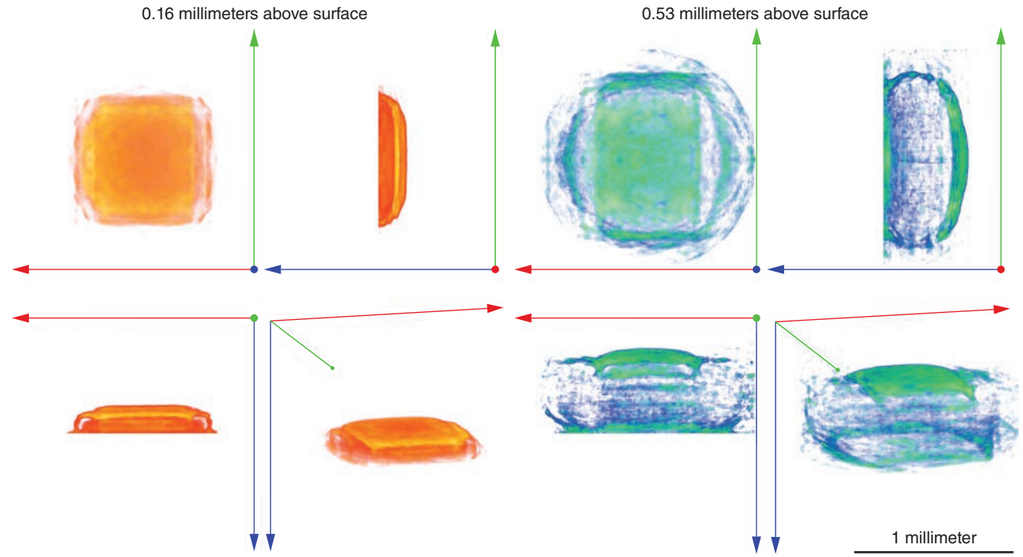
During the EFI experiments, APS's ultrafast pulsed x-ray beam provided high-resolution images measuring 1.5-by-1.5 millimeters at 153.4-nanosecond pulse intervals. EFIs were positioned at angles of 0, 15, 30, 45, 60, 75, and 90 degrees relative to the x-ray source and fired in these orientations. The resulting two-dimensional x-ray images, acquired at multiple angles, were input into a homegrown software package called Livermore Tomography Tools (LTT), which allows scientists to reconstruct 3D images of the EFI flyer at the pulse intervals. LTT's advanced iterative algorithms build 3D images of the object of interest from just a few views, in comparison to the typical thousands of views needed for computed tomography scans. As a result, the team captured the first detailed 3D images of flyers' kilometers-per-second motion during EFI operation.

Livermore's series of experiments on carbon condensates at DCS was no less compelling. Using the SAXS technique, the team resolved nanoscale details of the detonation. In this type of experiment, an intense but thin x-ray beam (approximately 50-by-100 micrometers) is fired directly through the sample. Scattering patterns for individual x-ray pulses were collected at 153.4-nanosecond intervals. Whereas previous studies showed condensate particle growth occurring over a few microseconds, the team's time-resolved SAXS imaging of HNS experiments demonstrated particulate growth within 400 nanoseconds after detonation. The Livermore team also observed that, once formed, graphite particulates generated from HNS detonations do not continue to change shape or size at microsecond timescales.

Determining particles' morphology and resolving their formation at faster timescales would not have been possible without the ability to perform SAXS on the four-camera array at DCS. In more recent experiments using other HEs, Willey and colleagues have observed nanostructures that range from complex and twisted to relatively flat. They have also noticed formation of nanodiamond particles and nanostructures with spherical shell graphitic layers resembling tiny "nano-onions." According to Willey, the team's data uncover possibilities for improving HE models and detonator performance. He says, "We're opening a new chapter in detonation science."

(a) An artist's rendering shows the setup for an experiment using an exploding foil initiator (EFI). A timing pin measures the time of the shock wave's arrival at the top of the charge. (b) A series of time-elapsed scatter-beam images, captured with the Dynamic Compression Sector's four-camera array, shows the upward progression of the detonation front.





The Livermore Tomography Tools software generates three-dimensional renderings of flyers in motion during EFI imaging experiments. Only seven views of the detonation were needed to create this reconstruction, which is viewed along x (red), y (green), and z (blue) axes.

Lighting the Fuse on New Experiments

Nanoscale characterization of HE processes has many applications. Commercially, nanodiamonds generated during HE detonations are used to seed synthetic diamond growth and are being explored for pharmaceutical purposes, fuel additives, and other uses. (See *S&TR*, March/April 2008, pp. 14–16.) In addition, the Laboratory's stockpile stewardship mission requires continual advancements to increase the safety, efficiency, and reliability of detonation technology. (See *S&TR*, July/August 2015, pp. 6–14.)

The team's tank setup has improved the fidelity and clarity of images showing flyers in motion during EFI detonation—data that will provide unprecedented feedback for new detonator designs. Future experiments will study changing detonation conditions to produce different pressure and temperature states for yielding supplementary postdetonation data on carbon condensates. Willey's team continues research with additional HEs, including DNTF (dinitrofurazanfuroxan), HMX (octogen), TATB (triaminotrinitrobenzene), and the Laboratory-developed molecule LLM-105.

Such breakthroughs in detonation experiments are inspiring new and early-career Laboratory scientists to pursue further advances in imaging and simulation capabilities. For example, researcher Will Shaw and colleagues are investigating another avenue related to EFIs by exploring in greater detail the initiation processes that occur when the flyer strikes the explosive. X-ray scattering expert Josh Hammons is coordinating construction of novel detector systems including camera configurations that capture two frames each to generate more images per detonation. Lawrence Fellow Mike Nielsen leads efforts to characterize the recovered detonation soot with transmission electron microscopy and related techniques. "Detonation is an interesting phenomenon," observes Willey. "With these technologies, we can conduct experiments that were not possible before."

—Holly Auten

Key Words: Advanced Photon Source (APS), carbon condensate, detonation science, detonator, Dynamic Compression Sector (DCS), exploding foil initiator (EFI), high explosive (HE), High Explosives Applications Facility (HEAF), Livermore Tomography Tools (LTT), small-angle x-ray scattering (SAXS).

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AGENT DEFEAT EFFORTS STRIKE GOLD

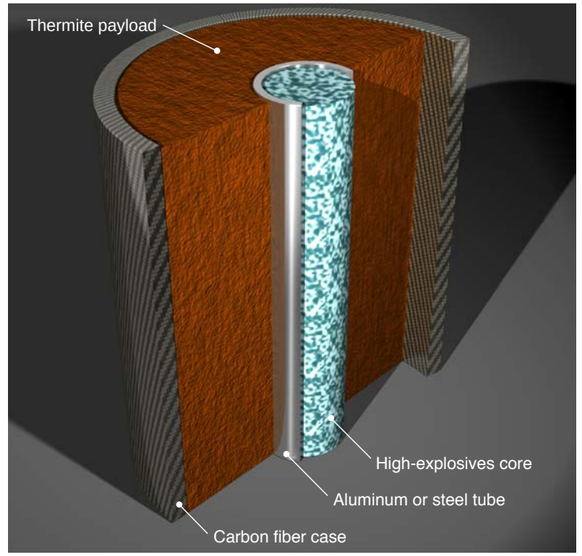
THE U.S. military must be able to deal with a broad range of contingencies, including some that are extremely challenging technologically. One such challenge is to destroy a stockpile of chemical or biological agents before they can be deployed. In this scenario, a specialized "prompt agent defeat" (PAD) weapon is required. The ideal PAD weapon contains payload materials that are thermally persistent—burning long and hot enough to rapidly and thoroughly eliminate the agents—and that produce minimal blast overpressure, which could liberate a chemical or biological agent before it is destroyed and thereby cause collateral damage. Such weapons usually contain a high explosive to initiate and disperse the PAD payload.

Both CrashPAD, developed in 2004 to destroy agents stored in lightweight structures, and Shredder, a more penetrating version developed in 2007, use a payload of white phosphorus. However, this pyrophoric material spontaneously combusts on contact with air and is therefore dangerous to handle and store. When the effort to create a replacement for CrashPAD began, Lawrence Livermore was tasked with helping develop a payload material with less risk than white phosphorus but without sacrificing effectiveness.

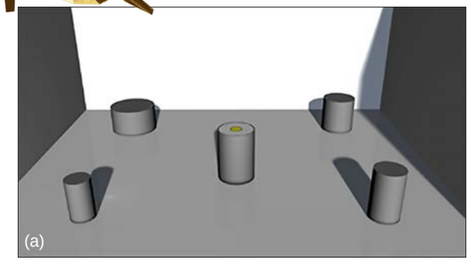
Lawrence Livermore has contributed to such agent defeat research and development efforts—including Shredder and CrashPAD—in various capacities since 1999. The Laboratory's tasks have included concept development, design, materials development, safety analysis, testing, and characterization. For its latest charge, the Livermore agent defeat team, in partnership with the Naval Postgraduate School (NPS), has developed a thermite-based payload that is far more effective than white phosphorus and much easier to work with. The breakthrough recently earned Livermore team lead John Molitoris and his colleagues their third Laboratory commendation for these efforts, a 2016 Gold Award from the Weapons and Complex Integration (WCI) Principal Directorate for exceptional innovation and excellence.

Formula for Success

Prior reactive materials experience and initial feasibility testing enabled the Livermore team to quickly determine that thermites, a type of pyrotechnic, were the most feasible payload replacement, potentially offering a level of thermal persistence and combustion comparable or superior to that of white phosphorus. Livermore's High Explosives Applications Facility (HEAF) provided the ideal environment for solving the project's two biggest scientific questions—the thermite formulation optimal for agent defeat and the best way to initiate the thermitic reaction. Molitoris observes, "We have a great facility and diagnostics to get the work done, but the true beauty of HEAF is that all of us—experimentalists, physicists, formulators, chemists, modelers, and technicians—are working under the same roof. Our scientific interactions are increased, and we get much more accomplished. For this type of work, there really isn't any other place like HEAF."



A cross-section drawing shows the components of the prototype agent defeat weapon that was subjected to performance tests in the firing tank at Livermore's High Explosives Applications Facility. (Rendering by Sabrina Fletcher.)

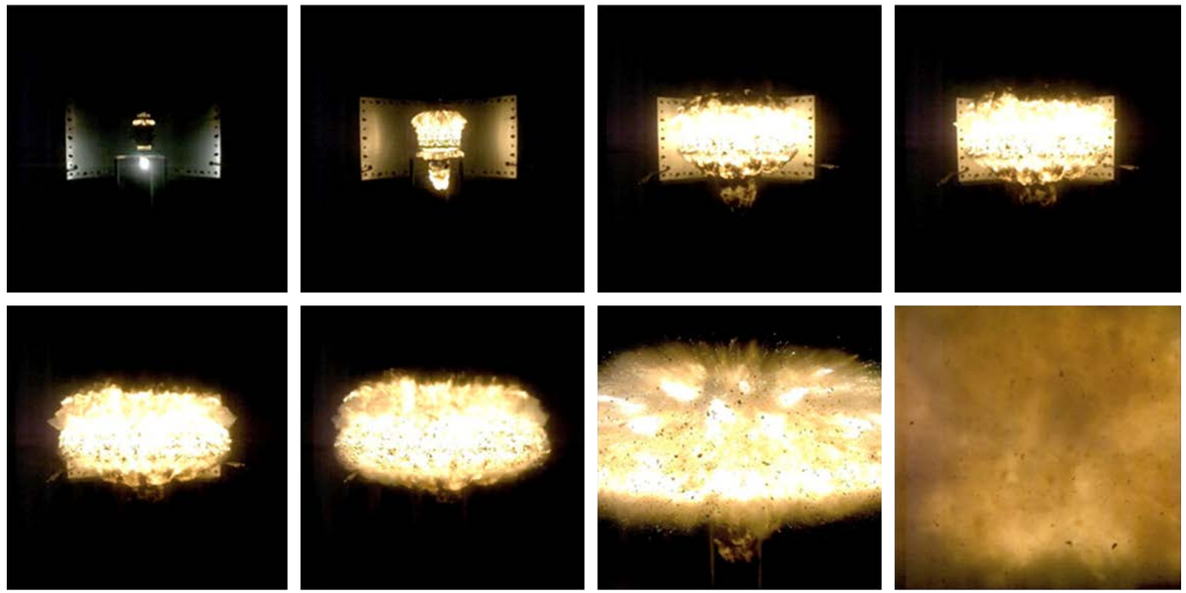


Livermore researchers are helping develop a weapon that can penetrate a storage facility and destroy chemical or biological agents inside before they can be deployed. Illustrations depict (a) a thermite-based payload (in the center of the space shown) delivered to a storage facility containing canisters of agents; (b) initiation of the weapon by high explosives; (c) creation of a thermitic fireball; and (d) establishment of a persistent thermitic cloud, which rapidly and efficiently destroys the agents. (Renderings by Sabrina Fletcher.)

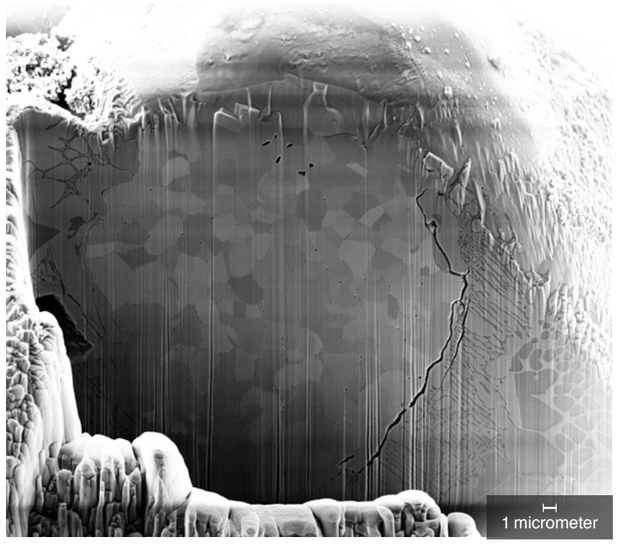
The team has changed its approach over the years in response to the myriad challenges it has addressed. “Initially, we had to build specialized diagnostics to do the research, but now the effort is more about formulations and performance testing for specific applications,” notes Molitoris. Materials scientists Alex Gash and Octavio Cervantes have contributed heavily to recent work, as has formulator Mark Hoffman, whose expertise is in polymers and plastic-bonded explosives. Once Molitoris has formed the right team for a given application, the team determines what material properties will be required and formulates an initial set of viable solutions. Critical performance testing then feeds back into development of the formulation until they reach the best possible solution.

“Every time we make a material, we have to conduct performance tests to see how it behaves,” explains Cervantes. “In this case, we were able to gather the needed information with relatively simple tests.” The team began testing candidate formulas by igniting samples in horizontally positioned, clear plastic burn tubes. When initiated, a thermite’s metal fuel and metal oxide components undergo a self-contained and self-sustained chemical reaction, producing a burst of flame. The team used a high-speed camera to document how long and how well each material burned, but they soon determined that burn tubes were too chaotic an environment to make the required measurements. Instead, they developed a new vertical platform in which the test material is sandwiched between a cylindrical metal base and an igniter and burns from the top down. This test arrangement, which took nine iterations to perfect, proved more satisfactory for studying flame propagation and temperature gradients.

The more promising formulations were further evaluated in HEAF’s spherical firing tank, which is equipped with pressure and temperature measurement instruments and high-resolution optical and x-ray imaging capabilities. These experiments employed a cylindrical carbon fiber case—which x rays can easily penetrate—packed with a donut-shaped thermite payload around a core of high explosives. The high explosives and thermites were separated by a metal liner. During performance tests, the tank’s multichannel flash x-ray system (see *S&TR*, December 2004, pp. 22–25, and March 2006, pp. 11–13) captured a sequence of radiographs to document the dynamic response of the PAD payload, from detonation to full thermite initiation and dispersal.



High-resolution images taken during firing-tank tests capture the evolution of a thermitic fireball. These images can be used to assess factors such as how efficiently the payload was initiated and dispersed.



Staff and students at the Naval Postgraduate School have characterized burn residue to help the Livermore team better understand the thermite reaction mechanism. A magnified sample is shown.

A First for Thermites

With the firing-tank test results, the researchers settled on a formula and initiation method that was both efficient and effective, producing a fireball that is hotter and more persistent, with less overpressure, than is possible with white phosphorus. Subsequent lethality tests performed with surrogate agents confirmed that Livermore’s thermite payload was better at capturing and destroying its target than CrashPAD or other possible payloads. “Thermites were even more effective than we imagined,” Molitoris says. The sponsors were very pleased with the results, but they soon challenged Livermore to take the research a step further—to create a plasticized (liquid) thermite that offered similar or identical performance to the newly proven granular (solid) formula, for even greater safety and ease of handling. If successful, the new payload would be used in a new incarnation of Shredder, dubbed the Agent Defeat Penetrator.

In addition to an accelerated timeline of only 15 months, the project entailed a high degree of risk because of the failure of all previous attempts by others to plasticize a thermite. Nevertheless, the Livermore team accepted the challenge. Even with the HEAF team’s collective experience with formulating energetic materials, significant effort was needed to find a binder that, in just the right proportions, would produce a substance with the desired viscosity—like toothpaste or soft wax—and with a shelf life measured in years, all without hampering performance. The Livermore team evaluated possible formulas for performance, while NPS professors Joe Hooper and Young Kwon and their students shed light on the thermitic reaction by characterizing residue from stack burn and explosive tests and exploring the influence of the carbon fiber casing on performance test results.

