Future research directions for interface engineering in high temperature plasticity

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Abstract

This paper summarizes briefly some of the conclusions arising from the workshop on Grain Boundary and Interface Phenomena in the High Temperature Plasticity of Solids and outlines possible directions for future research.

1. Introduction

The workshop on Grain Boundary and Interface Phenomena in the High Temperature Plasticity of Solids provided strong confirmation of the validity of combining apparently diverse fields within the broad framework of interface engineering.

In order to consider future research directions, it is useful initially to examine the use of grain boundary design as it applies to polycrystalline metals and ceramics, and then to consider separately the problems associated with three classes of materials where interface phenomena are often the dominant factor in determining the nature of high temperature plasticity: superplastic materials, nanocrystalline materials and composite materials.

2. Grain boundary design

Using high resolution electron microscopy on bicrystals with well characterized grain boundaries, it has been possible in recent years to make rapid progress in evaluating the atomistic structure and properties of grain boundaries and interphase boundaries (including heterophase interfaces between dissimilar materials). As a result of these studies, it is known that grain boundaries and interfaces have substantial structural variability and exhibit significant differences in their properties. It is now well established that the properties of grain and interphase boundaries depend strongly on the precise type and structure of the boundaries. Until recently, it was usual to consider the influence of grain boundaries in terms of their geometrical aspects, such as grain size (*i.e.* grain boundary density) and grain boundary inclination; an example is unidirectionally boundary-aligned materials produced by solidification. Thus, the role of boundary structure was generally not included.

An important current problem is bridging the gap between the structure-dependent properties of individual boundaries and the boundary-related bulk properties of a polycrystal. A new microstructural parameter has been introduced, termed the grain

boundary character distribution (GBCD), to bridge this gap and to provide a tool for designing and controlling the boundary-related bulk properties of polycrystalline materials.

By using SEM-ECP or SEM-EBSP techniques, it is feasible to characterize experimentally a large number of grain boundaries in a polycrystalline material. This type of statistical analysis is needed in order to understand the collective behavior of boundary-related bulk properties in polycrystals. Very recently, the use of grain boundary design has been developed for advanced polycrystalline materials, and this has permitted basic investigations of the GBCD in polycrystalline metallic, ceramic and semiconducting materials whereby the processing methods are modified appropriately in order to enhance the desirable properties (for example creep resistance and fracture toughness for high temperature structural materials). Using these procedures, some success has been obtained with metals and intermetallics. There is also evidence for improvement in stress corrosion cracking in nuclear reactor materials by control of the GBCD.

In general, the GBCD is closely related to the grain size and to the type and sharpness of the texture in metals produced thermomechanically. Moreover, the GBCD may be affected dramatically by microalloying with specific elements. These findings may help in understanding the microalloying effect in the bulk properties of some polycrystalline materials.

Present evidence suggests that the GBCD is not a sufficient parameter to control adequately the properties of advanced materials. Information is also needed on the connectivity between like or unlike types of grain boundaries in polycrystalline materials. For example, intergranular fracture occurs and propagates preferentially at and along high-energy random boundaries, giving a loss of ductility in polycrystalline materials. It is now possible to use GBCD analysis to determine the connectivity for a large number of grain boundaries (for example, a few thousands of grain boundaries) by using computer-aided analysis of the grain boundary character and the geometric configuration.

The effect of the grain boundaries on the bulk properties of polycrystals becomes more significant as the grain size decreases to the nanocrystalline scale. To date, little or no attention has been given to the use of GBCD in nanostructured materials, and instead discussion has centered on the size of the crystallites (and therefore on the density and volume of the grain boundaries) without attention to grain boundary type or structure. At present, it is not clear whether the structure of grain boundaries is similar between conventional polycrystalline materials with ordinary grain sizes and nanocrystalline materials. There is also the

possibility that triple junctions may play a greater role in nanocrystalline materials and a detailed characterization of triple junctions is therefore needed.

There appears to be much opportunity for grain boundary design and control in both nanocrystalline and conventional polycrystalline materials. By considering grain boundaries as two-dimensional lattice defects and incorporating their structural and geometric characteristics, it should be possible to design and control internal interfaces both geometrically and statistically, and thereby to attain higher performance in a wide range of advanced polycrystalline materials.

