Defense Intelligence Reference Document

Acquisition Threat Support

14 December 2009

ICOD: 1 December 2009

DIA-08-0911-012

Metallic Glasses: Status and Prospects for Aerospace Applications

Metallic Glasses: Status and Prospects for Aerospace Applications

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Administrative Note

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Metallic Glasses: Status and Prospects for Aerospace Applications

Summary

Metallic glasses combine some of the advantageous mechanical properties of metals—strength, stiffness, and in some cases toughness—with the processing flexibility usually associated with thermoplastic polymers. The absence of crystalline defects allows metallic glasses to be much stronger than conventional alloys but also means they have near-zero tensile ductility and poor fatigue resistance. In structural applications, therefore, metallic glasses are most likely to be useful in the form of composites consisting of ductile crystalline dendrites in a metallic glass matrix. These dendritic composites sacrifice some strength but can have exceptionally high fracture toughness, as well as good fatigue resistance, and could replace high-strength steels in certain load-limited structural components in aerospace vehicles where space is limited.

Because they are true glasses, thermoplastic forming near the glass transition temperature affords metallic glasses tremendous flexibility in processing. For instance, metallic glass components can be formed in a single step (for example, by injection molding) in complex geometries that would be difficult or impossible to produce with conventional alloys. In addition, metallic glass foams can be made with relative ease, raising the possibility of making structural foams with high strength and stiffness. Finally, because they lack a crystalline grain structure, metallic glasses can be used to form nanoscale features with high fidelity. This may make metallic glasses useful in a variety of micro-electromechanical systems (MEMS) applications.

Metallic glasses also have significant limitations for aerospace applications, however. Foremost among these is a lack of good glass-forming alloys; in particular, there are no good aluminum-rich glass-forming alloys, the known titanium-based alloys are either relatively dense (owing to high concentrations of alloying elements) or contain beryllium, and the known magnesium- and iron-based alloys are all quite brittle, with low fracture toughness. Although metallic glass matrix composites can have outstanding properties (particularly strength and fracture toughness), the number of good composite systems known at present is also quite limited.

Therefore, in order for metallic glasses (and their composites) to be of broad utility in aerospace structural applications, progress in the following areas is required:

- Development of new lightweight alloys and composite systems, preferably by computational and/or combinatorial approaches rather than by trial and error.

- Understanding of mechanical behavior, especially:

- - The effect of alloy composition and structure on plastic deformation.

  - Microstructural design of composites for optimal toughness.

- Development of processing techniques, including thermophysical processing of complex and/or nanoscale features as well as production of metallic glass foams.

It is highly likely that continued work over the next 20-50 years will result in significant advances in all these areas, and that metallic glasses and metallic glass matrix composites will see increasing acceptance as structural materials. Whether or not they achieve widespread use in aerospace applications, however, depends critically on the development of new, lightweight alloys.

Metallic Glasses

STRUCTURE

The atomic-scale structure of most metals and alloys is crystalline; that is, the atoms are arranged in a highly ordered manner on a lattice that is periodic in three dimensions, as depicted in Figure 1(a). In contrast to this crystalline structure, metallic glasses lack the long-range order of a lattice and are therefore said to be amorphous, as depicted in Figure 1(b). Although the word "amorphous" implies a complete lack of structural order, in fact the atomic structure of metallic glasses is not truly random. Constraints on atomic packing provide strong short-range order; for instance, on average the atoms have a particular number of nearest atomic neighbors at a well-defined distance. But this short-range order persists only over distances of a few atoms; there is no long-range order as there is in a crystalline alloy. In many ways, the atomic-scale structure of metallic glasses more closely resembles the highly disordered structure of a liquid than the structure of a crystalline alloy.