During their experiments, the researchers noticed that plasticized thermites burned less intensely in stack tests than did regular thermites but performed exceptionally well in the HEAF firing-tank experiments. “We saw better and more realistic results under confined conditions—inside a container—than in the open conditions of the stack burn tests,” notes Cervantes. “Flash x rays at HEAF have allowed us to understand scientifically how confinement makes the system work better.” The team was ultimately able to deliver a plasticized thermite—the first of its kind—suitable for PAD weapons. The material met or exceeded all requirements in Livermore’s performance tests and also exceeded expectations in the lethality tests. This successful plasticization of thermites for agent defeat is what earned the team its 2016 WCI Gold Award.

As the Agent Defeat Penetrator project transitions to a new stage—payload formula optimization and larger scale testing—Livermore researchers will continue to lend their considerable expertise in energetic and advanced materials development and testing. In collaboration with NPS, the team will further enhance the formula’s properties by fine-tuning ingredient proportions, particle size, and material mixture. They will also lead scaled-up tests at the Laboratory’s Site 300 facilities. Molitoris says, “Scaling up can be one of the most difficult tasks because of the need to preserve not only the defeat mechanism itself but all the other properties of the thermite fill, including performance, insensitivity, gas production, amenability to cast curing, and shelf life.” If their two-decade track record in agent defeat research and development is any indication, Molitoris and his HEAF colleagues will surely rise to the challenge once again.

—Rose Hansen

Key Words: Agent Defeat Penetrator, CrashPAD, Gold Award, High Explosives Applications Facility (HEAF), Naval Postgraduate School (NPS), prompt agent defeat (PAD), pyrotechnic, Shredder, thermite.

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S&TR March 2017 Payload Materials

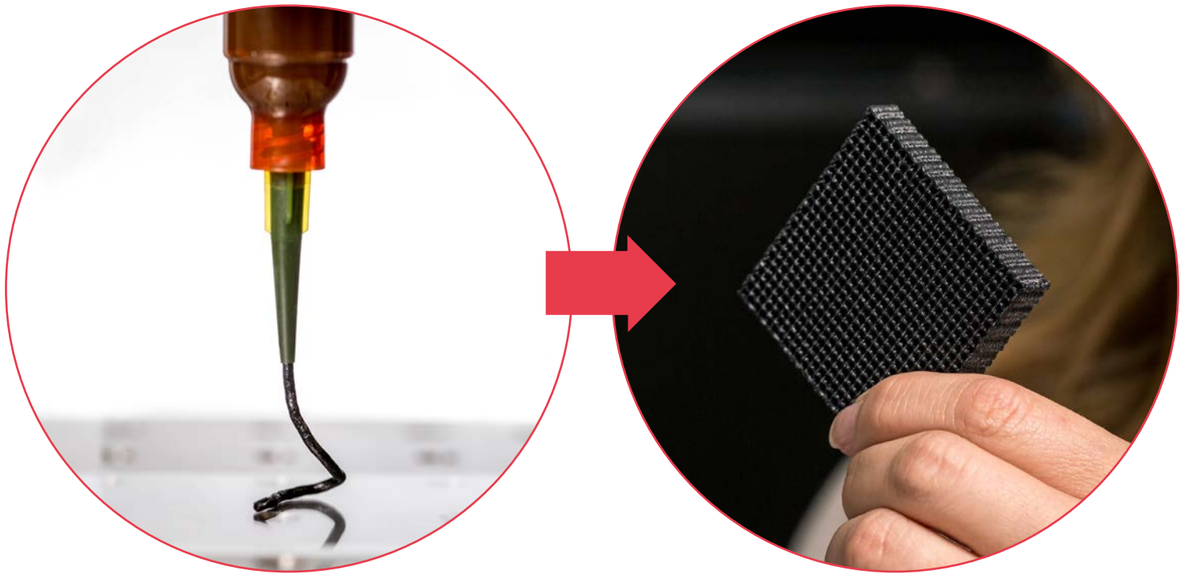
A NEW COMPOSITE-MANUFACTURING APPROACH TAKES SHAPE

Jennifer Rodriguez and James Lewicki examine a three-dimensionally (3D) printed carbon fiber part created using a Livermore-developed direct ink writing (DIW) process.

STRONGER than steel yet lightweight as plastic, electrically conductive and highly temperature resistant, carbon fiber composites have become the material of choice for many applications in aerospace, transportation, defense (see *S&TR*, March 2013, pp. 4–9), and energy storage. The heterogeneous nature of these mixtures of carbon fibers and resin allows for greater customization of structure and properties than with more homogenous materials, such as steel. However, the materials also pose significant manufacturing challenges. For instance, variability within and between parts can be greater than with homogeneous materials, and such variations can affect a part's properties and performance, which depend heavily on fiber orientation and distribution. Fabricators can compensate for this variability with a higher ratio of fiber to resin, but doing so makes the parts heavier and costlier and the process more wasteful than necessary.

Additive manufacturing (AM)—commonly known as three-dimensional (3D) printing—could eliminate many of these manufacturing concerns. By depositing a material layer by layer in a precise sequence specified in a computer file, AM enables greater precision, design flexibility, and repeatability than conventional manufacturing techniques. Plastic and metal AM technologies are well established, but printing carbon fiber composites is a tangle that scientists and engineers have only begun to unravel over the past few years.

Livermore chemist James Lewicki says, "Carbon fiber is the ultimate structural material. If we could make everything out of carbon fiber, we probably would, but it's been waiting in the wings for years because it's so difficult to make in complex shapes. With 3D printing, however, we could potentially make any shape." Lewicki leads a team of chemists, engineers, materials scientists, and computational experts who—with funding from the Laboratory Directed Research and Development Program—are working to improve the versatility and predictability of carbon fiber 3D printing and the performance of the resulting parts. Combining computational modeling and novel materials chemistry with AM techniques, the team has successfully demonstrated a new approach to producing high-performance carbon fiber composites.



In DIW, a type of additive manufacturing, (left) a tiny nozzle extrudes a liquid combining carbon fiber and polymer resin onto a platform in a pattern prescribed by a computer file. Layer by layer, as the 3D structure is built, the "ink" must extrude smoothly and solidify quickly to support the growing structure. (right) A completed 3D-printed part is shown.

A Better Glue

Carbon fiber composites are made of fibers just 5 to 10 micrometers in diameter, set in a polymer matrix known as a resin. The carbon fibers provide most of the material's strength and other performance characteristics. The resin binds the fibers together to prevent buckling but also represents one of the biggest obstacles to the 3D printing of high-performance parts using direct ink writing

(DIW). DIW is a high-speed, low-cost AM technique in which "ink"—a material in liquid form—is extruded through a tiny nozzle and onto a platform that is moved to deposit the ink where needed to build up the desired object, layer by layer, in three dimensions. (See *S&TR*, March 2012, pp. 14–20.) With DIW, manufacturers can print a wider variety of structures, geometries, and patterns than with conventional approaches, but existing DIW resins are not strong enough for high-performance applications such as aerospace. Nor are most high-performance resins suitable in another important regard—curing time. Conventional resins can take hours or days to harden, while the DIW process requires a resin that can hold its shape as the component is built up. Furthermore, most conventional composites would clog the nozzle of a DIW printer rather than extrude smoothly and continuously.

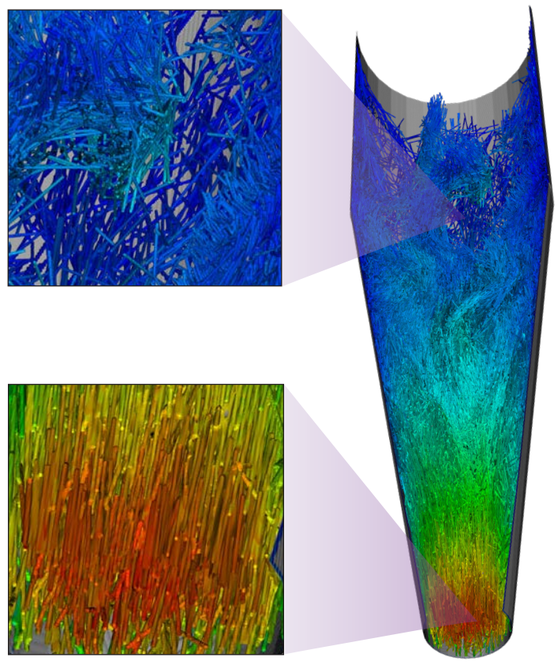
With no commercially available resin to meet their needs, Lewicki and his team created a resin specifically for high-performance component printing—one that gels in 5 seconds or less, fully cures with heat in 10 minutes, and offers flow characteristics suitable for AM. A low volume of high-surface-area silica nanoparticles yields an optimal resin consistency and allows the carbon fibers to orient themselves in the direction of the flow as they are squeezed through the nozzle, preventing clogging.

The resin formula is as much a product of computer simulation as innovative chemistry. In developing the resin, the team's computational experts used Livermore supercomputers to model the flow of carbon fibers through the ink nozzle at several scales. Lewicki notes, "Simulations of the actual printing process were important early on, as they helped show us the path forward with fewer experimental iterations." Fluid analyst Yuliya Kanarska adds, "With our code, we can simulate the evolution of the fiber orientations in 3D under different printing conditions to find the optimal fiber length and optimal performance." Simulation results both validated and explained what was observed experimentally—that with the right ingredients in the right ratio and the right nozzle size and shape, the resin can efficiently deliver carbon fibers without clogging the printer.

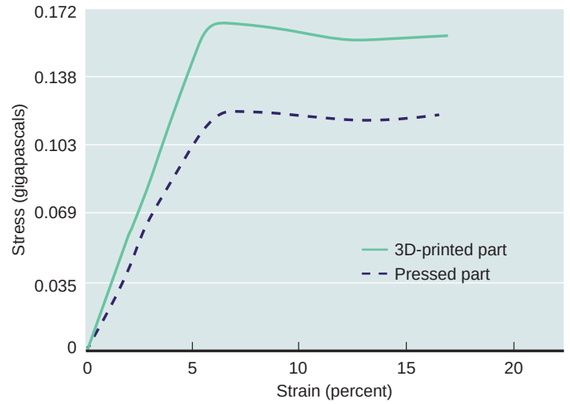
Designer Parts

Standard mold-based manufacturing methods and even some other DIW formulations produce parts with a more random fiber distribution and alignment than Livermore's approach does. Livermore parts, with fibers more consistently aligned in the flow direction, have superior mechanical properties compared to those with the same density of fibers produced by other methods. Recognizing this advantage, the team has gradually increased the volume of carbon fiber in their formula and can now create parts with the same level of performance as traditionally manufactured parts but with just one-third the carbon fiber volume that would be required by other carbon fiber composites. Engineer Michael King states, "We are now confident we can design parts that perform better on a per-fiber and an overall-part basis than other methods can."

Precise yet flexible, DIW offers researchers the freedom—and challenge—of tailoring a part's electrical, mechanical, and thermal response to a given application. Lewicki says, "With chemistry and engineering, we can purposely put carbon fiber exactly where we want it in a part, more so than other research groups can do. But then the question is, where *should* we put the material for the best performance?" For example, satellite components could be printed to be insulated on one side and conductive on the other to compensate for heat-induced warping.



To avoid nozzle clogging in DIW printing, Livermore researchers use high-resolution numerical simulations of carbon fiber "ink" to study the evolution of fiber orientations in three dimensions. The simulations, such as the one shown here, have helped researchers understand the relationship between fiber length, nozzle diameter, and degree of fiber alignment relative to flow direction. Colors reflect degree of alignment, with warmer colors indicating greater levels of alignment than cooler colors. Fibers approaching the nozzle at bottom start to orient with the direction of flow.



In mechanical testing, 3D-printed parts made with the Laboratory's carbon fiber composite—in which fibers are oriented in the printing direction—outperform conventional pressed parts, which contain randomly aligned fibers.

Because no existing composite-design algorithms could satisfactorily optimize performance, the team has been writing their own, building on team and institutional expertise in multiscale material modeling and systems optimization. Subsequent efforts to optimize fiber layout for greater strength and stiffness in certain directions yielded a 15 percent improvement in mechanical properties, with the potential for even greater improvements.

Computational optimization is an essential step towards making carbon fiber 3D printing predictable, repeatable, and highly customizable. Although still in its infancy, this effort aims to integrate process modeling and computational optimization with in-house tool-path planning algorithms, for a workflow of robust, computationally aided design, development, and manufacturing. The tool-path planning currently under way will assess a part's optimized design, confirm that the design is printable, and then translate the design parameters into instructions that the 3D printer understands. King says, "Essentially, we are building thousands of parts virtually to produce optimized machine instructions, so that we can ultimately get a highly buildable part." To this end, the team continues to investigate the structure and properties of the composite ink when used in DIW manufacturing. Characterization and modeling aim to better understand and control the properties and performance of the resulting AM structures.

From Idea to Product

With enhanced design flexibility, manufacturing repeatability, and part performance, AM technology is expected to spur wider adoption of the team's versatile carbon composite. Lewicki has been working with Genaro Mempin in the Laboratory's Industrial Partnerships Office to develop a commercialization strategy, including filing records of invention (ROIs)—the first formal step on the path to a patent. The ROIs expand Livermore's already sizable portfolio of AM-related innovations, underscoring the institution's core competency in advanced materials and manufacturing. Mempin says, "We have received more than 90 ROIs in AM from Livermore inventors since 2009. The Laboratory has filed patent applications for more than two-thirds of these ROIs, and more are in the pipeline being prepared to file."

Lewicki notes, "So many people are interested in a better, faster, cheaper way to make carbon fiber composites. To take this project further, however, we need to make the transition from scientifically interesting material to practical industrial product. For this, we need collaboration." The research team is exploring a range of opportunities. Other Livermore teams engaged in national and energy security research, along with potential U.S. defense partners and potential licensees in commercial aerospace, have already expressed an interest in Livermore's resin formulation and AM process optimization.

The secret formula behind the team's innovations, according to King, is actually quite simple: "We have a tight collaboration between computational experts, chemists, and engineers. Multidisciplinary teams are something the Laboratory does well and are what has allowed us to create a practical, high-quality technology."

—*Rose Hansen*

Key Words: additive manufacturing (AM), carbon fiber composite, design optimization, direct ink writing (DIW), Industrial Partnerships Office, Laboratory Directed Research and Development Program, record of invention (ROI), resin, silica nanoparticle, three-dimensional (3D) printing, tool-path planning.

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MIMICKING MOTHER NATURE TO MITIGATE CLIMATE CHANGE

ALTHOUGH carbon dioxide shoulders the majority of climate change blame, methane is the second most prevalent greenhouse gas. In addition, methane is 25 times more effective at trapping heat than carbon dioxide. This heat contributes significantly to Earth's changing climate, which can influence shifts in economic and agricultural trends and promote erratic weather patterns. (See *S&TR*, June 2012, pp. 4–12.) To help reduce methane emissions, Livermore scientists Sarah Baker, Joshuah Stolaroff, and their research team are developing an efficient way to convert methane to methanol—a liquid that has a wide range of applications.

Methane is emitted by wetlands, thawing permafrost, and grass-eating animals, and is broken down by soil microorganisms and atmospheric chemical reactions. Today, over 60 percent of the methane in the atmosphere results from human activity, throwing methane's natural cycle out of equilibrium. The decomposition of human-generated trash, for instance, is often overlooked as a source of greenhouse gases, yet this process releases massive quantities of methane through the degradation of volatile organic compounds and microbial action. Localized and stationary sources of methane such as landfills, natural gas extraction sites, and areas of rapidly thawing permafrost are the emission sources Baker's team is targeting with its innovative methane-conversion materials.

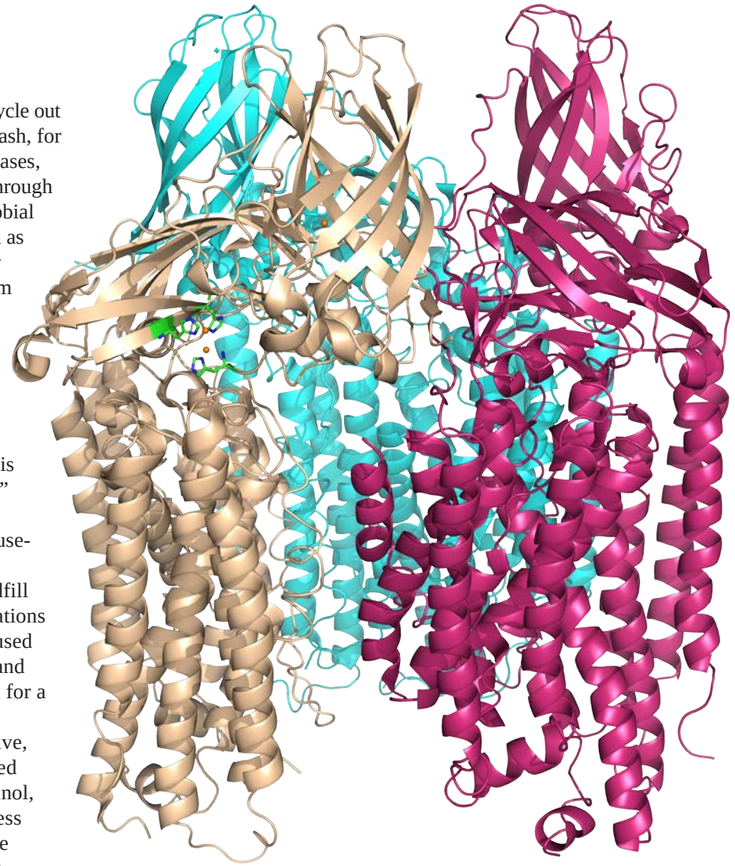
Scientist Jennifer Knipe holds an additively manufactured donut-shaped hydrogel that is being developed to trap methane for conversion to methanol. (Photo by Maren Hunsberger.)