3. Superplastic materials

Research into superplasticity has developed extensively in recent years, to the extent that there are now several important directions for future investigations. These various directions arise in large part because of the diversity of materials in which superplastic deformation has now been established. On the one hand, superplasticity is a well developed technology based on nickel, titanium, iron, and aluminum alloys. On the other hand, superplastic behavior has been observed recently in structural ceramics (including yttria-stabilized zirconia polycrystals and alumina), functional ceramics (including hydroxyapatite), ceramic composites (including alumina-reinforced yttria-stabilized zirconia, silicon carbide-reinforced silicon nitride, and iron carbide/iron composites), intermetallics (including nickel silicides, and nickel and titanium aluminides) and metal matrix composites. Based on the nature of this wide range of materials, it seems reasonable to conclude that there can be no single mechanism to explain the superplastic effect.

A consistent feature of the ceramic-based materials made superplastic to date is that they are all fine grained. The prime example is 3 mol.% yttria-stabilized tetragonal zirconia polycrystal (3Y-TZP), where elongations have been reported of up to 800%. An area of keen interest is whether a glassy phase is required at the grain boundaries in order to achieve superplastic deformation. Although glassy phases have been observed at grain boundaries in some superplastic ceramics, at least one study used high resolution electron microscopy and X-ray photoelectron spectroscopy to demonstrate an absence of any such phases. It was concluded from this study that the presence of a glassy phase is not necessary for a superplastic ceramic. However, the presence of a glassy phase can certainly affect the deformation behavior of superplastic ceramics and it is important to determine whether or not glassy phases are required.

Another new area is superplastic behavior at very

high strain rates in metallic alloys, metal matrix composites and mechanically alloyed materials. The normal rate of superplastic forming is relatively slow $(10^{-4}-10^{-3}\ s^{-1})$ compared with many manufacturing processes. The generation of a new set of microstructural conditions to make grain boundary sliding more facile, and to inhibit the slip creep process, can serve to increase the maximum strain rate for superplastic flow. The most straightforward approach is by microstructure refinement. Thus, ultrafine-grained (around 0.5 μm) mechanically alloyed aluminum alloys are found to exhibit elongations of more than 1000% at 50 s^{-1}. The precise deformation mechanism occurring in these materials is not understood and deserves further study.

An important processing area that has led to these ultrafine-grained materials is through the utilization of nanophase or even amorphous materials. Certain combinations of composites of Al alloys containing SiC, β-Si_3N_4 or α-Si_3N_4 whiskers have been shown to behave in a superplastic-like manner (up to more than 500% elongation) at high strain rates of 0.1–1 s^{-1}. In all of these cases, the phenomenon is observed at temperatures both above and below the solidus of the matrix. It is clear that this is potentially a very important area but much work is needed to understand the flow mechanisms and in particular the contributions of the grain boundaries, the metal–ceramic whisker interfaces, and the liquids in such materials.

In addition to the above fine structure superplasticity, there is also internal stress superplasticity. When internal stresses are developed, considerable tensile plasticity can take place (by a slip creep mechanism) under the application of a low external stress. Internal stresses can be generated by the thermal cycling of composite materials in which the constituents have different thermal expansion coefficients, thermal cycling of polycrystalline pure metals or single-phase alloys that have anisotropic thermal expansion coefficients, and by thermal cycling through a phase change. Experiments show that internal stress superplasticity can be utilized to enhance the ductility of metal-matrix composites, a Zn–30vol.% alumina particulate composite, zinc and α-U.

Much progress has been made recently in understanding both the role of cavitation in superplastic metals and the methods for suppressing cavity growth by imposing a hydrostatic pressure. Debate remains as to whether all cavities in superplastic metals are pre-existing or whether they are all nucleated during superplastic flow. It is also now becoming recognized that the maximum tensile elongations of superplastic ceramics are related to the flow stress rather than to the value of the strain rate sensitivity as is the case for metals. The reason lies in the fact that polycrystalline ceramics are susceptible to grain boundary separation.

In superplastic ceramics, there is a very clear need to expand the database to much wider ranges of strain rate and grain size. By comparison, the database for metals is far more extensive. In the area of models and mechanisms for superplastic flow, there are major omissions that should be addressed. For example, models for superplasticity do not incorporate the low or high angle nature of grain boundaries, the grain morphology or the occurrence of dynamic grain growth. Quantitative measurements of grain boundary sliding must be carried out with greater care than heretofore because recent analyses show that the measurements to date often tend to be in error.

