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MECHANICAL PROPERTIES OF NANOPHASE METALS*

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Abstract -- Nanophase metals have grain-size dependent mechanical properties that are significantly different than those of their coarse-grained counterparts. Pure metals are much stronger and apparently less ductile than conventional ones; intermetallics are also strengthened, but they tend toward increased ductility at the smallest grain sizes. These property changes are primarily related to grain size limitations, but they are also affected by the large percentage of atoms in grain boundaries and other microstructural features. Strengthening appears to result from a limitation of dislocation activity, while increased ductility probably relates to grain boundary sliding. A brief overview of our present understanding of the mechanical properties of nanophase metals is presented.

INTRODUCTION

The mechanical properties of materials depend fundamentally upon the nature of bonding among their constituent atoms and upon their microstructures on a variety of length scales. Mechanical deformation can be either elastic (reversible) or plastic (irreversible). Elastic deformation is effected through reversible changes in the interatomic spacings or the bending and stretching of bonds between atoms; it is governed by the elastic constants or moduli of a material, which indicate how easily such deformation occurs. For metals, such deformation is in general relatively easy owing to the non-local nature of metallic bonding, but for materials with strong covalent or ionic bonding, such as intermetallic compounds or ceramics, it is much more difficult.

In order to deform a material plastically, atomic ensembles must be displaced with respect to one another in a cooperative fashion. The easier that this process can be accomplished, the greater the ductility of the material. This deformation most frequently entails the motion of dislocations, the crystal lattice defects that facilitate such cooperative motion by localizing it. Dislocation motion then propagates this local displacement by a sequential disturbance of a much smaller subset of the atomic ensemble to be displaced. The unit displacement associated with a dislocation is defined by its Burgers vector, which has a magnitude that is usually on the order of an interatomic spacing and a direction that can vary between being parallel to the dislocation line (screw dislocation) or perpendicular to it (edge dislocation). Dislocation motion can be conservative ("glide") or non-conservative ("climb"); the former occurs without the creation or

annihilation of atomic defects, such as vacancies, whereas the latter requires such defects and is thus a process that requires thermal activation (1,2).

The ease of dislocation motion and creation at dislocation sources depends upon the nature of the atomic bonding in the material and also upon the material's microstructure. It is much easier (i.e., energetically favorable) to create and move dislocations, both of which involve bond bending and breaking, in metallically bonded materials than in either ionic or covalent solids. In ionic materials, charge neutrality conditions provide stringent constraints on the motion of such extended defects, while in strongly covalent solids, the breaking and bending of these highly directional bonds can require considerable energy. Even for metallic systems, where the degree of covalency can vary from essentially zero in a simple metal to moderate in a refractory transition metal to rather strong in an intermetallic compound, the difficulty in creating and moving dislocations can vary significantly, leading to very different mechanical behavior.

In some cases, plastic deformation can also occur by other mechanisms which depend more strongly on time and temperature than dislocation glide. Such deformation is usually called "creep" and may be effected by dislocation climb, atomic diffusion, and/or such a mechanism as grain boundary sliding, in which the grains of a polycrystal slide over one another, but remain fully bonded through the action of local diffusional healing processes in the interfaces between the grains. Creep rates in polycrystals depend strongly upon the grain size (d) and vary from d^{-2} behavior in cases where the mechanism is volume diffusion controlled (Nabarro-Herring creep) to d^{-3} behavior in cases in which the mechanism is interface diffusion controlled (Coble creep or Ashby-Verrall creep). Thus, as one enters the nanophase regime from conventional grain sizes and d is reduced greatly, the mechanical behavior can change dramatically (3,4).

In conventional metallic materials, strengthening during plastic deformation occurs with an increase in the dislocation density by dislocation multiplication mechanisms and the interaction between dislocations. A dislocation moves under the influence of a stress applied to the material; upon encountering an obstacle in its path, this stress must be increased to continue its motion. Obstacles to dislocation motion may be the stress fields of other dislocations or alloying elements, precipitates, or grain boundaries. It is thus common to strengthen these materials by a variety of methods to make dislocation motion more difficult. These include decorating them with impurities ("solute strengthening") that would have to be dragged along by the moving dislocation (or broken away from) or introducing obstacles to their motion, such as precipitates ("obstacle strengthening") or other dislocations ("work hardening").