(a)

(b)

Crystalline
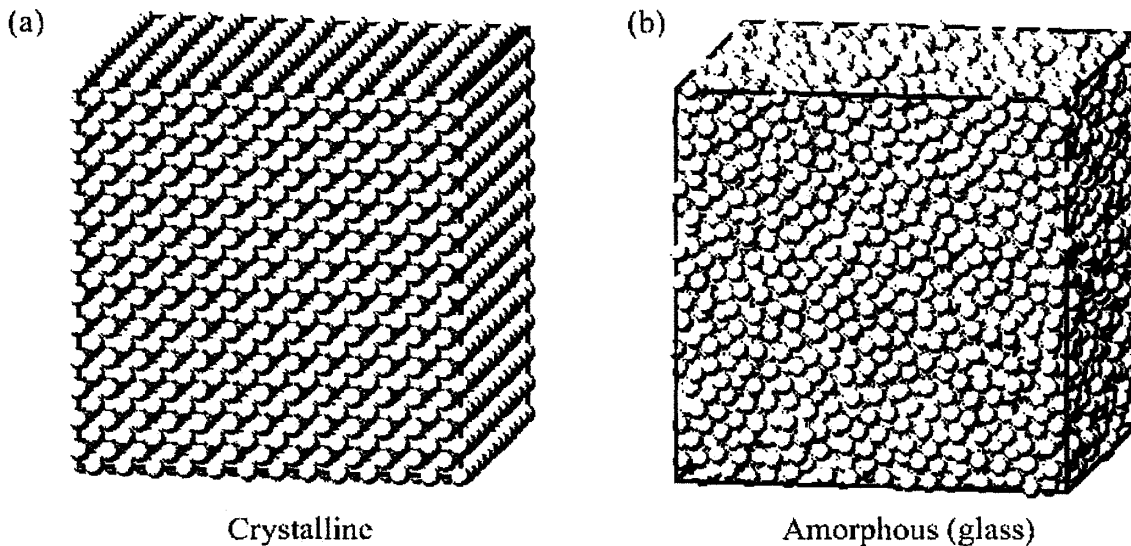
Amorphous (glass)

Figure 1. Amorphous Versus Crystalline Structure. Schematic atomic-scale structure of crystalline (a) and amorphous (b) metals. In a crystalline structure, order persists over long distances (many atomic dimensions). In a glass, there is short range order but no long-range order.

A corollary of this difference in structure is that the nature of structural defects is quite different between crystalline and amorphous alloys. Crystalline alloys, for example, have extended linear defects in the crystal structure, called dislocations, that are (in large part) responsible for determining mechanical behavior. The lack of crystalline order precludes the existence of dislocations in metallic glasses, but other sorts of defects can be present and may influence properties and behavior.

From an applications point of view, the amorphous structure of metallic glasses has two principal implications. First, the mechanical properties of amorphous alloys are significantly different from those of their crystalline counterparts; some of these differences are advantageous, but others are not. Second, because metallic glasses are

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glasses in the true sense of the word, rather than melting abruptly (as crystalline metals do), they soften and flow over a range of temperatures in a manner akin to common (oxide) glasses. This creates opportunities for tremendous flexibility in the processing of metallic glasses.