The combined superplastic-forming and diffusion bonding process (SPF–DB) has commercial importance in the manufacture of sandwich structure products. Although DB was demonstrated in titanium alloys, only limited success has been achieved to date in aluminum alloys using specialized techniques. An area of future study is clearly the development of SPF–DB for aluminum alloys, but this is very challenging because of the tenacious oxide layer existing on aluminum alloys. It is worth noting that some preliminary studies on DB of superplastic ceramics have now been carried out. There has been also the development of superplasticity in laminated composites containing at least one superplastic component.

Very limited quantitative information is now available to evaluate the variables involved in making bulk products from superplastic materials. Of special potential significance is the possibility of achieving new bulk shapes through powder metallurgy with the use of superplastic fine-structure powders. For example, sinterforging of ultrafine Y_2O_3-stabilized ZrO_2 powders has been successfully demonstrated.

4. Nanocrystalline materials

The study of nanocrystalline solids (metals, ceramics and intermetallics with grain sizes less than 100 nm) is a relatively new discipline, even though the groundwork for some of the current studies was developed over several decades of research in submicrometer-grained materials. Although the rapid expansion of the nanocrystalline field in the last 5 years has been accompanied by numerous difficulties and conflicting claims, it is clear that nanocrystalline materials provide a unique resource and an opportunity to solve historically difficult problems of both a scientific and technological nature.

As with any new field, the enthusiasm engendered by the initial reports of nanocrystalline solids has since been tempered by realism and practical experience. Thus, nanocrystalline materials are no longer seen as a

fundamentally new form of matter and a few of their remarkable properties reported in the early literature have since turned out to be artifacts of the difficult and unusual techniques employed to make the measurements. The initial problems of very small sample size, and the consequent difficulty of property measurements, have since been overcome by a plethora of new techniques designed to produce materials in ever greater quantities and in larger bulk dimensions. However, the variety of fabrication techniques leads to its own problems, since property variations due to differences in processing techniques may easily mask property variations due to the very fine grain sizes. Even when using the same starting materials, slight differences in sample fabrication may yield remarkably different results. A case in point is the controversy over whether hardness increases or decreases with grain size (positive *vs.* negative Hall–Petch slope) in nanocrystalline metals fabricated by different methods. Careful characterization of existing materials and methods of manufacture will be required before specific properties can be attributed unambiguously to the nanocrystalline nature of the microstructure.

From a scientific viewpoint, it is perhaps the length scale of nanocrystalline microstructures that will provide some of the most fascinating insights into mechanical behavior. Many of the existing theories for mechanical behavior rely on phenomena (*e.g.* long-range stress fields) or configurations (*e.g.* dislocation pile-ups, active Frank–Reed sources) that are too large to fit within 5 nm grains. If conventional behavior continues to persist even at these small grain sizes then clearly it will be necessary to reconsider the origins of conventional behavior in large grained polycrystals.

Nanocrystalline grain sizes also offer a unique opportunity to investigate the effects of boundary geometry on mechanical behavior. With such a high concentration of grain boundaries, the characteristics of the boundaries are expected to dominate the mechanical behavior. Thus it will be possible to observe the effects of high *vs.* low angle boundaries, special (low energy) *vs.* random boundaries, excess grain boundary volume, and tilt *vs.* twist components. The newly produced nano-amorphous intermetallics may allow a further distinction between grain boundary behavior relying on a reasonably ordered boundary structure and the behavior arising solely from the free volume considerations which are present even when the boundary is created by the impinging of non-crystalline grains. It will be a daunting challenge to fabricate nanocrystalline materials with specific well controlled grain boundaries, but hopefully this will be addressed in the next generation of studies.

Technological developments spurred by the field of nanocrystalline materials have been at least as significant as the scientific achievements. Several studies have shown that the manufacture of nanocrystalline materials often leads to the formation of novel phases which may, in turn, have unusual properties. Work on single-phase ceramics has indicated that nanocrystalline grain sizes confer enhanced superplasticity when the ceramic is essentially fully dense; the same ceramics in the porous state have very well defined pore size distributions that may permit their use as discriminating filters. In metals, near-nanocrystalline grain sizes are already being incorporated into Co–WC cutting tools for the machining industry, leading to substantial increases in strength and wear resistance. Finally, the sustained effort devoted to the manufacture of a solid with extremely fine grain sizes has led, in the case of ceramics, to a much better understanding of the processing issues involved in controlling densification and grain growth.