Grain size reduction can also yield improvements in mechanical properties, such as strength and hardness (3,4). This results at larger grain sizes from the introduction of additional grain boundaries that can act as effective barriers to dislocation motion and at the smallest grain sizes in the nanoscale regime from the paucity of existing dislocations and the difficulty in generating new ones (5,6). Hence, it has been found that grain size reduction from the conventional tens to hundreds of μm to the nanophase regime below 100 nm leads to improvements in these mechanical properties. However, grain size reduction may also have negative impacts on other mechanical properties, such as creep rate and ductility. On the other hand, in materials that are conventionally quite strong but very brittle, such as intermetallic compounds and ceramics, enhanced ductility from grain size reduction, through the increased probability of grain boundary sliding, can potentially offer considerable processing and performance advantages. Our current understanding of the mechanical properties of nanophase metallic materials is briefly reviewed here.

MECHANICAL BEHAVIOR

Hardness

Most extant experimental results on the mechanical behavior of nanophase metals are from measurements of hardness, which like strength typically derives from the difficulty in creating dislocations and the impedance of their motion by the development of barriers. It is commonly measured using a Vickers microhardness tester in which a pyramidal diamond indenter with a square cross-section is loaded with a specified force and applied to the sample surface for a given period of time. It has long been observed experimentally in conventional metallic materials that the hardness varies with the grain size through the empirical Hall-Petch relation:

$$H_v = \sigma_0 + k_0 d^{-1/2}$$

where H_v is the hardness, σ_0 is the intrinsic stress resisting dislocation motion, k_0 is a constant, and d is the grain diameter; the hardness variation with grain size is thus usually presented in a H_v versus $d^{-1/2}$ plot. A number of models have been proposed to explain this grain-size dependent hardness variation in conventional materials in terms of dislocations and other microstructural features (2,4). Recently, additional models have been proposed to explain whether metallic materials will harden or soften with grain size reduction into the nanophase regime (7-11).

The experimental results to date for room temperature microhardness testing of pure nanophase metals show these materials to be considerably harder, by factors of from 2 to 7, than their coarse-grained counterparts. Hardness increases are apparently independent of synthesis method; nanophase metals produced by gas condensation (12,13), mechanical attrition (14,15), electrodeposition (16,17), and wear (18), and a nanophase semi-metal formed by crystallization (19), all show similar trends shown in Fig. 1. But, the hardness of as-consolidated nanophase Cu and Pd has been shown to increase further with a modest anneal (20); thus, measured hardness variations can be dependent upon the method used to vary the grain size (21). Samples usually exhibit increased hardness with decreasing grain size when individual samples are compared; however, an apparent softening (an artifact) has been observed (22) for samples annealed to increase their grain size.

Several studies have shown that when intermetallic alloy samples are tested, initial hardening with decreasing grain size is also observed, but that at further reduced grain sizes either hardening at a reduced slope occurs or softening is often seen, as shown in Fig. 2. Nanophase intermetallics produced by gas condensation (23), mechanical attrition (24-26), electrodeposition (27), and crystallization from amorphous precursors (28-32) show that these effects are independent of synthesis method. The observed transitional behavior from hardening to softening with decreasing grain size can be quite complex, however, since thermal treatments of nanophase alloy samples and grain size variation itself may cause changes in the structure and composition of the grain boundaries, densification, phase transformations, and stress relief, any of which may affect the relationship between grain size and hardness.