PROCESSING

Glass-Forming Alloys

The key to making a metallic glass is to retain the disordered, liquid-like atomic scale structure during cooling from the melt. All materials have a tendency to crystallize upon cooling because the crystalline state is the most stable structure at any temperature below the melting point. But crystallization takes time, so if the cooling is fast enough, it is possible to bypass crystallization and form an amorphous structure at the glass transition temperature (Figure 2(a)). Glass formation and crystallization are therefore competitive processes; which one will occur depends on the material and the processing conditions.
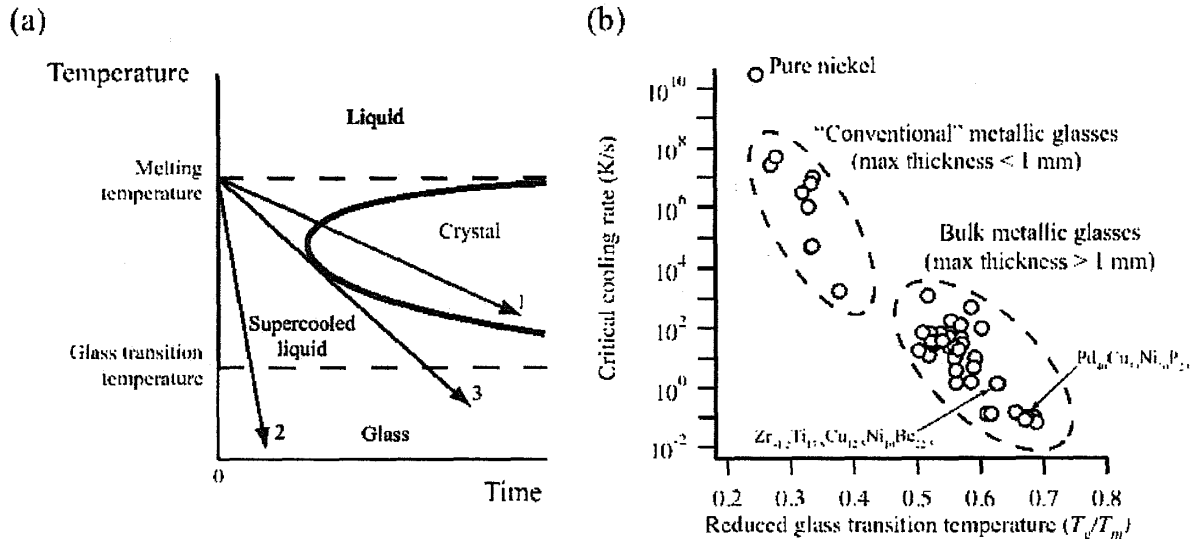
Figure 2. Critical Cooling Rate. (a) Effect of the cooling rate on glass formation – If the cooling rate is slow (path 1), then the melt crystallizes before going through the glass transition. If the cooling rate is fast enough (path 2), then the melt can form a glass. The critical cooling rate (path 3) is the slowest rate at which the melt can be cooled and still form a glass. (b) Critical cooling rates for various metallic alloys – The horizontal axis is the glass transition temperature normalized to the melting (liquidus) temperature.[1]

For some materials, such as silica (silicon dioxide) and most thermoplastic polymers, the crystallization process is slow because the crystal structures are complex and the basic structural units (for example, segments of polymer chains) are slow to rearrange into a crystalline form. These materials can therefore be produced in glassy form even at very low cooling rates; in fact, it can be difficult to crystallize them at all. Metals and alloys are another matter because the crystal structures are relatively simple and the basic structural units are individual atoms, which are highly mobile. Metallic crystals nucleate and grow quickly, making production of a metallic glass more challenging.

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One way to quantify the ability of a metallic alloy to be produced in glassy form is through the critical cooling rate—the slowest rate at which a metallic liquid may be cooled and still produce a fully amorphous structure, as shown in Figure 2(a). The critical cooling rate for a variety of metallic glass-forming alloys is shown in Figure 2(b). Early metallic glasses (discovered in the 1960s and 1970s) were binary alloys with critical cooling rates typically on the order of 104 to 107 K/s. Achieving such high cooling rates requires specialized techniques (such as melt spinning) and limits the maximum thickness of the metallic glass to < 100 µm because of the need to rapidly extract heat from the melt. As a result, these early metallic glasses could be produced in only a limited range of forms, including ribbons, foils, wires, and powders.

Extensive research efforts in alloy design over the past two decades have resulted in the development of multi-component alloys with much lower critical cooling rates (0.1 K/s or even lower). This has enabled the production of metallic glass specimens in larger sizes—in some cases exceeding 1-cm section thickness. Common practice in the field is to refer to any alloy capable of being cast into a section at least 1-mm thick as a "bulk" metallic glass. These alloys may be cast or molded into forms suitable for structural applications.

At present, it is not possible to predict a priori the glass-forming ability of an alloy of arbitrary composition. A variety of empirical rules for selecting alloying elements and compositions have been proposed, and techniques have been demonstrated for efficient searching of composition space. But identification of alloys with good glass-forming ability is still mostly a matter of trial and error. As a result, the number of truly outstanding glass-forming alloys (loosely defined as being able to be cast as a glass to a thickness of at least 1 cm) is quite limited (see Table 1).