Nature Inspires Better Design

Traditionally, most landfill methane is emitted into the atmosphere or is "flared off"—burned for energy in a process that releases carbon dioxide. "Obviously, this is not an effective solution to the climate change problem," comments Baker. More recently, several government agencies have recognized landfill emissions as greenhouse-gas sources that can be easily identified and reduced. In response to increased political pressure, some large landfill sites are building methane-recapture plants. These operations capture emissions and convert them into energy that is used onsite or sold to outside companies. However, the cost and complexity of these systems have limited their adoption for a majority of landfills and natural gas extraction sites.

When considering options for creating a less expensive, more feasible methane mitigation approach, Baker turned to nature for inspiration. "Converting methane to methanol, which is the liquid form of gaseous methane, requires less energy than purifying and condensing methane gas," she explains. "The liquid is also easier and more efficient to transport, and methanol can be used in manufacturing and as fuel." However, no commercially viable small-scale chemical methods exist to convert methane to liquid fuel. The most mature technique, called the Fischer–Tropsch process, requires many complicated steps, making it inefficient and costly. Other methods use traditional stirred-tank bioreactors, which are slow and energy intensive—the process occurs in batches, after which all equipment must be cleaned and all organic substances separated out for reuse.

To make a smaller scale process more commercially viable, the research team looked to bacteria. "We see methanotrophs—bacteria that consume methane as their energy source and turn it into methanol—performing exactly what we want to do," notes Baker. "They know how to perform this conversion, so let's learn from them."



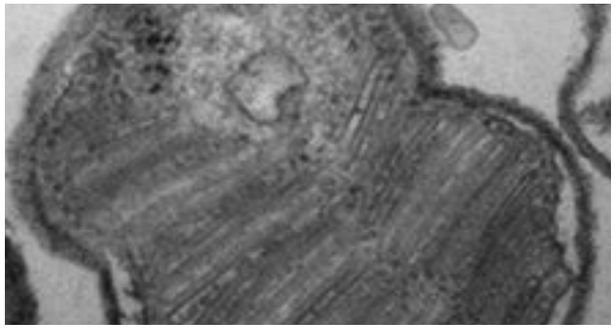
Particulate methane monooxygenase (pMMO) is an enzyme that methane-consuming bacteria called methanotrophs use to metabolize methane into methanol. Livermore researchers are focusing on pMMO as part of a scheme to trap methane as it is emitted from landfills and convert it to methanol. (Rendering by Edmond Lau.)

A Printable Structure

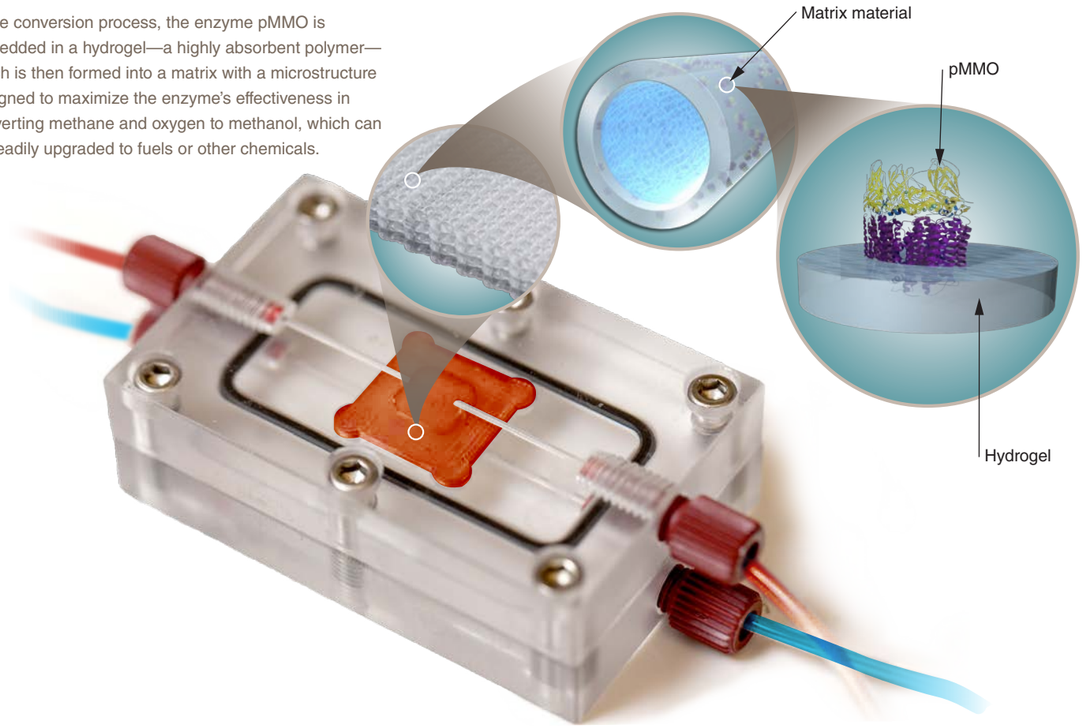
Methanotroph contain an enzyme called particulate methane monooxygenase (pMMO), which the organism uses to convert methane to methanol. This enzyme is embedded in folded lipid membranes that increase the surface area exposed to methane gas. Because pMMO is stored in a cell membrane, it is easy to extract and use. A partner research team at Northwestern University provided the pMMO for the Laboratory's experiments.

"Once we decided on this method of conversion," explains Baker, "the next step was to identify a more efficient way of introducing methane to the enzyme." Instead of forcing the gas into an enzyme-containing liquid, similar to the process used in conventional stirred-tank bioreactors, the team embedded pMMO in a hydrogel—a highly absorbent polymer made mostly of water—allowing them to increase the contact area between the enzyme and methane. Embedding pMMO in a printable hydrogel allows the team to mimic the bacteria's structure and also presents the possibility of using additive manufacturing to create the materials.

Jennifer Knipe, a postdoctoral researcher at Livermore and an expert in hydrogel formulation, was charged with finding the optimum hydrogel structure for methane–enzyme interaction. "The consistency of the hydrogel polymer we're using, called polyethylene glycol, is very similar to a brittle contact lens," says Knipe. "We've been studying the literature on fluid–gas exchange in contact lenses to better design our polymer. The problem is that the hydrogel on its own behaves a bit like jello in that it can't be disturbed too much or it will fracture—so we tested plastic matrices that would act as scaffolding to give it more strength and structure."



The methanotropic bacterium *Methylococcus capsulatus* (Bath strain) provides Baker and her team with a source of pMMO to use in their methane capture and conversion approach.



In the conversion process, the enzyme pMMO is embedded in a hydrogel—a highly absorbent polymer—which is then formed into a matrix with a microstructure designed to maximize the enzyme's effectiveness in converting methane and oxygen to methanol, which can be readily upgraded to fuels or other chemicals.

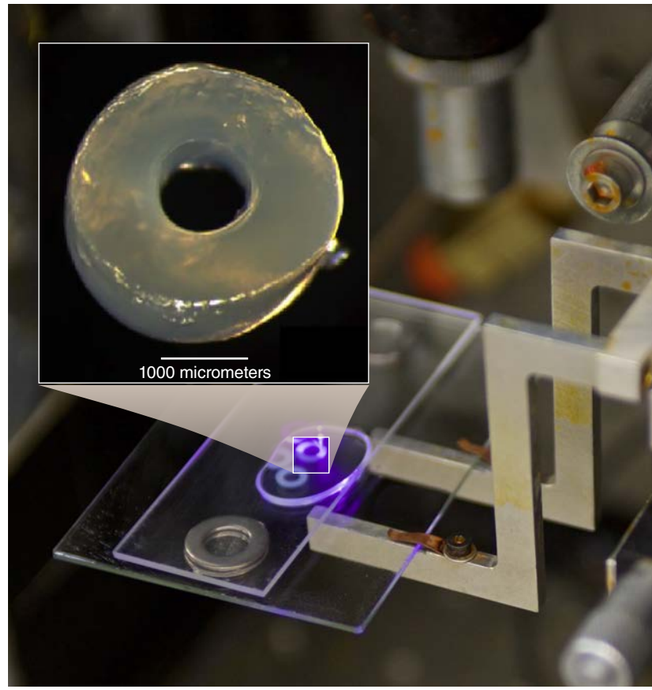
The team tested several structural designs for the matrix and found that a silicone mesh structure was effective but only when very thin. The methane–enzyme interaction is limited by diffusion and takes place within a few micrometers of the mesh's outside edge. The team also tested a hydrogel polymer without a matrix. Through their experiments, the team found that by making the polymer donut shaped, they could maximize its surface area and therefore increase methane conversion. "We're working on incorporating a silicone component into the donut-shaped polymer to keep it structurally sound," says Knipe. "The exciting part is that we're applying additive manufacturing to print the silicone matrices and the hydrogel quickly and simply, which could make this approach viable on a large scale."

The Future of Methane Conversion

Baker's team has already presented its findings on methane-to-methanol conversion at scientific conferences, and they plan to test other hydrogel polymers to determine whether any are less expensive and at least as effective as polyethylene glycol. Baker adds, "We also need to find an alternative to our cofactor," referring to an "assistant" molecule required for the enzyme to function properly in a laboratory setting. When the pMMO is removed from inside the bacteria, the molecules that naturally assist its function no longer surround it. The team used a reduced form of nicotinamide adenine dinucleotide (known as NADH) for their experiments, which is an expensive substance. Knipe notes, "Another limiting element is the enzyme itself. It breaks down after a certain period of time, and then we have to add a fresh batch. We're looking into why this breakdown occurs so we can preserve the enzyme's lifespan."

Although the process still needs to be refined and scaled up, the researchers are optimistic about its possible applications. "An efficient process could give industry more tools and incentives to reduce methane emissions," states Baker. The team will continue to draw inspiration from nature in its pursuit of mitigating one of the world's most potent greenhouse gases.

—Maren Hunsberger



A donut-shaped hydrogel is the most effective structure for trapping methane. Additive manufacturing can be used to fabricate the shaped hydrogel. The structure is then cured using ultraviolet light. (Photo by Maren Hunsberger.)

Key Words: additive manufacturing, biochemistry, bioreactor, climate change, Environmental Protection Agency, enzyme, greenhouse gas, landfill, materials science, methane, methane catalysis, methanogenesis, methanol, methanotroph, natural gas, particulate methane monooxygenase (pMMO), polymer.

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S&TR April/May 2016

REDUCING RELIANCE on CRITICAL MATERIALS

Livermore researchers support efforts to limit the need for rare-earth elements in U.S. clean-energy technologies.

HIGH-TECHNOLOGY products, from car motors to fluorescent lighting, often rely on small amounts of scarce raw materials that possess key properties, such as strength, thermal resistivity, and magnetism. No easy substitutes exist for these so-called critical materials, and as a result, demand for them can at times exceed available supply. Indeed, shortages of critical materials can impair entire industries and prevent the development and implementation of new products.

Critical materials include a group of related elements called rare earths, which traditionally include the lanthanide series of elements in the periodic table as well as scandium and yttrium (see the box on p. 7). Rare earths are essential to high-performance magnets and magnetic powders, catalysts, metallurgical additives, polishing powders, phosphors, glass additives, and ceramics used in a variety of industries, including health care, computer, automotive, communications, and optics to name a few. For example, at Lawrence Livermore's National Ignition Facility— the world's largest laser—optics made from ultrapure glass doped with neodymium atoms amplify laser light to the extremely high energies required for experiments.

Many rare-earth elements are also considered critical materials for the U.S clean-energy industry. Hybrid-electric vehicles, fluorescent lights, large wind turbines, and other clean-energy products all rely on small quantities of rare earths. The Department of Energy's (DOE's) Critical Materials Institute (CMI) was established, in part, to assure supply chains for these precious commodities, thereby enabling innovation in U.S. manufacturing and enhancing the nation's energy security. Established in 2013 with help from Livermore materials scientists, CMI is one of DOE's four Energy Innovation Hubs and is headquartered at Ames Laboratory in Ames, Iowa. A particular focus of CMI is to address the materials criticality issues

Many rare-earth elements are essential to the nation's clean-energy industry. Europium, a rare earth that has the same relative hardness as lead, is used to create fluorescent lightbulbs. With no proven substitutes, europium is considered a critical material to the clean-energy economy. (Photo courtesy of Ames Laboratory.)

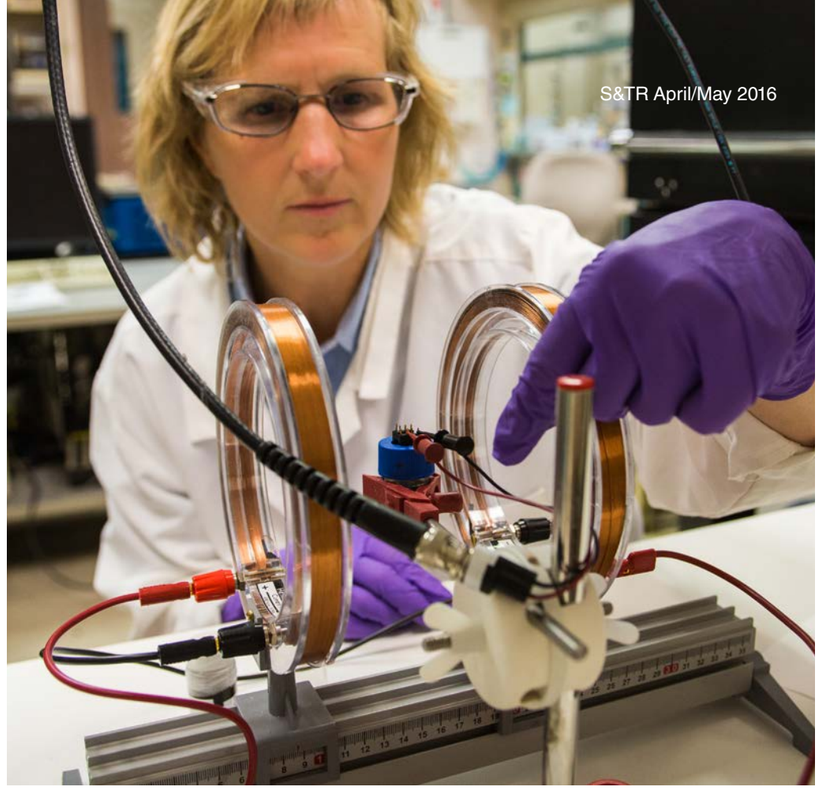
associated with five of the rare-earth elements: dysprosium, terbium, europium, neodymium, and yttrium.

CMI-sponsored research is conducted at national laboratories, universities, and U.S. companies. Lawrence Livermore physicist Eric Schwegler, who coordinates CMI-funded research at the Laboratory, notes that rare-earth research has implications for national security and economic vitality. More than 95 percent of rare earths are mined outside the United States. Occasional export restrictions by rare earth–producing nations have prompted concern about the effects a shortage could have on the U.S. clean-energy industry.

CMI is working to reduce the nation's dependence on rare earths through three research focus areas: diversifying supply, developing substitutes, and reuse and recycling. This work is further enhanced by cross-cutting research initiatives that range from establishing new additive-manufacturing technologies to conducting economic analyses of potentially new critical materials. Schwegler says, "Livermore's work for CMI has established the Laboratory's expertise in rare-earth materials synthesis, characterization, and modeling and has contributed to its mission of safeguarding energy security."

A More Varied Supply

Despite their name, rare-earth elements (with the exception of promethium) are found in relatively high concentrations across the globe. However, they seldom occur in easily exploitable deposits because of their geochemical properties. Schwegler adds that rare earths are chemically very similar and thus are generally found mixed together and are difficult to separate. In addition, the lighter rare-earth elements, such as cerium, are often present in greater concentrations than the heavier elements.



Laboratory materials scientist Christine Orme is helping develop exchange spring magnets—objects that are twice as strong, contain half the required rare-earth content, and operate more effectively at higher temperatures than existing permanent magnets. Such technology could drive design of smaller, lighter, and more efficient motors for cars and wind turbines. (Photo by Lanie L. Rivera.)

To better diversify supply, one strategy under consideration is finding novel applications for rare-earth materials that are relatively abundant but less used. Cerium, for example, is often discarded as a byproduct in the separation and extraction of the more valuable rare earths. If new, significant applications could be found for cerium, the economics of mining rare earths that occur in smaller concentrations could change considerably.