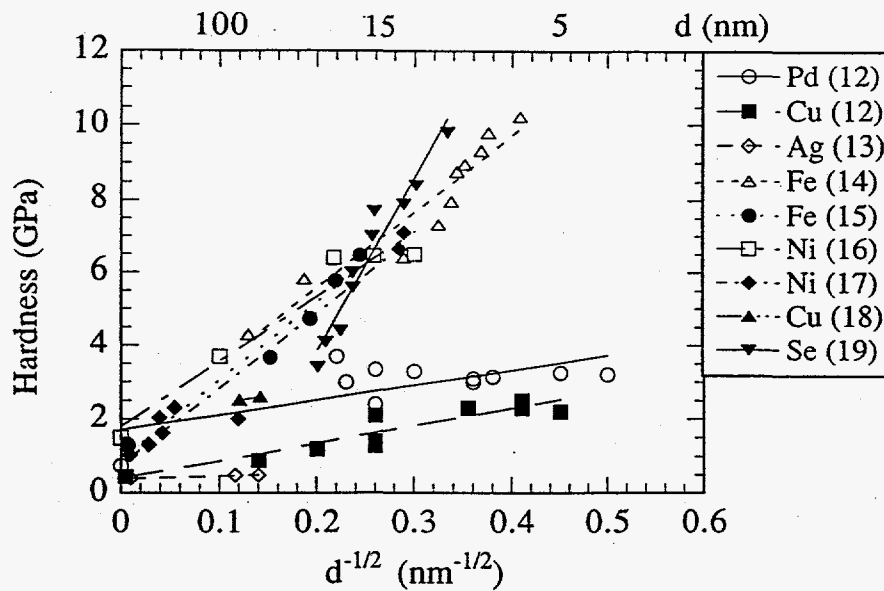


Figure 1. Room temperature hardness versus grain size for nanophase metals (12-19) compared with the hardness of their coarse-grained counterparts (values near origin).

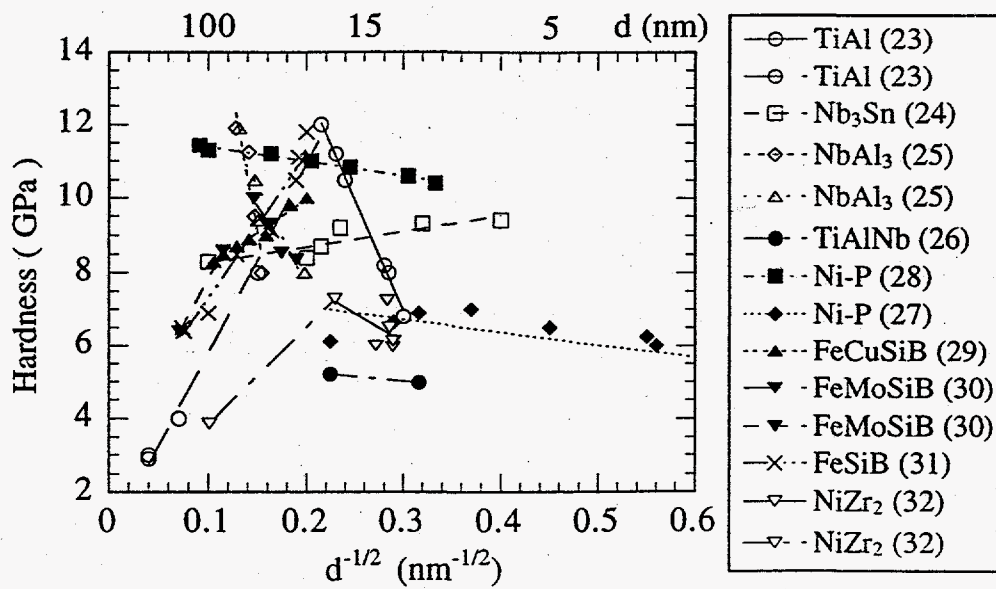


Figure 2. Room temperature hardness versus grain size for a variety of nanophase intermetallic alloys (23-26, 28-32) and a Ni-P solid solution (27).

While it is clear that the hardness of pure metals increases as their grain sizes are reduced into the nanophase regime, the full extent to which this hardening occurs is not yet clear. Insufficient data exist for a comparison of hardness measurements on the same nanophase material made by different methods. The presence of sample porosity, flaws, or contamination from synthesis and processing could influence the available hardness results, as could the nature of the grain boundaries and their state of relaxation. Nevertheless, the strong similarities among the grain-size dependent hardness data shown in Fig. 1 and also in Fig. 2 indicate that at least the trends appear to be reproducible from method to method among the data for pure metals and for intermetallic alloys.