Table 1. Selected Bulk Glass-Forming Alloys. Selected alloys reported to have excellent glass forming ability, quantified here as the maximum thickness of a fully amorphous casting.[2][3][4][5][6][7][8]

Composition	Maximum Thickness (mm)	Reference
$Mg_{65}Cu_{15}Ag_5Pd_5Gd_{10}$	10	2
$Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$	50	3
$Pd_{40}Cu_{30}Ni_{10}P_{20}$	72	4
$Cu_{47}Zr_{45}Ag_4Al_4$	10	5
$Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$	16	6
$Ti_{40}Zr_{25}Ni3Cu_{12}Be_{20}$	14	7
$Fe_{48}Cr_{15}Mo_{14}Er_2C_{15}B_6$	12	8

Moving from the laboratory to industrial practice, it is important to note that factors besides alloy composition can affect glass-forming ability. In particular, some alloys are sensitive to the presence of impurities; for example, the glass-forming ability of some zirconium-containing alloys is dramatically reduced by the presence of oxygen. Processing conditions also influence the ability to make a glass; these may include the material and surface finish of the mold and the temperature of the liquid prior to casting. Finally, glass-forming ability can be quite sensitive to small variations in composition, which may be difficult to control in industrial practice.

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Casting and Molding

Like other alloys, metallic glasses can be cast into net-shape or near-net-shape geometries. Die casting into a permanent (metal) mold—because it provides the rapid heat transfer needed to meet the requirement for relatively rapid cooling—is the most common casting technique. In most cases, casting is done in either a vacuum or an inert atmosphere to prevent formation of oxide particles that promote crystallization.

Conventional casting, however, does not take advantage of the flexibility afforded by the glassy nature of these alloys. If a metallic glass is heated to a temperature above its glass transition temperature, it becomes a supercooled liquid. In this state, the viscosity drops with increasing temperature over a wide range, making it possible to control the viscosity by controlling the temperature.[1] This ability to control the viscosity enables many of the processing techniques commonly used in molding thermoplastic polymers to be applied to metallic glasses (Figure 3).
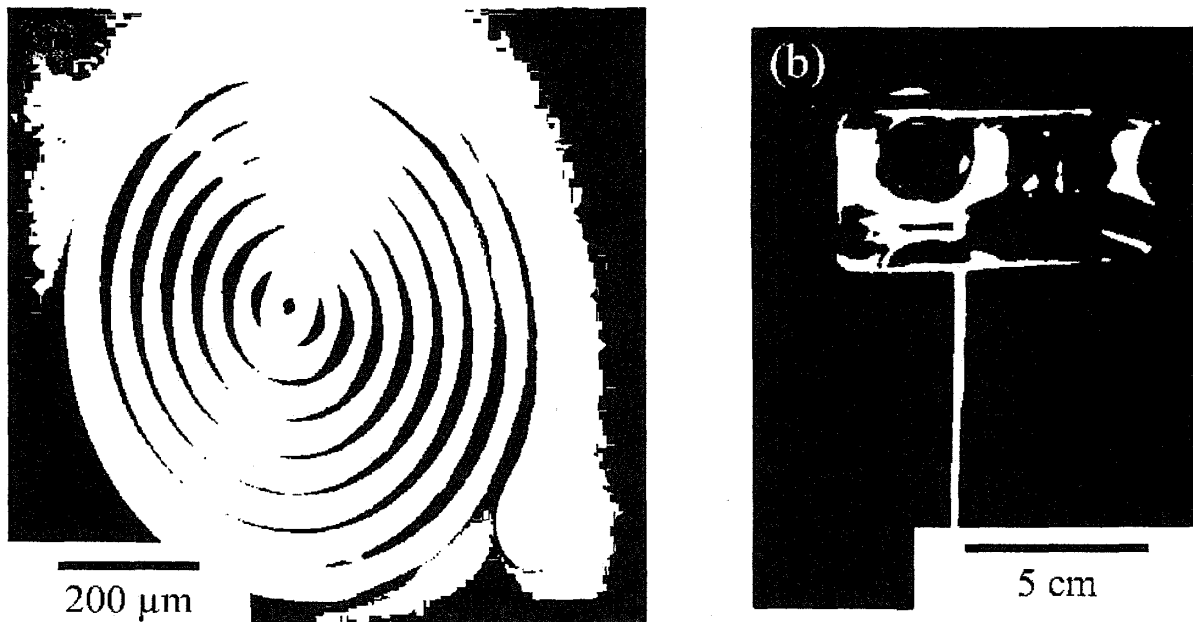
Figure 3. Examples of Processing of Metallic Glasses. (a) Microspring produced by lithography and (b) thin-walled bottle produced by blow molding. Images are courtesy of Professor Jan Schroers (Yale University).