A promising research avenue takes advantage of cerium's low demand to explore the element's suitability as an alloying agent. Currently, no low-cost aluminum alloys have been developed that can operate at elevated temperatures while maintaining the mechanical properties needed for high-performance automotive and aerospace applications. "By combining 10 percent cerium with aluminum and perhaps other elements, we could make stiff, lightweight materials for creating engines that operate at higher temperatures," says Livermore physicist Scott McCall. A high-performance aluminum alloy would enable design of higher efficiency internal combustion engines and lighter drivetrains, thereby improving fuel economy.

McCall is working with colleagues at Oak Ridge National Laboratory and CMI's strategic partner Eck Industries, Inc. of Manitowoc, Wisconsin. They are developing alloys containing cerium, along with appropriate techniques to efficiently manufacture them. Livermore researchers are testing the most promising alloys. "If the tests prove successful, the alloys could trigger a huge demand for cerium," says McCall. Early tests of aluminum alloys with cerium concentrations of 6 to 16 percent have proven that the material is castable and remains strong at room temperature.

Bring in the Replacements

Livermore researchers are also searching for rare-earth substitutes in magnets used in automobiles, especially hybrid-electric cars. Developed in the 1970s and 1980s, rare earth–based magnets are the strongest type of permanent magnets available. They are found in the more than 40 electric motors and actuators that control various vehicle devices from windshield wipers to speakers. In hybrid-electric cars, rare-earth magnets are part of the vehicles' regenerative braking system. These magnets are also found in lightweight motors for compact computer hard drives and even powerful hand tools. Large, megawatt-scale wind turbines contain approximately 1,000 kilograms of magnets, of which 25 percent by weight are made from rare earths.

Many of these magnets contain neodymium and the expensive rare earth dysprosium. "We want to make these motors cheaper and smaller while using fewer rare-earth elements," says McCall. He is working on a new class of magnet that offers high magnetic coercivity (ability to withstand an opposing external magnetic field without demagnetizing) and high magnetic remanence (the magnetization remaining when the magnetizing field is removed). Other team members include Jonathan Lee, Sarah Baker, Christine Orme, Joshua Kuntz, and Tony Van Buuren.

Rare-earth magnets, such as those made from neodymium–iron–boron or samarium–cobalt alloys, are hard magnetic materials that have high coercivity but only modest remanence. In theory, if these hard

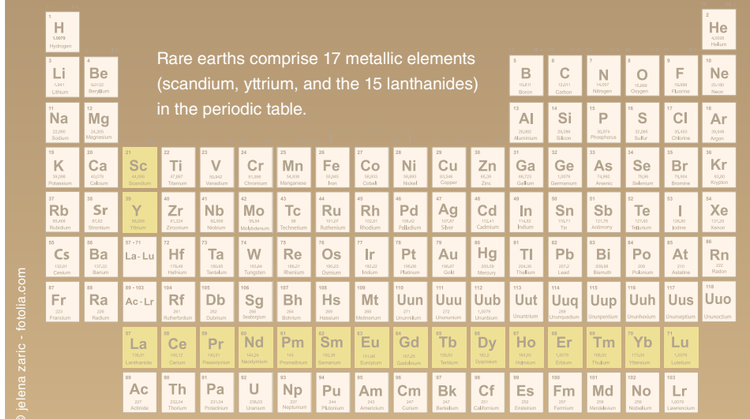
Rare Earths Have Special Properties

The rare earths comprise 17 metallic elements in the periodic table: scandium, yttrium, and the 15 lanthanides (lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium). Scandium and yttrium are considered rare-earth elements because they tend to occur in the same ore deposits as the lanthanides and exhibit similar properties. Used in various technologies from computer hard drives to speakers, rare earths are also essential for U.S. competitiveness in the global clean-energy industry.

Despite their name, rare-earth elements (with the exception of promethium) are found throughout the world. Cerium is particularly plentiful, about as abundant as copper. However, most rare-earth production is concentrated in China. A growing concern exists among scientists and high-technology industries regarding the future supply of five rare-earth elements—dysprosium, terbium, europium, neodymium, and yttrium. Shortages of these materials could affect clean-energy development in the coming years. For example, the largest wind turbines require very powerful neodymium–iron–boron magnets.

The atomic number of each rare earth is exactly one more or one less than its neighboring element along the periodic table. The nominal increase is the result of the successive addition of an electron to a material's 4f electron shell. Understanding the behaviors of these electrons is therefore central to determining how rare-earth elements produce the properties they confer to products. Better theoretical models for f-shell electrons, validated by experiment, are needed to accelerate the discovery and design of new products containing rare earths. In addition, studies of rare earths can provide insight into the properties of actinide elements, which have similar properties and are important for stockpile stewardship research.

When alloyed with other metals, rare earths provide enhanced magnetism, strength, thermal resistance, and other properties. Several rare-earth elements confer material properties that cannot be provided by anything else. For example, neodymium and dysprosium are used in high-strength magnets found in hard drives, speakers, and cars, all of which benefit from higher efficiency and smaller-size magnets.



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materials could be interspersed with a soft magnetic material that has high magnetic remanence, the resulting magnet could be twice as strong, contain half the required rare-earth content, and operate more effectively at higher temperatures. Called exchange spring magnets, these objects could drive design of smaller, lighter, and more efficient motors for cars and wind turbines.

"The exchange spring magnet idea has been around since the early 1990s," says McCall. However, their manufacture has posed significant challenges because the hard material must be distributed at the nanoscale within the soft material matrix. Additive-manufacturing techniques have made fabricating the magnets more feasible. In collaboration with Brown University and General Electric (GE), Livermore scientists are showing how hard and soft magnetic materials can be put down in a checkerboard array using electrophoretic deposition and nanomanufacturing technology. McCall says, "It's a very promising technique."

Exchange spring magnets could be commercially available within three to four years after laboratory demonstration. The development team is aiming to produce a prototype for testing by late 2016. Economists see a potential $10 billion market for these magnets. According to McCall, the market for high-strength permanent magnets is so large that even small improvements in magnet strength or reductions in the quantity of rare-earth elements required could save hundreds of millions of dollars annually.

Modeling Material Alternatives

In a separate project, physicist Patrice Turchi is combining quantum-mechanical simulations and thermodynamic modeling to estimate the phase stability, magnetism, and other properties of potential rare-earth alloys for hard magnet and structural applications. The effort takes advantage of progress in computational materials modeling and Lawrence Livermore's vast supercomputing resources to optimize design and development of new materials.

Livermore researchers Patrice Turchi (foreground) and Scott McCall review the phase diagrams of aluminum–cerium–silicon and cobalt–iron–samarium alloys. Quantum-mechanical simulations and thermodynamic modeling are used to estimate the phase stability, magnetism, and other properties of potential rare-earth alloys. (Photo by Lanie L. Rivera.)

Turchi and his team are developing a materials design simulator to accelerate the search for replacements to rare earths or rare-earth alloys that provide the same or enhanced materials stability and performance. Turchi says, "We want to find the optimum proportion of elements that will produce alloys with the best magnetic properties in the case of hard magnet applications, or mechanical properties in the case of structural materials applications."

By combining the team's modeling efforts with available experimental data, Turchi and his colleagues Per Söderlind, Alexander Landa, Aurélien Perron, and Vincenzo Lordi can validate quantum-mechanical simulations of rare earths and build a series of validated databases that include the thermodynamic and magnetic properties of rare earth–based materials. Toward this end, they are studying the permanent magnet that combines samarium with cobalt. These strong permanent magnets are similar in strength to neodymium magnets, but they can withstand higher temperatures and have higher coercivity. However, they are brittle and prone to cracking and chipping. The Livermore quantum-mechanical model computationally reproduces the properties of this magnet and gives researchers confidence as they search for solutes that could further improve the technology.

One goal of this effort is to partially substitute cobalt, a material sensitive to market price swings, with iron. The Livermore model has predicted the ideal mixture of iron and cobalt for maintaining the desirable properties of high-temperature and magnetic stability. "If stable, the material created from combining the rare earth samarium and iron could have fantastic properties," says Turchi. "We may want to add other rare earths as well as transition metals to fully stabilize the materials." For structural applications, thermodynamic modeling has been successfully used to optimize alloy composition in materials combining aluminum and cerium with other solutes. These models are helping guide the experimental efforts being conducted at Oak Ridge and Livermore.

Lighting the Way

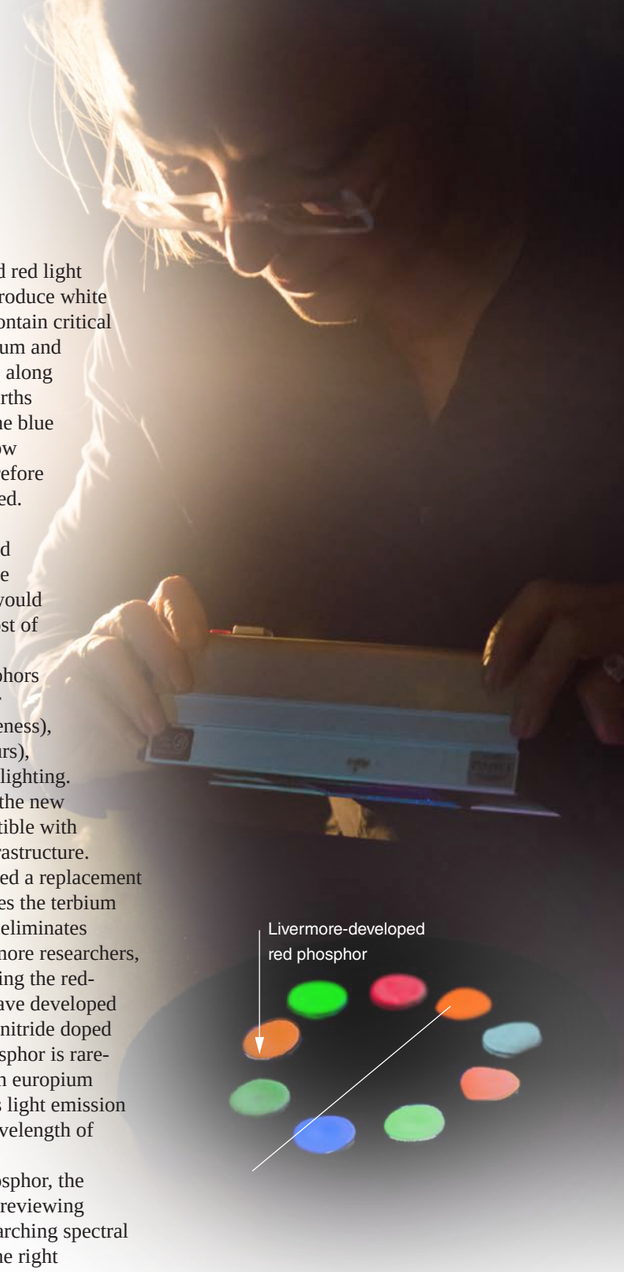
Advanced lighting systems are another technology that could benefit from rare-earth substitutes. Livermore researchers Steve Payne, Nerine Cherepy, Daniel Aberg, and Fei Zhou are working with colleagues from GE, Ames, and Oak Ridge to sharply reduce the rare-earth content of the three phosphors used in fluorescent lighting. Other Livermore team members include Zach Seeley, Kiel Holliday, Nick Harvey, Paul Martinez, Ich Tran, Alex Drobshoff, and several college summer students.

Current phosphors in fluorescent lighting consume more than 1,000 metric tons of rare-earth oxides yearly. GE, a major manufacturer of fluorescent lamps, has set a goal of reducing the quantity of rare earths in lighting by at least 50 percent without compromising the quality of the light or increasing the cost.

Cherepy and Payne explain that inside fluorescent bulbs electrons collide with atoms of mercury vapor. The excited mercury atoms emit energy in the form of ultraviolet photons (invisible to human eyes), which interact with three fluorescent phosphors coating the inside of the bulb. The current tri-phosphor blend uses a mixture of blue, green, and red light emitters that combine to produce white light. Fluorescent lamps contain critical rare-earth elements europium and terbium in their phosphors along with the lower cost rare earths yttrium and lanthanum. The blue phosphor has inherently low rare-earth content and therefore does not need to be replaced. However, europium and terbium are in high demand and eliminating them in the green and red phosphors would help stabilize the future cost of fluorescent lighting.

Any replacement phosphors must also sustain the color temperature (desired whiteness), lifetime (about 15,000 hours), and brightness of existing lighting. Further, the processing of the new phosphors must be compatible with current manufacturing infrastructure. GE scientists have identified a replacement green phosphor that reduces the terbium content by 90 percent and eliminates lanthanum entirely. Livermore researchers, responsible for reformulating the red-light emitting phosphor, have developed a compound of aluminum nitride doped with manganese. This phosphor is rare-earth free, eliminating both europium and yttrium oxides, and its light emission is close to the required wavelength of 610 nanometers.

In creating the new phosphor, the Livermore team began by reviewing scientific literature and searching spectral databases for emitters at the right wavelength. They then produced a small amount of candidate phosphors and tested them to determine their performance. In addition, physicists Aberg and Zhou performed quantum simulations of the prospective phosphors to calculate the substances' emission energies and various oxidation states. Much of their



Scientist Nerine Cherepy illuminates phosphor samples under ultraviolet light. Standard phosphors used in fluorescent lightbulbs (bottom right) could soon be replaced with those being developed by Livermore and collaborators that contain little or no rare-earth elements (top left). The Livermore-developed red phosphor is rare-earth free (Photo by Lanie L. Rivera.)

focus was on compounds containing manganese dopants.

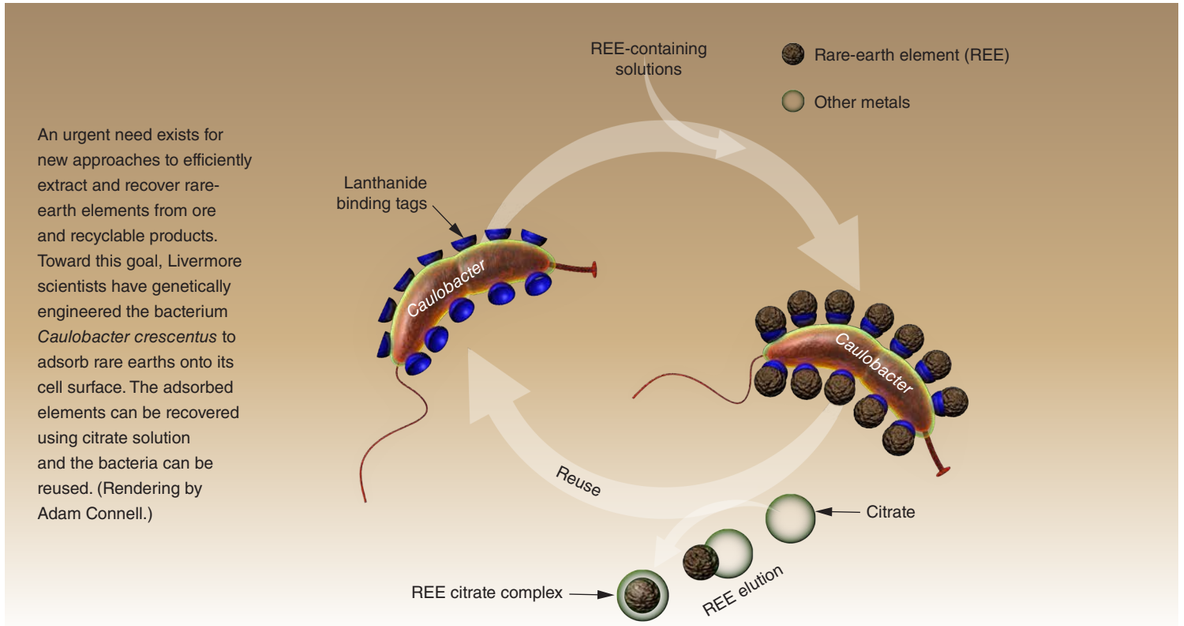
Cherepy points out that the original phosphor used in fluorescent bulbs was a mined mineral, willemite, which is naturally doped with manganese. Several decades later, in the 1970s, rare earth–containing phosphors became the standard. Aberg explains that depending on their oxidation state, manganese ions exhibit different colors and are often used as pigments. "Manganese is a versatile dopant," he says. "We focused on finding a host for manganese that allows the element to emit red in a phosphor."

Work is still underway to ensure the commercial feasibility of producing fluorescent lighting using these phosphors, but the future prospects look good. "The fundamental physics of the green phosphor being developed by GE as well as Livermore's red aluminum nitride–manganese phosphor is compelling," adds Payne. "We are taking the next steps in advancing this research by evaluating chemical issues such as slurry compatibility, improving procedures to synthesize the elements, and refining cost estimates."

Bacteria Create a Sticky Situation

The increasing demand for rare earths in emerging clean-energy technologies has triggered an urgent need for new approaches to efficiently extract these materials from ores and recyclable products. Livermore staff scientist Yongqin Jiao and colleagues are leading a project to develop a bioadsorption strategy for rare-earth recovery using genetically engineered bacterium.

Caulobacter crecentus is a common bacterium found in soil and lakes. (See *S&TR* April/May 2014, pp. 13–16.) The research team's genetically engineered *C. crecentus* has lanthanide binding tags attached to its outer cell wall. The tags have molecules called ligands that bind to metal atoms with 1,000 times greater affinity for rare earths than other metals. They also have an adsorption preference for heavy rare-earth elements relative to light elements.