Tensile Strength and Fracture

Just as hardness typically derives from the difficulties in creating dislocations and the provision of barriers to dislocation motion, similar mechanisms are responsible for strengthening conventional materials. The challenge to date for nanophase materials has been the acquisition of sufficient volumes of material for tensile strength testing. The testing of a material in uniaxial tension consists of extending a specimen whose longitudinal dimension greatly exceeds the cross-sectional dimensions, all of which need to be large compared with the grain size for reliable measurements to result. This test measures the strength of the material in tension, and typically the data are plotted as stress σ (load per unit cross-sectional area) versus strain ϵ (longitudinal displacement per original or instantaneous longitudinal length); such a plot shows typical regions of elastic and plastic deformation. The slope of the elastic portion of the stress-strain curve is an indication of the elastic stiffness of the material and is the Young's modulus in a pore-free, flaw-free material. The limit at which the deformation becomes permanent or plastic usually is taken as 0.2% strain, and the stress at which this occurs (σ_y) is the yield strength of the material. The total strain to fracture as well as the stress level at which the sample fails, the fracture stress, are other important parameters that can be obtained from such data. Work hardening, in which the material becomes increasingly stronger after yielding because of dislocation interactions, can also be observed if present.

Enhanced tensile strength of nanophase materials may be expected solely from the difficulty in generation and motion of dislocations (12) in their ultrafine grains, which has led to their increased hardness. The nanophase materials tested in tension thus far have been face-centered cubic metals; they have exhibited similar improvements in strength as those seen in their hardness behavior (see Fig. 3), but they have also showed limited ductility. Relative to their coarse-grained counterparts, the tensile strength of the nanophase metals increased by factors ranging from 1.5 to 8 depending on their grain size and the material (12). The extent to which the tensile strength improved with grain size refinement to about 25 nm, for example, is on the order of that produced by cold working polycrystalline material (13). The limited levels of ductility exhibited by nanophase metals may possibly arise because of difficulties in creating, multiplying, and moving dislocations, but may as well relate to the presence of significant flaw populations in these materials (12,33). Retesting of larger grained ($d=50$ nm) nanophase Ag did show enhanced ductility and some evidence of work hardening (13). Annealing after consolidation has resulted in improved ductility of cluster consolidated nanophase metals (34) and of mechanically attrited submicron grain-size materials (35).

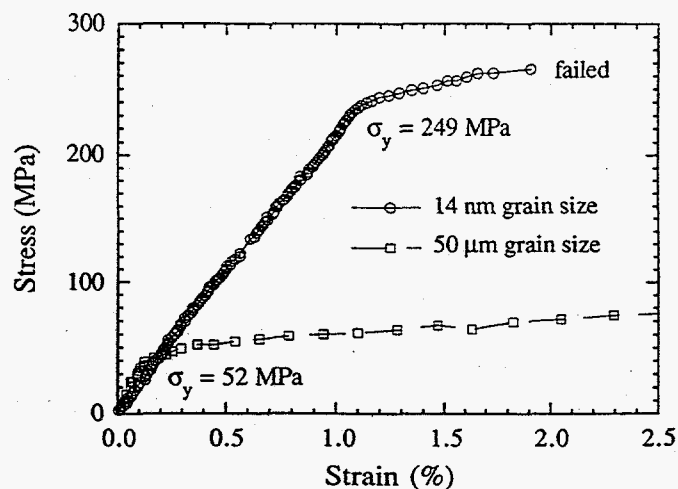


Figure 3. Stress-strain curves for nanophase and annealed coarse-grained Pd (36).

Elastic modulus changes can be expected as materials enter the nanophase regime; however, reduced apparent modulus values can also result from sample porosity. The apparent elastic moduli measured to date on nanophase materials (12,37) have been decreased in value relative to those in their coarse-grained counterparts, probably because of porosity and flaws resulting from processing (36). For nanophase Pd samples with residual 4-16% porosities, for example, the apparent Young's modulus values were 2-6 times smaller than that of coarse-grained Pd (12). This reduction in Young's modulus may be a result of the enhancement of the stress intensity factor from pores in the material (38); in contrast, the Young's modulus of pore-free, electrodeposited nanophase Ni-P yielded a value comparable to that for coarse-grained Ni.

In the practical application of materials, often it is not the inherent yield strength of the material which limits its application, but its fracture strength. A material can yield and sustain itself against imposed stresses by taking advantage of microstructural features like dislocations and grain boundaries which prolong plasticity. However, a material which has inherently high strength can also fail in a sudden and brittle manner with little plasticity, thereby hindering its usage.