There are two important limitations on processing of metallic glasses in the supercooled liquid region. First, supercooled liquids are metastable and have a tendency to crystallize, so there is a limited window of time (typically on the order of minutes) in which the processing must be completed if the glassy structure is to be maintained. Second, the viscosity of many glass-forming alloys near the glass transition temperature is too high for convenient processing. The viscosity can be reduced by increasing the processing temperature, but higher temperatures promote crystallization

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1 A crystalline metal, in contrast, melts abruptly, going from a rigid solid to a low-viscosity fluid very quickly.

and thus reduce the window of time available for molding. In practice, therefore, successful molding requires careful control of the processing conditions.

Joining

Structural applications inevitably require joining of components, for instance by mechanical fasteners or adhesives or by welding, soldering, or brazing. The use of fasteners and adhesives is much the same for metallic glasses as for any other metal. Techniques such as welding, soldering, and brazing are potentially problematic because they involve heating the glassy alloy, running the risk of crystallization (which could make the joint more brittle). In welding, for instance, the metal to be joined is actually melted and then resolidifies upon cooling. In the case of a metallic glass, care must be taken to ensure the cooling rate is fast enough to avoid crystallization. There is also a risk that the glassy material in the heat-affected zone (near to but not in the molten region) might crystallize. Laboratory tests of a variety of welding techniques have been performed on several glass-forming alloys with mixed results, and it is clear that much remains to be done in this area.

Foams

One particularly promising recent development is the ability to produce metallic glass foams. Here, the relatively high viscosity of glass-forming alloys is an advantage in producing a stable foam structure that can be solidified, leaving a high-porosity foam with metallic glass ligaments.[9] These foams have high specific strength (that is, strength normalized to density) and specific stiffness and could have excellent damage tolerance, although this has not been demonstrated.

Thin Films and Coatings

The discussion above focuses on the processing of free-standing metallic glasses, with an emphasis on structural applications. However, it is also possible to produce amorphous alloys as thin films or coatings using techniques such as physical vapor deposition or electrodeposition. Although the thicknesses of material that can be produced in this way are limited, they are useful for making amorphous alloy coatings (for wear and corrosion resistance) or for thin films for magnetic or micro-electromechanical system (MEMS) applications. A distinct advantage of the thin film techniques is that because the effective cooling rates during vapor deposition are extremely high, a much wider range of alloys can be produced in amorphous form than is possible with casting. This allows the alloy composition to be tailored for optimization of functional properties, with less concern about glass-forming ability.

Mechanical Behavior Near Room Temperature

When a material is subjected to a stress, it can experience both elastic and plastic deformations. Elastic deformation occurs at lower stresses and is recoverable when the applied stress is removed. The limit of elastic deformation is defined by the yield stress—the point at which plastic (nonrecoverable) deformation begins. Much of the current interest in metallic glasses arises because their yield stresses (that is, their strengths) can be much higher than those of crystalline alloys of similar composition; this difference is a direct result of the novel atomic-scale structure of metallic glasses. The fracture and fatigue characteristics of metallic glasses are also different from those

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of conventional alloys. In this section, we review the mechanical behavior of metallic glasses, with particular attention to properties of interest for aerospace applications. We consider actual properties in detail in the section below on applications, where we compare the properties of metallic glasses with those of other advanced structural materials.

Stiffness: Elastic Deformation

Stiffness is the resistance of a material to elastic deformation and is quantified by either the elastic modulus (for tensile or compressive loads) or the shear modulus (for shear loading). Metallic glasses tend to be somewhat (20-30 percent) less stiff than crystalline alloys of similar composition. The lower modulus is a consequence of the amorphous structure, in which atoms are (on average) slightly farther apart than in a crystalline alloy, enabling certain atomic relaxations that are not possible in a crystal. The lower modulus of amorphous alloys is clearly a concern in applications where stiffness is a primary criterion, but it does present some advantages. For instance, some applications (springs, for example) require the ability to store elastic strain energy (resilience), and here metallic glasses do quite well. Resilience is also a key figure of merit for snap-fit assembly of materials without fasteners. Overall, however, for structural applications, the low stiffness of metallic glasses is a disadvantage.