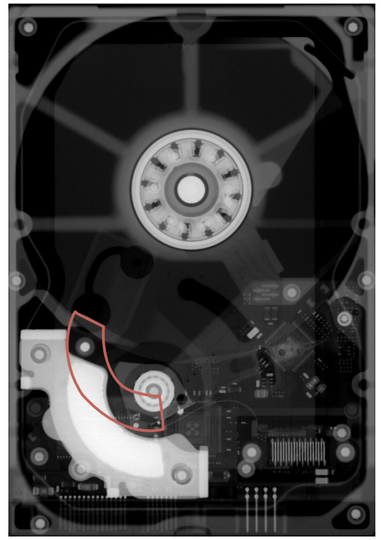
An urgent need exists for new approaches to efficiently extract and recover rare-earth elements from ore and recyclable products. Toward this goal, Livermore scientists have genetically engineered the bacterium *Caulobacter crescentus* to adsorb rare earths onto its cell surface. The adsorbed elements can be recovered using citrate solution and the bacteria can be reused. (Rendering by Adam Connell.)

The rare earths adsorbed by the bacteria can be washed off with a solution of citrate (a derivative of citric acid). In addition, citrate is harmless to the bacteria so it can be reused many times. "Our results have demonstrated a rapid, efficient, and reversible process for rare-earth adsorption with potential industrial applications," says Jiao, who adds that the novel technique would be applied mainly to low-grade waste material left over from mining. The rare earths would be leached from mine tailings, and the engineered bacteria would be added to the slurry to extract all the rare earths.

Extraction and Retrieval

If discarded materials can be mined for their rare-earth content, these materials can also find new purpose. For example, magnets in computer hard drives are made with neodymium. Data centers for companies like Google and Amazon.com use millions of hard drives per center. Industry practice suggests one-third of hard drives be retired and recycled yearly to ensure data integrity, making them an ideal source for rare-earth retrieval.

Researchers Karina Bond, Jeffrey Kallman, William Brown, and Harry Martz are developing a method to automate the recovery and recycling of neodymium–iron–boron magnets from discarded computer hard drives. Bond's prototype test bed for the method subjects hard drives to 160-kiloelectronvolt x rays, similar to those used in airport x-ray scanners. The magnets can be easily seen on the recorded x-ray images. Unfortunately, the magnets are located in different places depending on the hard drive. In addition, their size and shape can vary from one manufacturer to another. To facilitate an automated "punch" mechanism for extracting the magnets, machine-vision techniques are applied to locate their position and shape from the x-ray images. Bond says, "We need to demonstrate we can achieve a processing throughput of greater than 100 hard drives per hour to make this method economically feasible."



An x-ray radiograph of a hard drive shows the rare earth–containing motor magnet outlined in red. X-ray images such as the one shown here are part of a Livermore-developed method to automate the recovery and recycling of magnets from discarded computer hard drives.

Once extracted, a magnet could be reused in its entirety or chemically processed to recover just the neodymium. Oak Ridge is responsible for developing methods to extract magnets given their location in the drives. Scientists at the Colorado School of Mines and Ames Laboratory are researching chemical processing methods to recover the rare-earth elements from the extracted magnets. Co-locating this type of magnet-extraction machine with data centers would eliminate logistics and supply chain challenges for rare-earth recycling. One idea is to design and install such a machine in the back of a truck for processing discarded hard drives at various server farms.

Promoting Research Success

In addition to coordinating CMI-funded research at the Laboratory, Schwegler also leads CMI's cross-cutting initiatives. This work, which involves researchers at eight different institutions, focuses on developing tools and techniques that are useful in three areas: enabling science, environmental sustainability, and supply chain and economic analysis. By creating validated predictive simulation tools and materials databanks, conducting environmental impact assessments of new technologies and strategies for mitigating deleterious effects, and evaluating supply chain and future materials criticality issues, cross-cutting research enables CMI's overarching goal to diversify supply, develop substitutes, and reuse and recycle rare earths.

As demand for rare earths continues to grow commensurate with growth in clean-energy technologies, Livermore's support of CMI and its critical materials research is ever more important. For the U.S. clean-energy industry, the payoff is reduced negative effects from a supply disruption and strengthened assurance of new products and technologies.

—Arnie Heller

Key Words: Ames Laboratory, *Caulobacter crecentus*, cerium, clean energy, cobalt, Critical Materials Institute (CMI), exchange spring magnet, fluorescent lighbulb, neodymium, phosphor, quantum mechanics, rare-earth element, samarium.

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SOLVING THE MYSTERIES OF METAL HARDENING

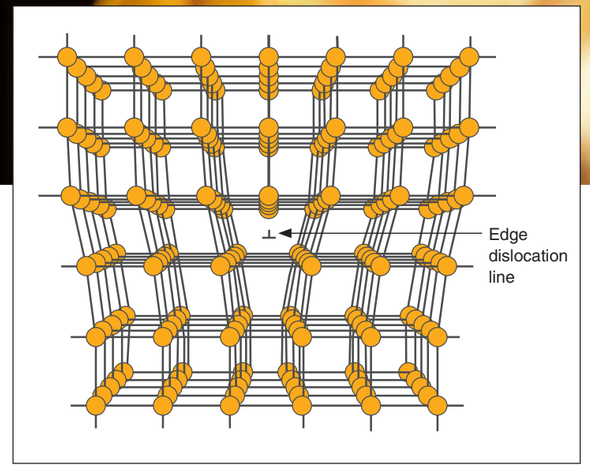
WITHOUT understanding why, metalsmiths have known for centuries that repeatedly heating and folding a block of metal would strengthen the material. Incorporating this technique into their craft, the master swordsmiths of medieval Japan forged elegantly curved, razor-sharp katanas for samurai warriors—blades exceptionally strong for their light weight. Around the same time, Damascus steel, hardened in similar fashion, became the metal of choice for the fearsome blades used in the Near East. In Russia and other countries, the metal was called bulat steel and formed the weapons carried by Genghis Khan's armies.

However, an understanding of the science behind this metal-hardening process has only recently begun to emerge, thanks to modern theoretical investigation, observational tools, and computer models. At Lawrence Livermore, materials simulations using high-performance computation are peeling back the layers of mystery, revealing some surprising insights into how metals behave under extreme pressure. Driving this research is the Laboratory's mission of stewarding the nation's nuclear stockpile. The simulations also contribute to basic science and may have applications in aerospace, astronautics, and other fields where materials are used under high-stress, high-temperature regimes.

Vasily Bulatov, a Livermore computational materials physicist, leads a research team working to simulate how metals behave under high pressure. Bulatov, who has studied the behavior of metals for more than two decades, says, "Our mission is to predict the strength of materials under extreme conditions. We are funded by the National Nuclear Security Administration's Advanced Scientific Computing Program, which seeks precise computations instead of some of the measurements previously obtained through nuclear testing."

The Dynamics of Dislocations

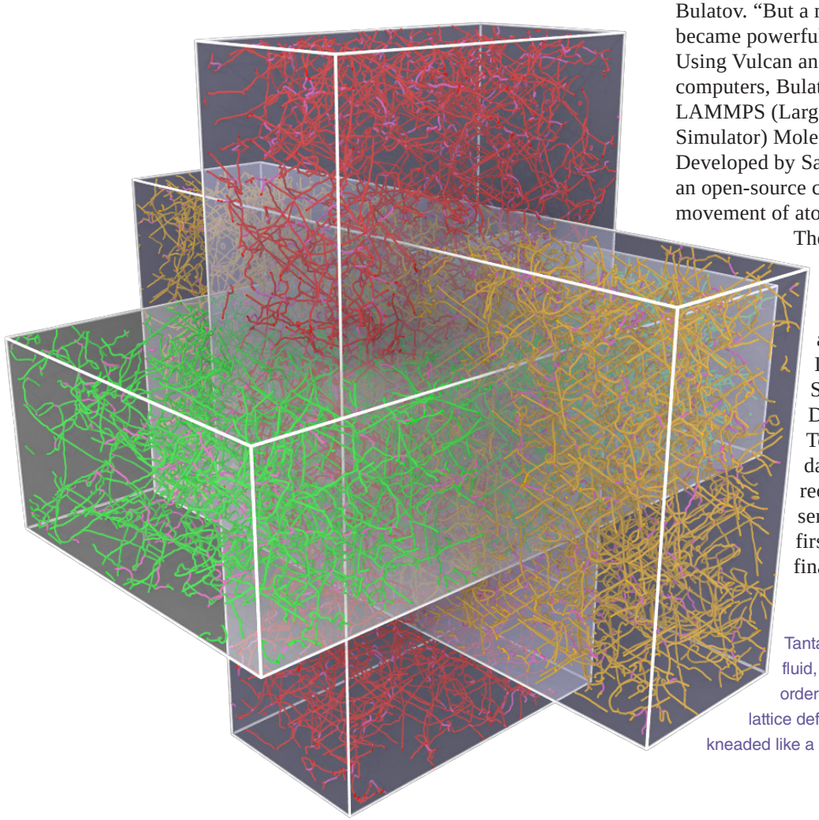
Arriving at the Laboratory from the Massachusetts Institute of Technology in 1999, Bulatov realized that a model was needed to predict metal strength. "None of the existing codes at that time could even form the basis of such simulations," he explains. He assembled a research team that eventually developed ParaDiS (Parallel Dislocation Simulator), which modeled the dislocation dynamics of metals. Dislocations—irregularities in the crystalline structure of atoms—help explain the strength and ductility of metals. Metallic atoms typically arrange themselves into regular stacks as tennis balls do in a crate, with the centers of the atoms aligning in parallel planes.



This schematic of an edge dislocation in a metal crystal shows how the extra half-plane of atoms interrupts the regular stacking of the crystalline structure. The edge dislocation line is the bottom edge of this extra half-plane.

In one type of dislocation, some planes of atoms are slightly displaced relative to their neighbors such that their centers form a half-plane that displaces the adjacent stacks of atoms to either side. The line formed by the edge of this malformed plane is called an edge dislocation. Another major type of disarrangement is an angular variety called a screw dislocation. Characterizing dislocation patterns is the first step in modeling metals under high pressure.

When a metal is compressed through repeated blows by a metalsmith's hammer, for example, the force pushes existing dislocations through the material and creates new ones, as well. As these irregularities migrate, some collide with each other, merging or forming junctions that actually strengthen the metal by resisting further strain. Bulatov says, "Take the classic example—an aluminum paper clip. Bend it back and forth a few times, and eventually it starts to harden. The more you bend the metal, and the more dislocation lines are created and collide with each other, then the harder it becomes for the lines to move. This response to stress defines the material's strength."



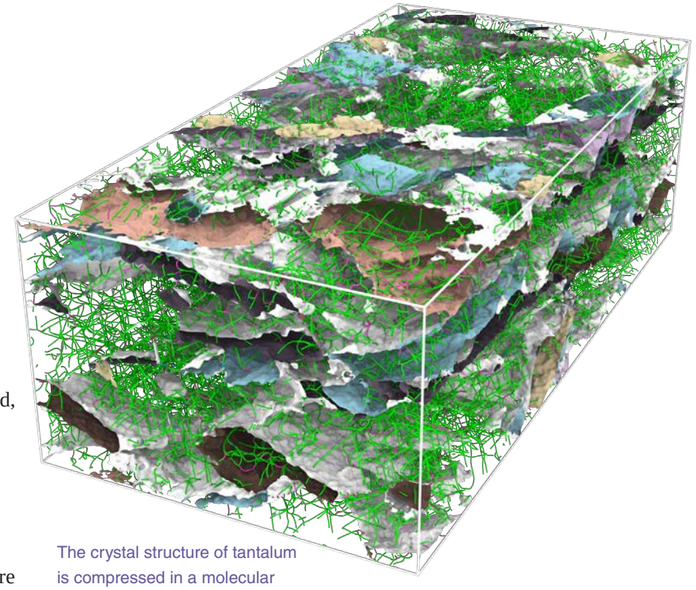
Tantalum crystals can flow indefinitely, similar to a viscous fluid, while remaining stiff and strong and retaining their ordered lattice structure. Three juxtaposed snapshots depict lattice defects—dislocation lines—developing when the material is kneaded like a piece of dough.

In 2006, Bulatov's team simulated the element molybdenum. Their results suggested that the behavior of dislocation lines under stress explained the material's crystal strength, but he more to the story remained—that only an atomistic model could reveal whether any other phenomena influenced hardness. However, even the Laboratory's fastest computers of the time could not model a large enough number of individual atoms to achieve a fully atomistic simulation of metal strength, also known as a molecular dynamics simulation.

The Need for Speed

"When I began investigating the problem, computers were seven orders of magnitude slower than they are today," recalls Bulatov. "But a moment came two years ago when computers became powerful enough to make an atomistic model a reality." Using Vulcan and Sequoia, Livermore's two most powerful computers, Bulatov and his team began using software called LAMMPS (Large-Scale Atomic/Molecular Massively Parallel Simulator) Molecular Dynamics Simulator for this purpose. Developed by Sandia National Laboratories, LAMMPS is an open-source code that allows users to study the physical movement of atoms and molecules.

The team ran simulations of tantalum (Ta), a hard yet ductile, corrosion-resistant metal with applications such as electronic components, jet engines, and surgical instruments. Starting from atomic configurations generated by Bulatov, Livermore's Luis Zepeda-Ruiz and Alexander Stukowski of Germany's Technische Universität Darmstadt ran the simulations. The Laboratory's Tomas Oppelstrup optimized the code and data management. In one of the simulations, rectangular bricks of Ta atoms were compressed serially in three directions—stresses were applied first lengthwise, then along the width, and finally along the height of the blocks repeatedly, "kneading" the metal like a lump of dough. In simulations consisting of up to 268 million individual Ta atoms, the team each day generated approximately five exabytes (10^{18} bytes) of atomic trajectory data, comparable to all the data that Google currently has stored on servers worldwide.



The crystal structure of tantalum is compressed in a molecular dynamics simulation. All atoms are removed for clarity, and the structure is represented by lattice defects—dislocations (green and red lines) and interfaces of twin particles (surfaces of various colors).

A Swift, Distinct Transition

This work, published in 2017, yielded two significant scientific findings. First, the team found that as Ta is compressed, its dislocations extend and collide with each other, moving actively to prevent the metal from breaking. This behavior imparts ductility to the metal—but that was not all. "Something else rather dramatic happens," says Bulatov. "If you strain the metal very quickly, the dislocations are unable to keep up, and whole chunks of the crystal rotate, a phenomenon called deformation twinning. We showed a very precise threshold where this transition from dislocation to twinning takes place."

During twinning, planes of atoms do not slide past one another as happens with moving dislocations. Instead, regions of material twist in opposite directions from one another, resulting in volumes with distinct crystal orientations. Scientists had previously theorized that this transition was possible, but simulations by Bulatov's team revealed the precise atomistic mechanism and the conditions under which the transition occurs.

The second key finding announced in 2017 concerns Ta behavior during slow compression. "When tantalum deforms slowly enough that that the dislocations can keep up with the applied forces, the crystal reaches a steady state that persists forever," explains Bulatov. If the metal is compressed in such a way that the transition to twinning is not reached, dislocations will continue to migrate through the material endlessly, and this mechanism will remain dominant, preventing the metal from breaking. Kneading thus ensures that no other changes will happen, and that the metal will retain the same strength indefinitely. This may be the molecular secret to the famously strong swords.

Even Larger Simulations

Metals subjected to force often harden in stages, undergoing a low level of hardening upon initial compression, then high-strength hardening, and back to low-level hardening until breakage occurs. The reasons for this three-stage process are not fully understood, but further simulations may elucidate what is happening at an atomic level. Since reporting their work, Bulatov's team has run an even larger simulation involving more than two billion atoms. The results are still being analyzed. Because these simulations generate so much data, Bulatov is planning to use machine learning to identify the significant data and detect patterns in data sets too large for humans to comprehend. Recent simulations have generated a volume of data equivalent to seven to ten times the data on Google's servers worldwide.

Bulatov is optimistic about solving the remaining mysteries of metal hardening. He states, "As both computing power and the accuracy of atomic models steadily increase and, at the same time, the spatial and temporal resolution of experimental methods in materials science improve, we are increasingly seeing the complete confluence of experiments and atomistic simulations." For solving the mysteries of their ancient craft, the swordsmiths of yore would be impressed indeed.

—Allan Chen

Key Words: Advanced Scientific Computing Program, bulat steel, Damascus steel, deformation twinning, dislocation dynamics, edge dislocation, high-performance computing, katana, LAMMPS (Large-Scale Atomic/Molecular Massively Parallel Simulator) code, metal hardening, molecular dynamics, molybdenum, Parallel Dislocation Simulator (ParaDIS) code, screw dislocation, tantalum.

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SUDDEN CHANGES AT ULTRAHIGH PRESSURE

LOWER water's temperature to its freezing point and it turns to ice. Raise it to its boiling point and it becomes water vapor—a gas. At one atmosphere of pressure (101.3 kilopascals), which prevails approximately at sea level, these phenomena are familiar to everyone. However, at much higher pressures and temperatures—up to hundreds of thousands of atmospheres and several hundreds to thousands of degrees—water and other matter behave in complex ways. Under such conditions, a solid of the same composition may assume different crystalline structures, and the molecules that form liquids may order themselves in various configurations. These changes in molecular arrangements are called phase transitions.