The results to date on the fracture properties of nanophase materials have been limited in scope and hindered by the presence of porosity or interfacial phases in the samples tested. Bending tests of fully-dense Ni-P showed that the grain size reduction into the nm regime resulted in higher values of the fracture stress and the strain to fracture (39). The variations in the fracture properties due to grain size were attributed to the changes in the volume fraction and density of the interfaces. However, the acknowledged presence of additional phases of free Ni and Ni₃P complicates the interface-controlled fracture behavior (40). HREM studies of in-situ fracture of nanophase Au and Au/Si composite films on Al substrates showed a strong dependence of the fracture behavior on the grain size (41). For grain sizes below 25 nm and slow strain rates, the deformation and fracture were driven by diffusional mechanisms bridging the crack formation and propagation. When the grain size was increased above 35 nm, the cracks

grew both through and around the grains. In both grain size regions, the contribution to plasticity by dislocations was deemed negligible because dislocations were not imaged during the testing.

Compressive Strength and Creep

The unique microstructures of nanophase materials are likely to have significant effects on their mechanical behavior. The intercrystalline region composed of grain boundaries and triple junctions can comprise almost 50% of the volume fraction of 5 nm grain size material (42). This extensive intercrystalline region is expected to have a profound effect on the bulk mechanical behavior, such as ductility and grain boundary migration and sliding, in nanophase materials. Since creep is primarily controlled by diffusion, it is expected to occur readily in nanophase materials because of the large volume fraction of uncontaminated grain boundaries and the extant short diffusion distances. Diffusion along the intergrain contacts is very rapid, and mechanisms similar to those that drive sintering and neck formation at room temperature in nanophase metals may enhance also the creep rates in these materials. Creep rates may also be influenced by the level of porosity in nanophase samples, since free surfaces tend to increase diffusion rates relative to grain boundary rates.

Nanophase ceramics have demonstrated greatly enhanced ductility (43,44). True compressive creep testing of nanophase intermetallic materials, although limited in the number and variety of materials tested, has substantiated this enhanced plasticity and also increased compressive strength. As shown in Fig. 4, after the mechanical attrition of 75 μm grain size Fe-28Al-2Cr powder to produce 80 nm grain size nanophase material, and subsequent shock consolidation, the samples, when tested in compression at room temperature, exhibited extreme plasticity (true strains >1.4) and increased yield strength (almost 10 times that of the coarse-grained material) (45), as well as a further average grain size reduction to ca. 10-15 nm.

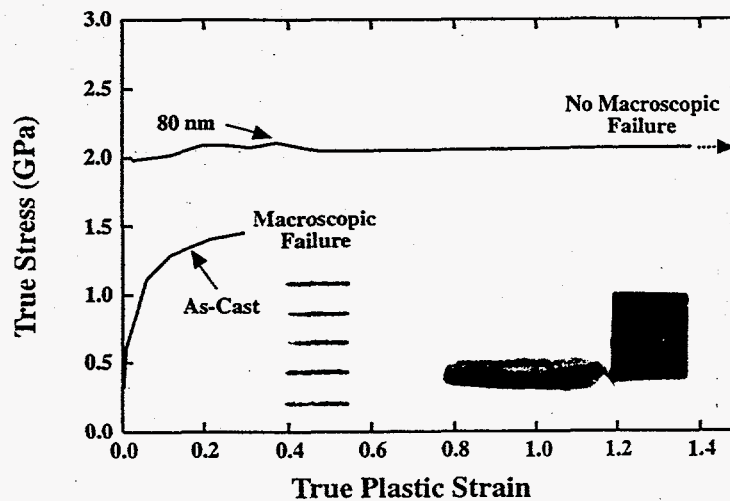


Figure 4. Nanophase Fe-28Al-2Cr sample before and after compression (inset) along with the stress-strain curves for the nanophase and coarse-grained, as-cast material (45).