Strength and Ductility: Plastic Deformation

The theoretical strength of perfect, defect-free crystalline metals is several orders of magnitude larger than strengths measured in typical laboratory experiments. The difference exists because metallic crystals inevitably have crystalline defects (dislocations) that are able to move at relatively low stresses and cause plastic (nonrecoverable) deformation. Because dislocations cannot exist in an amorphous structure, in principle the strength of amorphous alloys should approach theoretical limits based on the inherent strength of the atomic bonds. As shown in Table 2, the strength of aluminum-based metallic glasses can be two or three times greater than those of conventional (crystalline) high-strength aluminum alloys. Similarly high strengths are seen for other amorphous alloys; for instance, the best iron-based alloys have a strength of approximately 4 GPa—again, two or three times greater than those of conventional high-strength steels.[10] Such high strengths create great interest in potential structural applications of metallic glasses.

Table 2. Comparison of Strengths of Amorphous and Crystalline Aluminum Alloys. Compared with the theoretical maximum strength (taken to be $\mu/30$, where μ is the shear modulus of pure aluminum).

	Yield Stress (MPa)	% of Theoretical Strength
Theoretical Strength (Defect-Free Crystal)	1,600	-
Typical High-Strength Aluminum Alloy (7xxx Series)[11]	400–500	25–31%
Best Crystalline Aluminum Alloy[12]	770	48%
Aluminum-Based Metallic Glass[13]	1,280	80%

Unfortunately, the lack of dislocations in amorphous alloys is also their Achilles' heel. In crystalline alloys, dislocations move and multiply in response to applied stresses, resulting in dislocation tangles that increase the resistance to further dislocation motion. This process, called strain hardening, is of crucial importance because it makes plastic deformation stable. If one region of a crystalline material yields and begins to plastically deform, the deforming region strain hardens, and so another region will deform instead. The result is that the plastic deformation is not concentrated but rather spreads through a large volume of material. Metallic glasses, lacking dislocations, do not strain harden and in fact strain soften in response to plastic deformation. This means that as soon as any one region yields, any further deformation will occur in the same region. This process, known as shear localization, leads to the formation of shear bands (Figure 4). In any loading geometry where the metallic glass experiences significant tensile loading, fracture occurs on a single dominant shear band with essentially zero tensile ductility.[2] Metallic glasses therefore fracture in an abrupt, apparently brittle manner on the macroscopic scale (even though there can be significant plasticity on a microscopic scale). This lack of ductility is of obvious concern to designers interested in structural applications. Furthermore, it limits the ability to fabricate metallic glasses into different shapes by deformation processing (by rolling or forging, for instance) after casting.