Livermore physicist Jon Belof and a team of physicists, engineers, and computational scientists are subjecting matter to extreme conditions and simulating experiments with high-performance computers to study phase transitions at ultrahigh pressures. Examining how matter arranges itself and behaves at these levels may reveal new underlying physics principles. The work also supports the Laboratory's mission in stockpile stewardship by improving models that are used to simulate stockpile components.

Exploring a New Frontier

Belof has been studying phase transitions in elements since 2010, when he was a postdoctoral researcher at Lawrence Livermore. In January 2017, Belof was one of 100 scientists in the nation to receive a Presidential Early Career Award for Scientists and Engineers. This honor is the highest bestowed by the U.S. government on outstanding scientists and engineers who are early in their independent research careers. "The study of material phase transitions at extreme conditions could be a new scientific frontier," he says. "We can now study these phenomena in ways that were not possible five years ago, both experimentally and computationally, allowing us to gain insights into the atomistic physics of material transformations."

Livermore's increasingly powerful high-performance computers and new tools for shocking matter at ultrashort timescales have enabled Belof's team to peer into the physics of phase transitions at an unprecedented scale—occurring as fast as tens of picoseconds (trillionths of a second). With these capabilities, Belof and his team are developing a predictive theory of nonequilibrium phase transitions. In such cases, a material has had its pressure and temperature changed so rapidly that it enters a state far from stability. In an effort to return back to equilibrium, the stressed material changes its phase, but when that process begins and how quickly it occurs are not well understood. By developing a predictive theory for phase evolution, scientists can greatly improve simulation capabilities, and thus achieve more accurate results of a material's behavior and physical properties.

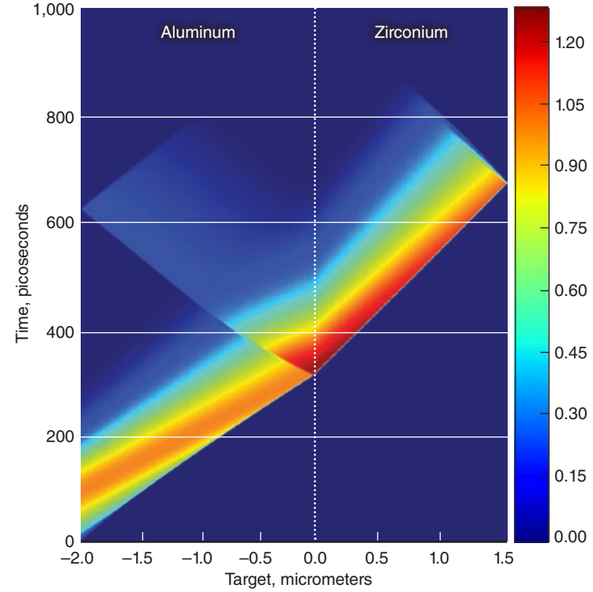
The Secrets of Shocked Zirconium

Recently, Belof's team turned its attention to zirconium (Zr). This metal, which has a high melting point (1,855ºC), is used for heat-resistant applications in the aerospace and nuclear industries. It also has biomedical applications, such as in dental implants and hip replacements.

Funded by Livermore's Laboratory Directed Research and Development Program, Belof and his colleagues partnered with SLAC National Accelerator Laboratory (previously called Stanford Linear Accelerator Center) to run Zr experiments. Using SLAC's Linac Coherent Light Source (LCLS), the team subjected 1.7-micrometer-thick Zr samples (each deposited onto a 2.2-micrometer layer of aluminum) to high-energy laser pulses. During the experiments, the Zr samples underwent more than 100 gigapascals (GPa) of pressure for a duration of less than 1 nanosecond (one-billionth of a second). For that very brief period, while the Zr was compressed, LCLS delivered an intense x-ray pulse to probe the atomic structure of the material by diffraction.

Livermore's Mike Armstrong, co-leader of the experiment, says, "The real power driving this experiment is the LCLS x-ray pulse, one of the brightest sources of x rays in the world." Bombarding the sample with x-ray pulses and recording how the x rays scatter provides a record of the sample's phase transitions. "The distinguishing feature of our experiments is the ability to observe the details of phase transitions at very short timescales," he adds. Since the window of opportunity to examine the shocked material is so small, researchers need to record the diffraction patterns in the briefest intervals possible, less than 100 picoseconds.

The results of the experiments were striking. The known shock Hugoniot—a set of high-pressure, high-density states



Simulation data from one of the team's experiments using the Linac Coherent Light Source at SLAC National Accelerator Laboratory show how pressure on the target—aluminum ablator (left) and zirconium (right)—changes over time. The x-axis shows the length scale of the target. The laser pulse is passing through the target from left to right, and the color gradient represents the increased pressure from the energy of the pulse. The pressure units are normalized to 27 gigapascals.

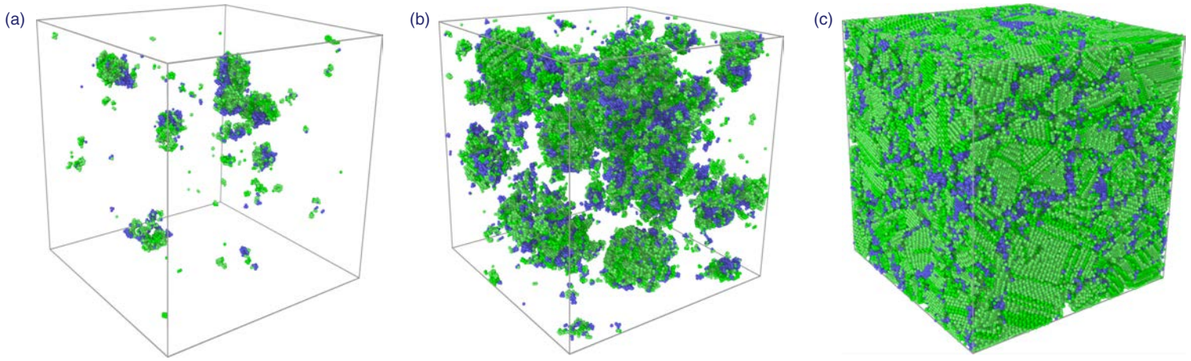
achieved when a shock wave is driven at constant velocity through a sample—for Zr indicates that the material passes through multiple solid phases. “However, if the drive is rapid enough, the zirconium can melt directly out of its ambient pressure phase without going through its intermediate phases, suggesting that the transformation pathways are different when the material is subjected to very rapid compression,” says Belof. “The kinetics seem to dictate that the relaxation to an equilibrium state is nontrivial.”

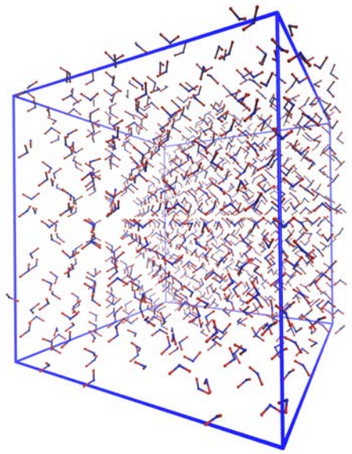
Typically, a material’s phase transitions are explained by classical nucleation theory (CNT), first developed in the 1920s. During the formation of a new phase, such as the transition from a solid to a liquid, tens of thousands of molecules organize themselves into the new phase first, forming clusters which then seed the transition. More molecules then aggregate to these nucleation sites until the changeover from liquid to solid is complete. The laws of thermodynamics govern when the change potentially starts and where it ultimately ends (the equilibrium state). At the pressures and temperatures produced during the experiments, CNT begins to break down. Belof says, “At this very short timescale, we could be seeing new physical principles at play that we are just starting to uncover.”

Modeling Nucleation at the Atomic Scale

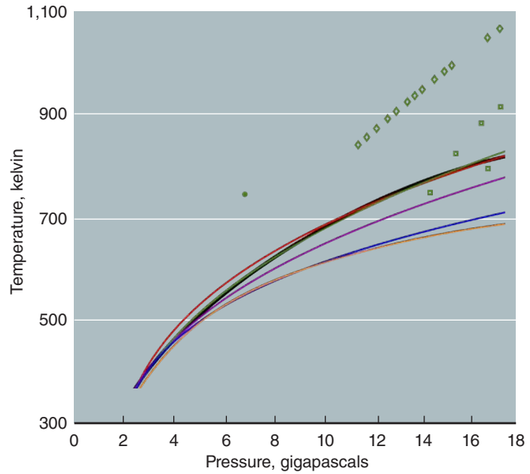
To better understand the physics required for modeling phase transitions, Belof and colleagues are using massively parallel codes on Livermore supercomputers to model the details of each step. Computational materials scientist Luis Zepeda-Ruiz is applying these codes to model systems involving tens of millions of atoms and to follow individual atoms as they change from one phase to another. “For atomistic-level simulations, we still cannot reach the length and timescales associated with most experiments, with a few exceptions,” he says. Molecular dynamics simulations are limited by the time step used to propagate the equations of motions. The faster the physics, the smaller the time steps. “However, at extremely high deformation rates, processes happen rapidly. We can acheive greater simulation accuracy at these very short timescales.”

A visualization of homogeneous nucleation according to classical nucleation theory shows (a) crystals begin to form clusters in a liquid at nucleation sites. (b) Each site grows as more molecules aggregate to the clusters. (c) Growth stops when the phase change to a solid is complete. (Liquid atoms are removed for clarity.)





This visualization depicts a molecular dynamics (MD) simulation of the high-pressure water polymorph ice VIII. Oxygen atoms are blue and hydrogen atoms are red. The applied pressure is 10 gigapascals and the temperature is 200 kelvin. MD simulations such as this are making it possible to develop models for phase transformation kinetics in hydrocodes.



A portion of the phase diagram for water shows the approximate boundary between liquid water and ice VII. The many curves illustrate boundaries reported by different research teams, indicating that the boundary is still imperfectly known. The Livermore team’s theoretical model of the boundary is the black solid line.

Zepeda-Ruiz is modifying a code called the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) to routinely simulate 30 to 40 million atoms, and at times more than 200 million, during a phase transition. “We can pinpoint the interface between a solid and a liquid with good accuracy,” he says. The atomistic-level LAMMPS code provides parameters, such as nucleation and growth rates, that are used in other hydrodynamics codes—SAMSA, developed by Belof, and ARES—to model the material at the continuum level. Together, these codes provide multiscale coverage. Livermore’s high-performance computing (HPC) infrastructure makes the work possible—few laboratories in the world have the computing power needed to pursue this research systematically.

The Wonders of Water’s Phases

Improved simulation has also allowed the research team to model the solidification of water at ultrahigh pressures using, for the first time, a physics-based model for the phase transition. “Water is one of the most complex substances in existence, so simply determining its equation of state (EOS) is difficult—and we need the EOS before we can attempt to solve the mysteries of kinetics,” says Belof. The EOS describes the phases of a material at varying pressure and temperature. Water has at least 17 solid phases.

One reason why this research is important is that water may exist at ultrahigh pressures on some of the many super-Earths detected by NASA’s Kepler Mission, a few of which may harbor life. *Escherichia coli* bacteria have been shown to survive at pressures as high as 2 GPa. Furthermore, many scientists believe the majority of the universe’s water exists as an ultracold glassy state, a particular phase of water that is of intense interest.

Postdoctoral researcher Philip Myint, working with Belof and colleagues, has explored the solidification of water into ice phases at ultrahigh pressures. “We are trying to implement CNT in a code and use that to understand dynamic compression experiments as well as make predictions. Past models of phase transitions in shock physics have been empirical,” says Myint. After successfully modeling a number of shock physics experiments on water, several long-standing controversies on the compressive freezing of water are closer to being resolved.

At pressures above 2.2 GPa, water freezes into ice VII, a state in which the molecules order themselves into a cubic crystalline form (unlike the hexagonal form of ice typical at Earth’s surface). Ice VII forms through nucleation clusters that grow until all the material has solidified. This form of ice could be common at the high pressures of extrasolar super-Earths and can exist at temperatures well above 600 kelvin.

Through HPC simulations, Belof, Myint, and colleagues have observed a breaking point at about 7 GPa. “At this pressure, ice VII may form through a homogeneous nucleation process where the clusters contain fewer than a dozen molecules—perhaps as few as two or three—instead of thousands,” says Myint. In contrast to freezing initiated by heterogeneous nucleation, which occurs along the plate walls and may take hundreds of nanoseconds to complete, freezing initiated by homogeneous nucleation occurs within the bulk of the water and is completed in less than 10 nanoseconds. “The liquid is being driven so rapidly that it’s approaching instability,” says Belof. “The dynamic freezing of water to ice VII is shedding light on the fundamental physics of nucleation, since this magnitude of undercooling cannot be achieved without rapid compression.” Exploring this new frontier of phase transitions will reveal how nature transforms matter away from equilibrium.”

—Allan Chen

Key Words: ARES, classical nucleation theory (CNT), equation of state (EOS), heterogeneous nucleation, high-performance computing (HPC), homogeneous nucleation, ice VII, Laboratory Directed Research and Development Program, Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS), Linac Coherent Light Source (LCLS), phase transition, SAMSA, SLAC National Accelerator Laboratory, super-Earths, ultrahigh pressure, water, zirconium.

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COMPUTATION BOOSTS MATERIALS DISCOVERY

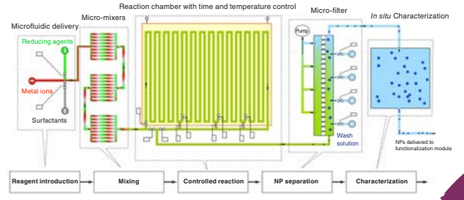
In the area of materials science, the hunt is on for revolutionary new materials to use in applications such as flexible electronic displays, higher capacity batteries, efficient catalysts, and lightweight vehicles. At Lawrence Livermore, such materials are needed for stockpile stewardship, inertial confinement fusion experiments, radiation detectors, and advanced sensors. Ironically, although materials themselves have become more sophisticated, their development process is still rooted in 19th-century techniques. These techniques rely on the knowledge, experience, and intuition of scientists using a trial-and-error approach to synthesis and testing that is iterated until researchers achieve a material with the desired properties.

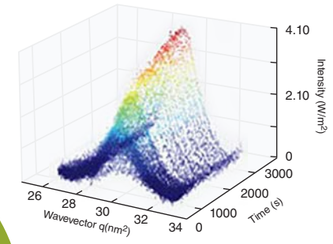
A group of Livermore materials and computation scientists and engineers have come together to create a more modern development approach that applies machine learning, high-performance computing, and big data analytics to accelerate materials discovery. Their effort is a perfect fit for Livermore, where interdisciplinary teams of researchers work together to solve difficult problems of national importance. The team, led by materials scientist T. Yong Han, is conducting a three-year project funded by the Laboratory Directed Research and Development Program to deploy advanced materials faster and at a fraction of the cost by integrating computational and experimental tools, digital data, and collaborative networks into the synthesis and optimization process.

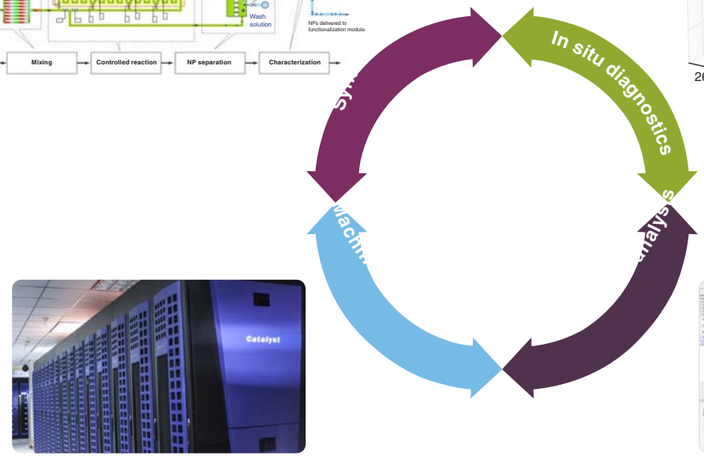
Synthesizing a material involves many reaction parameters, including specific chemicals, chemical concentrations, temperatures, additives, reaction times, and solvents. Scaling up a high-quality material from the laboratory to more commercial applications is often hindered by the challenge of experimentally pinpointing the material's most critical reaction parameters to obtain the desired results. Han says, "If we can discover the most relevant critical reaction parameters from existing literature using computational and data-processing techniques and experimentally verify their veracity, we will have made a significant leap in the field of materials synthesis and materials informatics."

Following the Recipe

Materials scientists publish tens of thousands of papers every year that contain useful information about the "recipes" they used to generate new materials. Each recipe includes the list





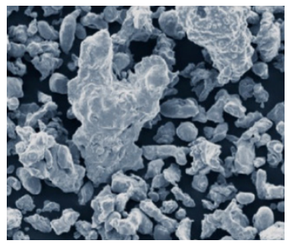


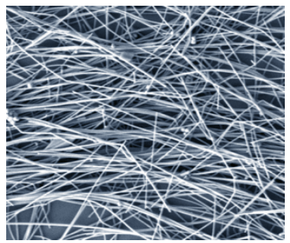
A Livermore research team is developing a new structured knowledge base and application programming interfaces to analyze, query, discover, and optimize processes for quickly deploying novel advanced materials.

of ingredients, how the ingredients were synthesized, how much of each ingredient was needed, and the method used to create the final material. "The amount of data in this area of research is enormous and constantly growing," says Han. "We want to set up an ingest pipeline for large numbers of papers so that we can tease out relevant and important correlations in synthesis parameters, including chemicals and process conditions, to speed materials discovery, synthesis, and optimization."