Hardness testing at elevated temperatures can also indicate compressive creep behavior of nanophase materials. Although typically used as a static tool, by increasing the loading times with a constant load and at temperature, the indentation size can be monitored to yield dynamic compressive behavior. In such a way, the indentation sizes on nanophase TiAl with ca. 10 nm average grain size were seen to increase rapidly and then more slowly, indicating that a diffusion-controlled deformation process was occurring (46). The data obtained (see Fig. 5) appear to follow the Ashby-Verrall creep model (47) with a threshold stress occurring for a load >100 g. At low temperatures, the nanophase TiAl (23) showed little change in hardness until the temperature rose to the point that thermally activated deformation by diffusional creep started. An observed drop in hardness with temperature was attributed partially to densification under the indentation load and primarily to enhanced flow of the material (46).

To date the sole tensile creep measurements on nanophase metals have been for Cu and Pd (12) at room temperature, which exhibited stress-strain behavior logarithmic with time that apparently resulted from dislocation activity (48). No evidence for significantly enhanced Coble creep, as suggested by some earlier measurements on nanophase metals (22) and ceramics (49), was observed at room temperature for either Cu or Pd.

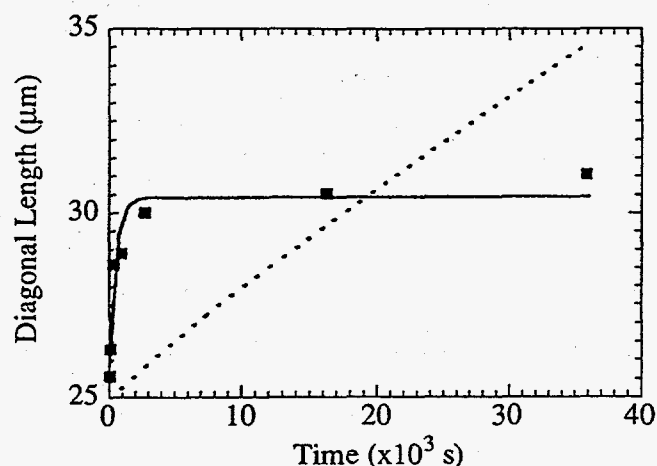


Figure 5. Diagonal length of a hardness indent on nanophase TiAl measured at 25°C for a 200 g load as a function of time compared with the behavior expected from Coble (.....) or Ashby-Verrall (—) creep (23).

DISCUSSION AND CONCLUSIONS

The presently available body of data on the mechanical properties of nanophase metallic materials, while still rather limited, has now grown to the point where a certain consistency is emerging and some general conclusions can be drawn.

It seems apparent from the generally observed increase in hardness with decreasing grain size, as well as from the observations of work hardening, decreased ductility, and logarithmic creep, that dislocation activity still dominates the mechanical behavior of pure nanophase metals

over the grain sizes that have been investigated. However, the dislocation activity appears to continually decrease with decreasing grain size from those levels normally found in conventional pure metals owing to a combination of the decreased availability of dislocations and the decreased ability to create new dislocations in the increasingly confined nanophase grains. Conventional Hall-Petch hardening from the introduction of increasing numbers of grain boundaries as barriers against dislocation motion seems to play an insignificant role in this grain size regime. The paucity of mobile dislocations in nanophase grains has been well documented experimentally (50) and is simply a result of the long known and well understood image forces that act on dislocations near surfaces and hence in confined media (51). The difficulty in creating new dislocations within the spatial confinements of ultrafine crystallites has also long been evident (5,6) from earlier research on single crystal whiskers and wear debris. Since the minimum stresses required to activate common dislocation sources (such as a Frank-Read source) are inversely proportional to the distance between dislocation pinning points, these stresses will increase dramatically with decreasing grain sizes into the nanophase regime owing to the limitation of the maximum distance between such pinning points. As metal grain sizes shrink down to ca. 1-2 nm (the actual number depends upon the specific value of the shear modulus), the theoretical yield stress of a dislocation free metal may be approached. Thus, it appears that the increasing hardness and strength observed in pure nanophase metals with decreasing grain size is simply a result of diminishing dislocation activity. While other mechanisms that have been recently suggested (7-11) might also play a role, no substantial experimental evidence for metal softening in this regime has yet been produced.