The field of nanocrystalline materials has the potential to contribute substantially to the scientific and technological knowledge base. Additionally, the initial problems due to the lack of large-scale production methods are now being overcome. For example, it is possible to manufacture large ingots of 10 nm grained metallic alloys by thermomechanical processing, and numerous techniques have been developed for the large-scale production of nanocrystalline powders (high temperature pyrolysis, spark erosion, chemical synthesis, continuous stream gas phase condensation, *etc.*). Unfortunately, few of these techniques have been adopted to date in industrial practice.

The field of nanocrystalline materials now faces different challenges. Careful characterization is becoming increasingly important, so that grain size effects can be distinguished from the microstructural effects due to impurities or the presence of residual porosity. The processing of nanocrystalline materials from nanometer-scale powders needs to be better understood. Finally, a major challenge is the inherent diversity of the field, which ranges from the production and consolidation of ultrafine powders to the potential development of superplastic forming techniques. Often, the successful development of a nanocrystalline material relies on working partnerships between chemical engineers, physicists, materials scientists, and process engineers. If this diversity of expertise becomes recognized as an integral component of interface engineering, it may be possible even in the reasonably short term, to develop a coordinated approach that covers all aspects of the nanocrystalline field from production to ultimate utilization.

5. Composite materials

The term "composites" refers to a class of materials that is extremely diverse. Consequently, it is challenging to find unifying principles that govern mechanical behavior and thereby to apply general concepts. Nevertheless, a consideration of the high temperature plasticity of composites and associated interface phenomena reveals a set of problems and requirements that appears to be common to most, if not all, composites. The materials systems are vastly different, including matrices of all varieties of ceramics and metals, and various reinforcement materials in geometries that range from continuous fibers to whiskers to particles. The problems, however, are often similar or at least related.

One of the pervasive difficulties is that composites deforming at high temperatures are subject to environmental effects. In particular, these effects often involve thermal oxidation of the reinforcements. Nearly all of the presently available reinforcements for high-temperature composites are carbides, specifically silicon carbide, and SiC is susceptible to oxidation at high temperatures. For SiC reinforcements, the reaction products generally involve silica glass and carbon monoxide gas, and these phases are deleterious to nearly all composite properties, including creep resistance, fracture toughness, fiber strength, and fracture resistance. Several approaches are possible to deal with this problem. New fibers of oxides or oxidation resistant compounds would be valuable, although the development of such fibers may prove costly and time consuming. There is at present a growing interest in alumina and YAG (yttrium aluminum garnet) fibers, although cost, availability, and consistency are often prohibitive factors. A second approach involves protective coatings on fibers or on composite components although this may add a prohibitive cost to the material. Finally, matrix additives that modify the properties of intergranular glass films and/or boundaries is an option that has had some success in monolithic ceramics, and it is useful to consider this approach as an example of "grain boundary design".

A second problem with composite materials is the need to develop simple and consistent testing methods in order to evaluate interface properties. One approach to this problem is to construct interfaces in model geometries that, while far different from typical composite geometries, offer the prospect for a fundamental understanding of interface behavior. The results of these investigations must be subsequently extrapolated or linked to real composite morphologies. A second approach is to accept the given material geometry and to develop methods to probe the individual fibers by either pulling them or pushing them out of the matrix. The so-called "push-out" test is gaining wide acceptance because the sample preparation is relatively tractable compared with the pull-out test, and sophisticated load- and depth-sensing indenters are now commercially available to achieve the push-out. However, interpretation of these results is not trivial and elevated temperature testing may be difficult. Furthermore, the test does not necessarily provide all of the required information on interface properties.

Finally, it is apparent that the interface characteristics required for one property may conflict with the requisites for a second property. For example, it is widely accepted that a weak interface is desirable for high fracture toughness at room temperature whereas a strong interface is required for creep resistance and strength at high temperatures. The challenge for materials designers is to meet two (or more) apparently contradictory requirements in one material. This requires novel approaches and the use of interface engineering to design interfaces with selected properties. For the example posed above, it is possible to consider fiber coatings with a thermal expansion coefficient such that at high temperatures the fiber experiences high frictional forces during sliding while at low temperatures the sliding (or pull-out) is relatively easier. The prospect of being able both to design interfaces and to implement these designs in selected composites is now feasible and this approach will undoubtedly play a major role in future composites research.