The goal is to develop an extensive computational knowledge base that will enable researchers to query desired material properties. The knowledge base may not contain the exact recipes for a given material, but with the help of machine-learning algorithms and big data analytics, it may provide a way to narrow down the possibilities or even predict the synthesis pathways, significantly reducing the time needed to produce the desired materials. Livermore computer scientist Brian Gallagher, an expert in machine-learning algorithms, says, "One of the major challenges is re-creating the experimental procedure from the original write-up. The steps are not always described in order or even in the same portion of the article. Authors also leave out essential steps that may be viewed as 'understood' by trained scientists."

As part of the process, the team will use machine-learning algorithms running on Livermore computation clusters to identify the experimental procedure sections in scientific papers—the section where most materials' recipes are located. The researchers will then "train" the machine-learning tool to look for typical recipe-related sentences, initially focusing on synthesis methods for silver nanowires. This material is key to developing technologies such as water-resistant flexible displays, wearable electronics, optoelectronic circuits, more efficient solar cells, and nanomaterial-based sensors.

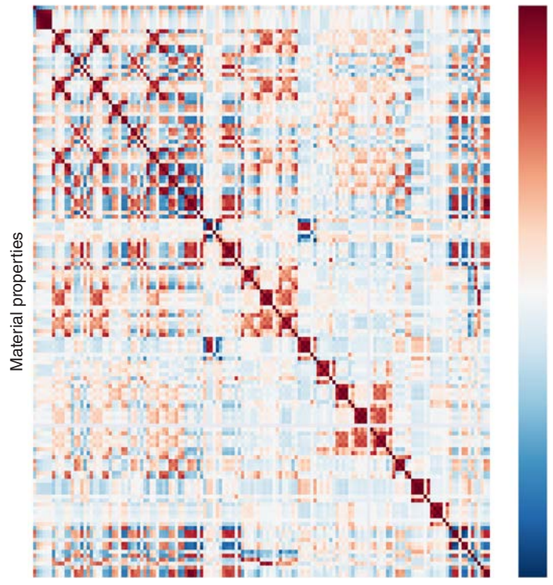




Material "recipes" included in scientific literature describe how researchers develop a new material in a laboratory. (left) A commercial copper powder compared with (right) copper nanowires produced at Livermore show how recipes yield different results. Livermore's structured knowledge base will allow researchers to more quickly identify the common synthesis parameters needed to develop a material with desired properties.

A Strategy Takes Shape

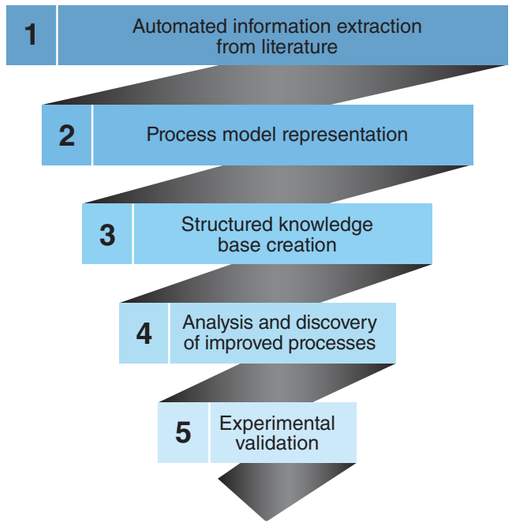
"One of the hardest parts of a project is gathering the data," says team member and computer scientist David Buttler, a specialist in information management systems and natural language processing. Obtaining access to a useful number of papers required negotiation and extensive Web searches. Thanks to an agreement with scientific publisher Elsevier, the team has assembled a collection of 70,000 papers on the synthesis of silver nanomaterials. The team's Kansas State University collaborators, led by Professor William Hsu, are developing an application engine to determine which papers are beneficial, a capability that will speed up Web crawling for relevant work beyond the Elsevier study. With the data gathering infrastructure in place, the team has begun developing and training machine-learning algorithms to analyze the papers.



Machine-learning algorithms can learn different materials properties—for example, thermodynamic constants and atomic information—and their correlations. This chart shows 145 material property correlations for 600 compounds. Positive (red) and negative (blue) correlations are indicated. The diagonal line represents a 1-to-1 correlation in the properties.

With supervised machine-learning techniques, human operators provide the software with thousands of examples of words and images labeled by names, as well as rules about data relationships. In the case of Han's project, the team is training the machine-learning tool to search for the chemical ingredients and the relationships of the chemicals to one another—that is, the procedures the scientific teams used to synthesize their materials. This information will enable the software to differentiate procedures relevant to silver nanowires from those for other nanomaterials—for example, silver nanospheres or nanocubes.

The researchers are modifying two open-source chemistry codes, OSCAR (Open-Source Chemistry Analysis Routines), a chemical names recognition tool for natural language texts, and ChemicalTagger, used for data extraction from chemistry literature, to pull out the material recipes. Buttler says, "We're rewriting the identifier section of ChemicalTagger from scratch to improve its 70-percent accuracy rate. It must be able to convert the text into something that is easier for the machine-learning algorithm to identify."



The team has a five-step approach for accelerating materials synthesis, optimization, and scale-up. Machine-learning algorithms first extract information from the scientific literature, providing information that can be used to develop process models. These process models are integrated into a structured knowledge base to analyze and discover optimized procedures and conditions for materials synthesis. Users can query the knowledge base for a particular material and then experimentally validate synthesis processes in the laboratory.

Perhaps several dozen papers on silver nanowire synthesis will have procedural elements in common to create a process model representation. The team will analyze and bin the papers into categories based on material types, resulting in a structured knowledge base of the procedures used to synthesize these materials. Users can then query the knowledge base for a material with the critical parameters they seek, fin d the recipes closest to possessing the material properties they want to develop, and then conduct experimental validation and scale-up in the laboratory. This workflow could help eliminate much of the trial-and-error process typical of materials research today. Ultimately, it may also enable predictions of synthesis pathways for new materials. Buttler says, "As far as we know, an automated process to identify and assemble the relevant text and convert it into steps that form a coherent recipe does not exist today."

Not Just for Nanowires

The team—which also includes materials scientists Jinkyu Han and Anna Hiszpanski, computer scientists Bhavya Kailkhura, Peggy Li, and Hyojin Kim, and engineer Erika Fong—is excited about the technology's capabilities. In its infancy, the machine-learning tool is designed specifically to help materials scientists working with nanomaterials, but the technology has broader applications. "The machine-learning pipeline is agnostic to the process—we are developing it for materials synthesis, but it could be used for any other process," says Han.

Machine-learning algorithms could help the pharmaceutical industry by screening papers describing natural products with medicinal properties. The technology could also assist the medical profession, increasing the speed at which life-saving modifications to medical procedures make their way into general practice. Han says, "If we are successful, the technology will help younger scientists gain knowledge more quickly from the experiences of many people—it will reduce the number of real-life experiments we need to conduct to obtain a result, and we will achieve desired results faster."

—Allan Chen

Key Words: algorithm, big data analytics, ChemicalTagger, informatics, machine learning, materials discovery, OSCAR (Open-source Chemistry Analysis Routines), silver nanowires, structured knowledge base, supervised learning.

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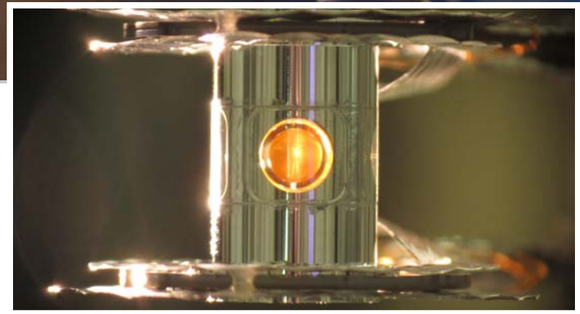
BIG IDEAS FOR TINY TARGETS



(top) A Livermore scientist tests the tensile strength of carbon nanotube yarn used to support target capsules for experiments at the National Ignition Facility. (Photo by Jason Laurea.) (bottom) A target capsule, only 2 millimeters in diameter, is visible through a port in a hohlraum. (Photo by Eduard Dewald.)

FROM the 10-story-high building that could hold 3 football fields (each 48.5 meters by 109.1 meters) to the 130,000-kilogram target chamber that brings together 192 laser beams, nearly everything about Lawrence Livermore's National Ignition Facility (NIF) is gigantic—except the targets themselves. Nestled inside a cylindrical hohlraum is a spherical capsule only 2 millimeters in diameter. For inertial confinement fusion (ICF) experiments, the capsule contains a fragile, volatile mix of deuterium–tritium fuel. This sphere must rest securely in its berth until the laser beams converge inside the hohlraum and the capsule implodes, becoming the "star" of the experiment. (See *S&TR*, January/February 2016, pp. 4–11.)

Research and development efforts focused on designing, simulating, constructing, and testing NIF targets include a multidisciplinary team responsible for one of the smallest and most important pieces of the target assembly—the material supporting the capsule inside the hohlraum. As group leader for target fabrication science and technology, Michael Stadermann describes this work as a multipronged challenge. "Supporting the capsule is a materials problem, an engineering problem, and a physics problem," he says. "How do we make a material strong enough to withstand fabrication, handling, storage, and positioning, yet weak enough that the material doesn't influence the fusion reaction? A successful capsule mount must provide sufficient support without interfering with the experiment."

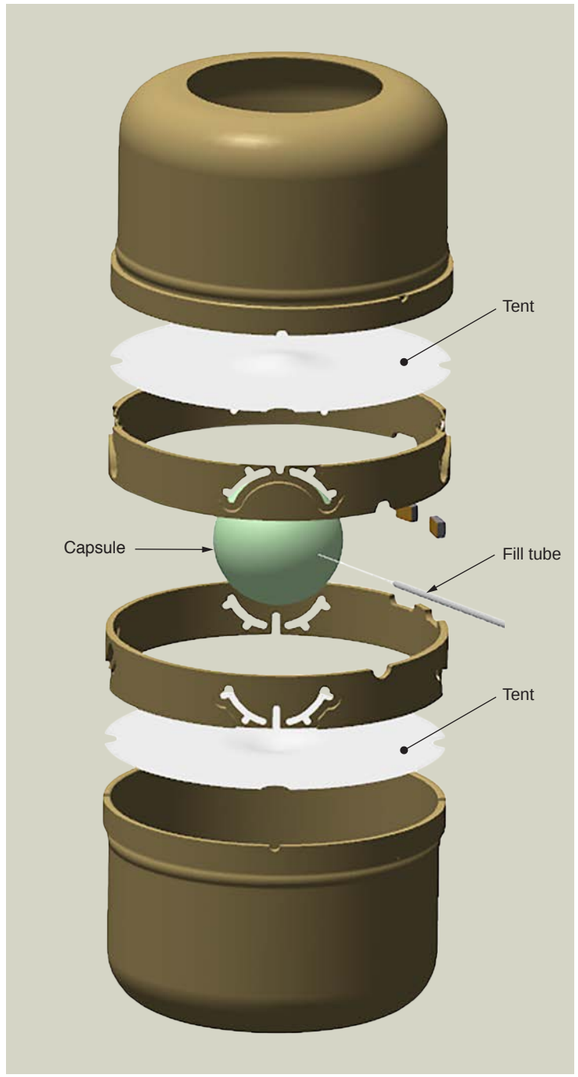
Stadermann underscores the collaborative effort necessary for fielding new target components. He notes, "All difficult problems at NIF need a dedicated team to solve them." Physicist Vladimir Smalyuk adds, "ICF is a complicated process. To achieve ignition, we need to understand how all features in the target affect implosion, then mitigate those effects if needed. It is a team effort from beginning to end." Through careful coordination with specialists at each phase of development, advancements in capsule support technologies are as much about the process as the product.

From Sketch Pad to Target Chamber

A capsule support design usually begins as a drawing accompanied by physics calculations. Designers, engineers, and target fabricators weigh in as Smalyuk and other NIF experimentalists develop experimental platforms to define the test parameters, such as which data to measure and which diagnostic techniques to use. Stadermann says, "Deciding which concepts to pursue is a challenge." Not every idea outlives the sketch pad, and no detail is too small for consideration. Changing even a single variable could have multiple effects on implosion, so the team uses computer simulations to predict a design's performance. Smalyuk emphasizes the importance of focused experiments to complement computational results. He says, "Every experiment reveals something you did not expect."

Once initially approved, a design then undergoes rigorous evaluation. A series of target fabrication tests is conducted, including materials testing to measure specific properties and determine feasibility, assembly testing to check for centering and static stability, dynamic testing for vibration and other factors, and cryogenic layering tests using Livermore's Integrated Target Proofing System. Stadermann notes, "We have to demonstrate that the device can survive assembly before going any further. A design passes through many hands before proving its value." A prototype that performs well in this stage moves on to the NIF target chamber, where shots are conducted to measure perturbations and implosion efficiency. Data produced by these shots are used to validate and augment simulation codes.

NIF experimental designs need time to mature. Simple capsule support designs can be ready for the target chamber in less than



A rendering shows a design for target support that splits the hohlraum into four segments to minimize contact between the tents and capsule. Each tent is secured at its edge by two segments. Notches and holes in the hohlraum accommodate other aspects of target assembly and placement, such as a port for the capsule's fill tube. One risk of this design is energy leakage through the ports or seams between two hohlraum segments.

a year, whereas more complicated designs may require two or more years of preparation. Iterations can take another six months of development, even if only a minor modification is made, such as repositioning a piece by a few micrometers. “Each iteration increases our understanding of ICF,” says Smalyuk. “Nature is always more complex than our imagination.”

Supporting Something with Nothing

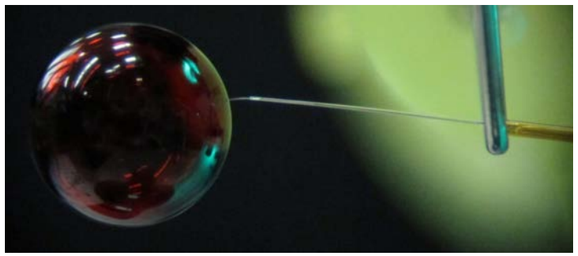
A decade ago, thin polymer tents provided an early solution to the problem of capsule support. In this setup, two membranes are attached to the walls of the hohlraum, one above the other, with the capsule suspended between them. The membranes are bent into tented shapes around the capsule’s peaks. Over time, NIF researchers realized that the tents caused pressure and density asymmetries, decreasing implosion efficiency. Smalyuk says, “Tents produced surprisingly large modulations.” Using x-ray radiography, scientists determined that these perturbations increased with tent thickness. However, thinner tents also had limitations—because of confinement, a film’s mechanical properties changed as its thinness approached a single layer of the molecules. These changes both led to film failure after target assembly and were predicted to offset the benefits of reduced thickness, so Stadermann and colleagues began exploring alternate approaches.

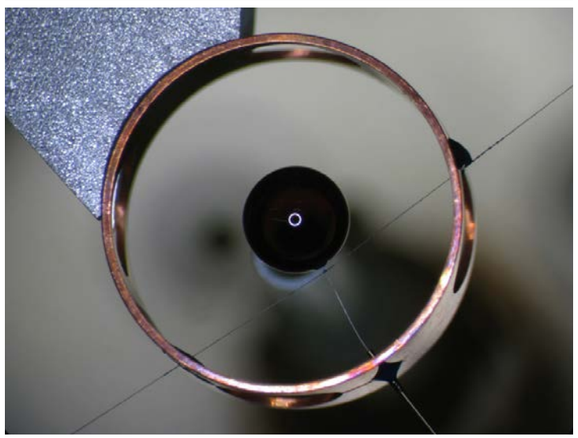
By 2014, the team had come up with dozens of ideas involving a variety of materials and attachment techniques. Stadermann explains, “From there, we evolved our process to find common denominators and eliminate duplicates.” A major problem to solve with any target-supporting approach is reducing the amount of supporting material touching the capsule, thereby decreasing perturbation. Stadermann explains, “How can we support the capsule with as little material as possible? To put it more simply, how do we hold something with nothing? Making a material thinner or exposing it to cryogenic temperatures changes its mechanical properties. Designs that initially show potential can be eliminated because of this change.” Three solutions have come far in recent testing—a four-part hohlraum with polar tents, a supported fill tube, and the tetra cage.

Promising Approaches

Despite earlier outcomes, the team decided to continue exploring tents. The idea of sandwiching the capsule between two tents to reduce surface contact led to the four-part hohlraum, in which the walls of a hohlraum segmented into four parts clamp the tents’ edges. With a stabilized perimeter, the membranes touch only the capsule’s poles. Stadermann acknowledges the miniscule margins of error that come with fine-tuning the four-part design. He says, “When we reduce the amount of deflection, or bend, in the tents, the tents must be stiffened to have sufficient force for holding the capsule. However, if made too stiff, the tents can break during assembly.” This tradeoff, combined with the added task of stocking more hohlraum parts, is proving worthwhile. Data from multiple shots conducted at NIF show improvement over the original two-tent design, and the four-part hohlraum is now part of standard target production.