The situation regarding the observed mechanical behavior of nanophase intermetallic alloys or compounds is more complex, but also appears to have some degree of consistency. This is the case even though significant questions can and should be raised regarding the various effects of the grain size dependence of phase stability and solute segregation in the nanophase regime in these materials and even regarding the definition of grain sizes in these frequently multiphase systems. Nevertheless, for a number of the nanophase intermetallics investigated thus far, the mechanical response in the larger end of the nanophase grain size regime seems rather similar to that for the pure metals. However, a number of these typically harder and more strongly bound materials exhibit a clear transition from hardening behavior to softening behavior with decreasing grain sizes or, in some cases, only softening. The softening behavior or increased ductility appears to be related to an increase in grain boundary sliding with decreasing grain size as evidenced by stress-strain (46) and creep (23) measurements, although direct metallographic observations of grain boundary sliding are still lacking in these materials. The mechanical response of these intermetallics thus appears to be transitional between that of pure nanophase metals at larger grain sizes and approaching at smaller grain sizes that observed for nanophase ceramics (4,43,44). Thus, grain boundary sliding mechanisms, accompanied by short-range diffusion assisted healing events, appear to increasingly dominate the deformation behavior of strongly bound and conventionally brittle materials in their nanophase forms. This deformation by grain boundary sliding also appears to have its analogue in the cluster consolidation process for creating nanophase materials (50,52,53) in which the typically equiaxed clusters formed by gas condensation retain both their general morphologies and random orientations during consolidation by means of diffusional events akin to Ashby-Verrall creep.

The mechanical behavior of nanophase metallic materials reviewed in this paper suggest that a qualitative framework, shown in Fig. 6, for understanding the mechanical properties of nanophase materials in general may be useful to consider. It appears that with decreasing grain size into the nanophase regime, the frequency of dislocation activity decreases and that of grain boundary sliding increases. Which of these effects dominates depends upon the grain size regime, the specific type of material, and most importantly on the nature of its interatomic bonding. Thus, metals (e.g., Al) with essentially free-electron-like, non-directional bonding would fall at the left of Fig. 6 and those with more covalent bonding (e.g., Cr) would lie further toward the covalently bonded intermetallic alloys or compounds, which themselves lie in the transitional region where diminishing dislocation activity yields to increasing grain boundary sliding; nanophase ceramics with their strong ionic or covalent bonding would lie in the region to the right dominated by grain boundary sliding.

Much work, of course, remains to fully elucidate the mechanisms responsible for the mechanical behavior of nanophase materials and to test whether such a simple framework as that proposed here is truly applicable. Critical experiments will need to be performed on a wide variety of nanophase materials with different bonding characteristics to identify the actual atomic mechanisms responsible for their observed mechanical properties and how these fit within the scheme shown in Fig. 6, or whether a totally new framework will need to be introduced. Nevertheless, the very different mechanical behavior already observed for nanophase materials compared with conventional grain size materials, and the already demonstrated possibilities to engineer this mechanical behavior through grain size control in the nanophase regime, indicate that such research endeavors will be both scientifically interesting and technologically important.

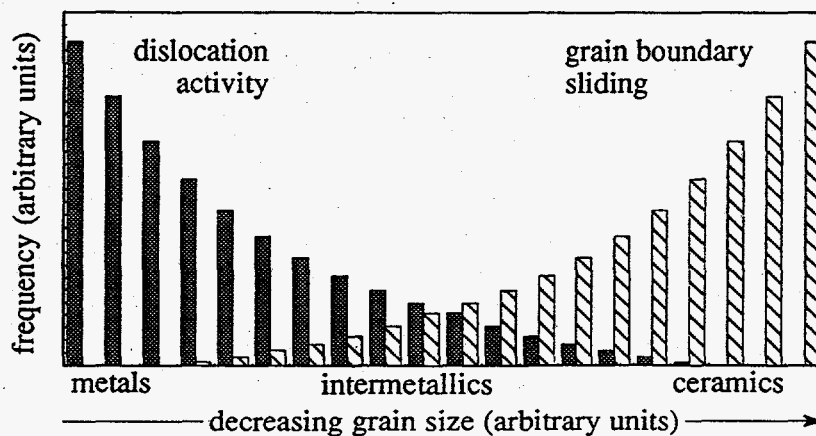


Figure 6. Schematic framework for the grain size dependence of dislocation activity and grain boundary sliding contributions to the deformation behavior of the various classes of nanophase materials. The nature of its interatomic bonding determines the appropriate location for a particular material.

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