For another method of capsule support, the team looked more closely at the 10-micrometer-diameter glass tube that fills the capsule with fuel. A conventional fill tube is too flimsy to hold the capsule in place without drooping and causing vibrations. Furthermore, the capsule’s weight stresses its bond with the fill tube. Consequently, Stadermann’s team attached a rod to the hohlraum walls, running it perpendicular to the fill tube, with the tube resting on top. Testing revealed an issue with the cantilevered design: The closer the rod is to the capsule end of the fill tube, the more the rod affects implosion. In a modified concept called a “fishing pole,” the team expanded the fill tube to a thickness of 30 micrometers over most of its length, returning to the 10-micrometer diameter just short of the capsule’s surface. Again, the team discovered an unexpected effect. Smalyuk explains, “The fill tube produced shadows on the capsule from the hohlraum x-ray drive. These shadows would interfere with x rays angling off the walls, introducing asymmetry into implosion.” Therefore, these and related designs for fill tube supports continue to undergo stability modifications and hydrodynamic growth radiography testing.





Livermore researchers are also exploring enhancements to an existing device used in target assembly, instead of supporting the capsule itself. (top) One approach involves creating a fill tube with a thicker diameter for all but 200 micrometers of its length. (bottom) Another method of supporting the fill tube includes a perpendicular cross-piece.

A third approach to capsule support began with spider silk, an ultrathin substance known for its high density and excellent tensile strength. The team examined silk taken from live spiders caught in Stadermann’s garden and specimens ordered on the Internet but found the creatures’ silk to be inconsistent. The researchers therefore decided to make synthetic fibers using carbon nanotechnology. The process begins with a seeded catalyst subjected to thermal chemical vapor deposition, yielding a multiwalled “forest” of nanotubes. By twisting millions of such nanotubes together, the team generates thin, sturdy yarns that are then fortified with vapor-deposited polymers. Four yarns come together inside the hohlraum in an orthogonal configuration called a tetra cage. This innovative design supports the capsule between two pairs of carbon nanotube yarns—one pair under the capsule and one pair above. Stadermann states, “Now we are trying to shrink these yarns to less than 1 micrometer in diameter to reduce perturbations even further.”

Other capsule support concepts are in development. For instance, the team is working on a solution that uses magnets to levitate a capsule coated with a superconducting material, eliminating the need for a fill tube or tents. Another fill tube design positions the tube tangentially to the capsule instead of connecting perpendicularly to the surface. In another recent accomplishment, a 5-micrometer-diameter fill tube sufficiently supported the capsule while achieving the highest total neutron yield to date. Smalyuk notes, “Behind each split-second shot are years of teamwork. This neutron yield milestone was achieved because of all the hard work that came before.”

—Holly Auten

Key Words: capsule, carbon nanotube, deuterium–tritium fuel, fill tube, hohlraum, implosion, inertial confinement fusion (ICF), National Ignition Facility (NIF), target science and technology, tetra cage.

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(top) Carbon nanotubes are produced in a densely packed forest. Individual strands are separated and pulled together into a wedge shape, then twisted into a yarn. (bottom) Four yarns make up the tetra cage formation, with the capsule suspended between two pairs.

LOOKING FOR TROUBLE ON OPTICAL SURFACES

HIGH-ENERGY pulsed lasers, including the world's most energetic laser at Lawrence Livermore's National Ignition Facility (NIF), rely on finely calibrated optics for accuracy. The lenses, mirrors, and crystals that make up a laser's optical system serve various functions, from guiding a beam toward a reflective surface to correcting distortions. NIF's 192-beam system includes tens of thousands of optics that amplify and focus energy for hundreds of shots every year. In the high-energy-density regimes of these experiments, optical integrity is paramount.

Compromised optics are an expensive liability for laser performance. Debris and other damage initiators, also called precursors, can affect optical surfaces through laser–material interactions and subsequent material response, including etching, pitting, cracking, and melting. Degradation can lead to delamination of protective coatings as well as distortion, diffraction, blocking, or scattering of the laser beam. The Laboratory's Optics and Materials Science and Technology (OMST) organization manages efforts to analyze damage precursors, improve fabrication and processing, and repair flaws. (See *S&TR*, September 2011, pp. 17–19; January/February 2015, pp. 19–22; January/February 2016, pp. 21–23; and July/August 2016, pp. 12–15.)

Recently, a team of OMST scientists, with input from collaborators at Lawrence Berkeley National Laboratory and the University of Rochester's Laboratory for Laser Energetics, completed a project funded by the Laboratory Directed Research and Development (LDRD) Program to examine in detail coupling mechanisms between lasers and contaminants on optical surfaces. Livermore physicist Manyalibo (Ibo) Matthews led the project, which aimed to understand how contaminant particles interact with laser beams, how particle shape and particle-induced damage affect beam propagation, and how damage morphology evolves in the presence of high-energy lasers.

Wear and Tear

Like many sensitive instruments, optical components are susceptible to dirt, debris, and defects at all phases of their production and operation, including fabrication, processing, handling, and installation. In addition, airborne particles generated during laser operation or present in a laboratory environment can relocate to other areas, potentially contaminating optical surfaces.

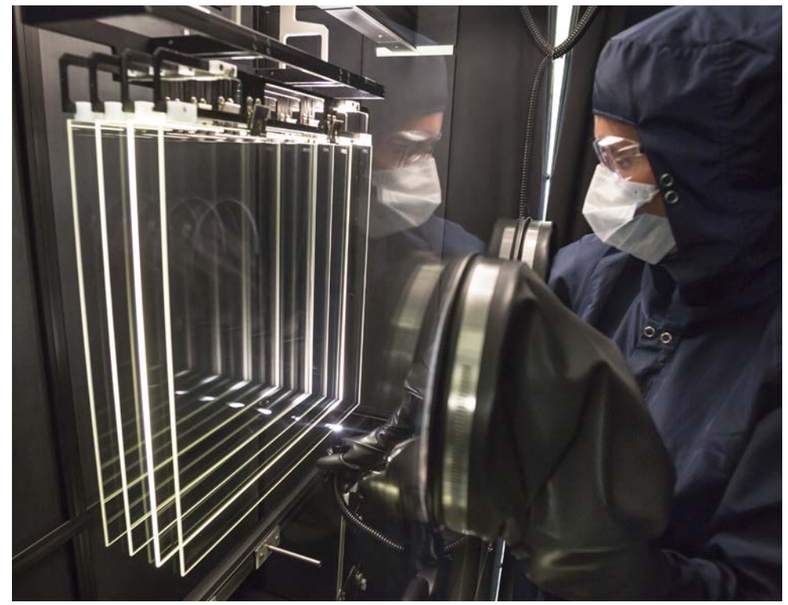
Optics closer to the laser's target encounter additional threats. At NIF, a disposable debris shield positioned between the final optics and the target can begin to break down with use, potentially introducing glass shards and particulates into the optical field. In addition, during an ignition shot, the target (a gold hohlraum containing a deuterium–tritium fuel capsule) is compressed as its holder is blown apart, generating fragments that can threaten the nearest optics.

Besides sustaining damage from surrounding materials, optics are directly affected by the high-energy laser beams. Repeated exposure over time contributes to accumulated defects. Furthermore, debris on the input side of an optical component can diffract incoming laser light, altering the beam path and promoting damage initiation on the exit side of the optic. Ironically, just as an attempt to clean eyeglasses might smear a substance across or grind particles into the lenses, dry laser cleaning—using a low-energy laser pulse to clear off debris—can also damage optics by creating shallow pits.

A Complex Approach

Matthews' LDRD team took a multifaceted approach to investigating the interaction of laser energy with micrometer-scale metallic and glass particles on optical surfaces. The researchers conducted experiments to measure particle velocity, plasma formation, and ejected material, and computer simulations were used to predict laser absorption and damage effects on beam propagation and performance. Livermore's robust diagnostic capabilities included a time-resolved imaging method that exposes nonuniformities in materials, and plasma emission spectroscopy, which measures spectral wavelengths of light generated during laser ablation of particles on optics.

Multilayer dielectric (MLD) coatings are an integral part of high-power laser systems for beam combination, beam steering, wavelength separation, and diffraction gratings. Team member Roger Qiu led tests to determine titanium particles' effects on the capping materials of MLD coatings.Titanium particles in general



At the National Ignition Facility, a low-cost disposable debris shield (several are shown here) protects the final optics from debris and contamination. However, the disposable shield is susceptible to damage, which, in turn, can cause glass shards and particulates to be introduced into the optical field.

can be generated in high-power pulsed-laser systems through laser ablation within beam dumps and the subsequent deposition of condensed metal vapor on nearby optics. By combining large-aperture laser damage testing, scanning electron microscopy, and numerical modeling, Qiu's team uncovered the responses of different capping materials on specific MLD mirror layers to laser–particle interactions. Qiu says, "The knowledge we gain from these experiments will guide new materials development to guard against laser-induced damage of MLD coatings."

Laser-induced pitting scatters the light from the laser and causes the optical surface to become hazy, but the team was not sure how problematic such effects were to overall laser performance. "We learned that metal contamination could cause shallow pits on the glass surface," explains physicist Eyal Feigenbaum, comparing the typical pit to the shape of a margarita glass. Feigenbaum created simulations of pit formation and morphology and developed models to characterize the resulting beam degradation. Further tests with large-aperture beams, in which large numbers of particles were evaluated simultaneously, enabled Feigenbaum to assess debris-caused damage characteristics.

A Range of Results

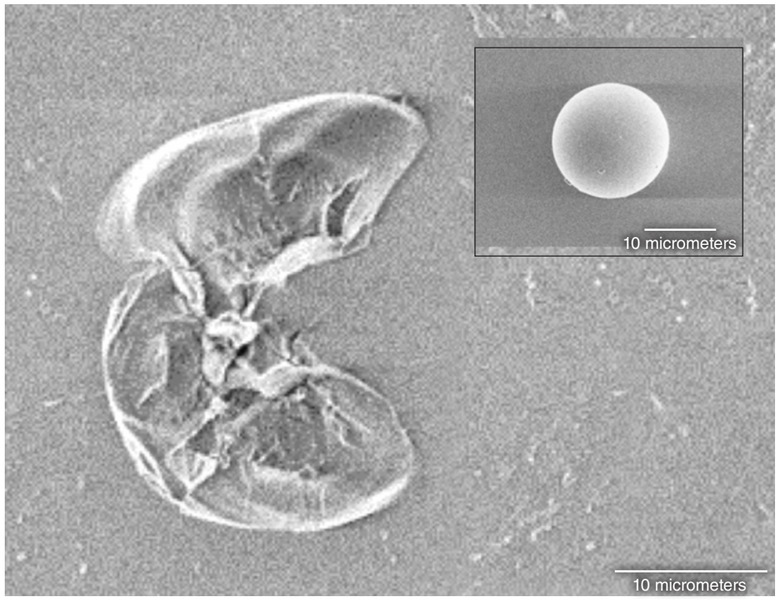
Matthews and colleagues found that the mechanisms governing laser–particle interactions depend on multiple factors. Regarding particle shape, the team saw a range of dispersal patterns following a laser pulse. In some cases, the momentum of a beam hitting a spherical particle yielded a donut-shaped distribution of fragments. Irregularly shaped particles, such as those formed by mechanical abrasion, produced a shielding effect via dispersion fields that mimicked particle shape. In the MLD experiments, Qiu observed a relationship with the coatings' properties. He notes, "Contaminant-driven damage of MLD coatings is strongly dependent on the shape of particulates and the thermal expansion and mechanical strength of the coating materials."

A particle's opacity also affects its behavior, as does the location of debris relative to the incoming beam. On an optical component's input surface, opaque particles tend to compress and disperse along the surface as the beam is obscured, whereas transparent particles tend to blow away from the substrate because more light energy is deposited into their interior. On the exit surface, the opposite occurs. Essentially, opaque particles are ejected while transparent particles break into shards and, under certain circumstances, fuse to the substrate, promoting damage initiation. Thus, opaque debris causes more damage on the input side, and transparent debris causes more damage on the exit side. These behaviors were key findings of the LDRD study.

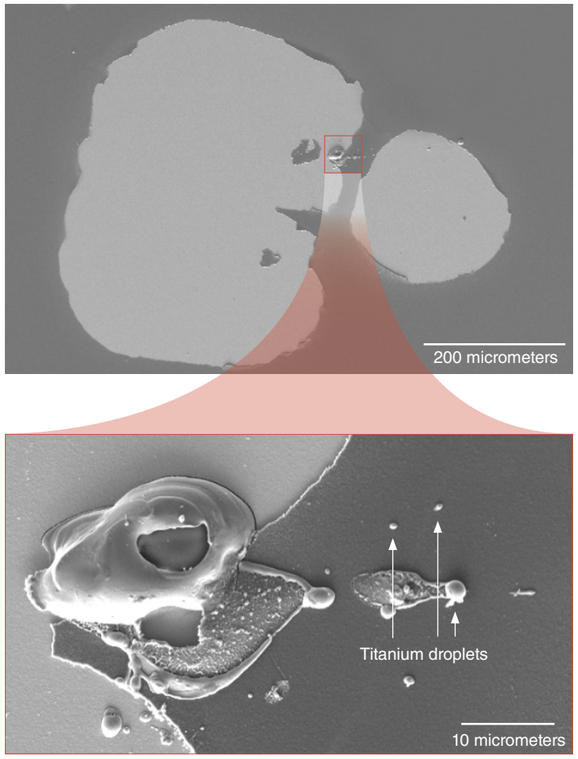
The team's experiments and simulations also revealed interesting features of particle ejection and dispersion. Some particles move from one location on the optical surface to another without ejecting. Others disperse quickly or slowly depending on the intensity of beam fluence, and still other particles liquefy and spray out from the surface. Calculating particle velocity and trajectory helps estimate the strength of ejection mechanisms, including secondary effects such as shockwaves reverberating inside and breaking apart particles. "Ejected material has to go somewhere," observes Matthews. "These findings can inform upgrades to laser-ablation processes with a goal of removing ejecta from optical surfaces."

As energy transfers from the laser beam to the particle—a mechanism known as pulsed-laser momentum coupling—plasma forms between the surface and the particle. Matthews' team studied the shockwave generated by the laser and the resulting plasma plume. They found that different types of particles vary in their reaction to the shockwave, and plasma flow changes as the particle moves. By measuring the speed and temperature of plume formation, the team showed that plasma is sensitive to laser fluence, wavelength variations, and beam angle.

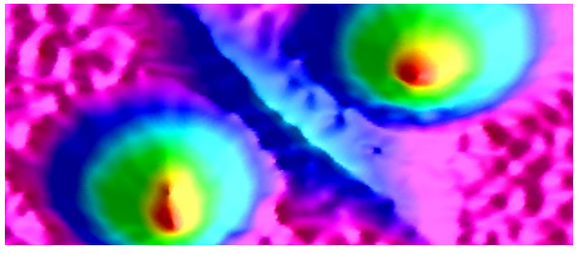
As for pits carved by metallic particles, Feigenbaum observed surprising behavior. "These shallow pits do not tend to grow with subsequent laser shots, so their effect is limited." But when the laser fires at higher energies, he warns, "Another mechanism kicks in, and deeper surface fractures are created. These fractures do grow with subsequent laser shots and limit an optic's lifetime." This relationship between beam intensity and pit and fracture formation allows scientists to evaluate beam-scattering effects on the system's performance. "The scattering model for the hazed-glass surface has been instrumental to operations and usability of NIF laser optics," says Feigenbaum.



A scanning electron microscopy image shows damage on a fused-silica surface following laser irradiation of fragments left behind by an initial laser pulse irradiating a spherical borosilicate particle (inset). Glass fragments remaining on a pristine optic in high-power laser systems can lead to catastrophic damage if left untreated.



Scanning electron microscopy images show damage to a multilayer dielectric surface contaminated with titanium particles. (inset) A close-up view reveals the surface's complex morphology and indicates the formation of molten titanium droplets.



A false color, three-dimensional rendering shows two laser-induced shallow pits (LSPs) on a silicon-dioxide optical surface. A cluster of LSPs also creates the linear-like groove in the center. Typical dimensions for LSPs are up to a few tens of micrometers in width and hundreds of nanometers in depth.

Damage Control

In keeping with the spirit of the LDRD Program, the team's experiments serve a larger purpose of innovation in optical design and laser performance. Understanding laser–matter interactions can inspire design improvements, such as vapor chemistry treatments, to make optics and coatings more impervious to damage or repellant to debris. Scientists can use these data to develop debris-removal techniques without compromising optical integrity and to enhance the Laboratory's computational capabilities to better predict contamination scenarios and prevent overuse. Cost savings naturally follow life-extension efforts.

Livermore's Directed Energy Program is poised to reap the benefits of this LDRD project in developing new types of laser technology, such as continuous wave and diode-pumped alkali lasers. Matthews also cites industrial settings in which optical surfaces play an important role, such as in lasers used to generate patterns or for machining materials with holes. He also recognizes the value of his team's findings for the next-generation of durable optical elements. He states, "Continuing our efforts to understand and control laser damage in high-power laser systems is crucial to maintaining NIF and supporting our missions for the National Nuclear Security Administration."

—Holly Auten

Key Words: debris, high-power laser, Laboratory Directed Research and Development (LDRD) Program, National Ignition Facility (NIF), optic, optical damage, optical system, Optics and Materials Science and Technology (OMST) organization, particle, plasma formation, surface contamination.

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