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2 This assumes there is no geometrical constraint preventing fracture. Some geometries (such as simple bending) can involve tensile loading, but there can still be significant plastic deformation because the geometrical constraints inhibit propagating of shear bands across the specimen.
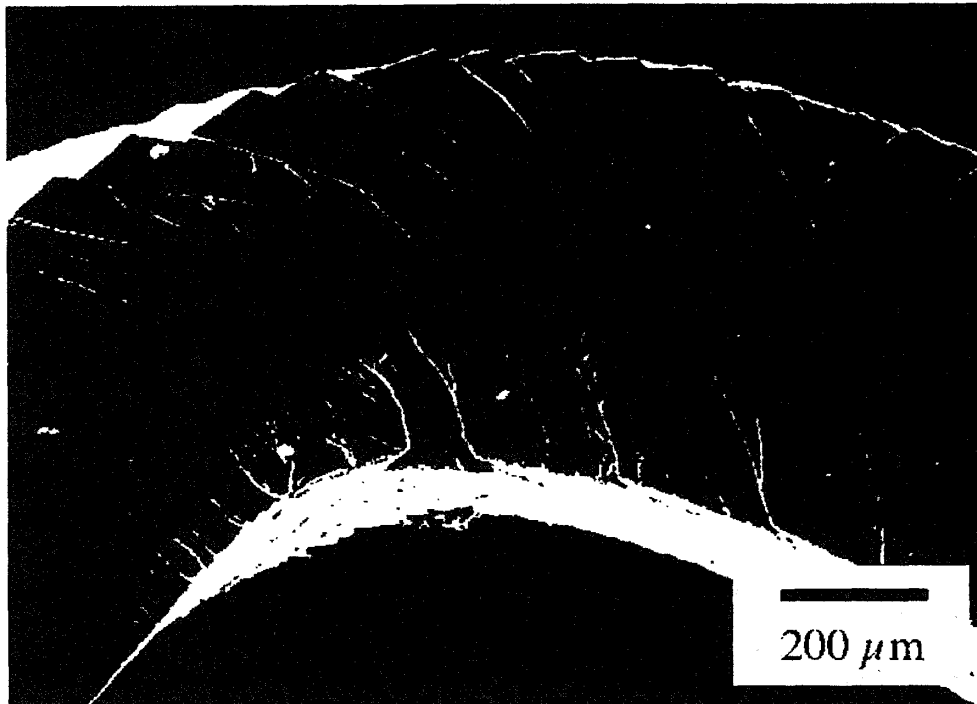
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Figure 4. Shear Bands. Produced by bending of a zirconium-based metallic glass.[14]

Fracture Toughness

Fracture toughness is a measure of a material's resistance to growth of cracks, a critical property for structural materials subjected to tensile loading. In very tough metals, the toughness usually results from plastic deformation that occurs near the tip of the advancing crack; plastic deformation requires energy, and the need to provide this energy translates into resistance to crack growth.[3] Despite their lack of tensile ductility, at least some metallic glasses are not brittle in the same sense that ceramics are, for example, because they can experience significant plastic deformation around the crack tip during fracture. For instance, the fracture toughness (K_{1c}) of zirconium-based metallic glasses is about 20 $MPa \cdot m^{1/2}$ [15]—somewhat lower than the ~ 55 $MPa \cdot m^{1/2}$ typical of crystalline zirconium alloys[16] but much greater than the fracture toughness of ceramics (typically 1-5 $MPa \cdot m^{1/2}$). The fact that metallic glasses are reasonably tough despite their lack of tensile ductility suggests structural applications are not out of the question.

However, some metallic glasses appear to be intrinsically brittle in that they fracture with only limited plastic deformation near the crack top and thus have very low values of fracture toughness. For this reason, some alloys that would otherwise be highly desirable, such as iron-based metallic glasses (for their high strength and low cost) and magnesium-based glasses (for their low density), fall into this category. The physical origins of the difference between intrinsically brittle metallic glasses and those capable of limited plastic deformation (and thus some toughness) are not well understood.

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3 In other materials, notably polymer-matrix composites, other mechanisms of toughening can be more important.

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Even some metallic glasses with reasonable toughness may be embrittled by exposure to elevated temperatures. This may occur in the heat-affected zone during welding (as discussed above), or it may be a by-product of processing in the supercooled liquid region (as in injection molding, for instance). The causes of embrittlement are also not well understood, and there is no known way to reverse embrittlement once it occurs.

Fatigue

Fatigue is a process by which materials can experience incremental crack growth owing to cyclic loading, even at stresses well below the yield stress. If unabated, fatigue cracks can grow to a critical length at which abrupt catastrophic fracture occurs. Up to 90 percent of failures of structural components in service are estimated to be caused by fatigue, making fatigue resistance of obvious importance to designers.

The fatigue resistance of metallic glasses is not very good. A common measure of fatigue resistance is the fatigue limit—the stress amplitude (range) below which no fatigue failure will occur, regardless of the number of loading cycles the material experiences. The fatigue limit for high-strength crystalline alloys is typically about 40 percent of the tensile strength, but for metallic glasses, it is only about 5 percent of the tensile strength (Figure 5). The reason for this difference has to do with the structure of the material. In a crystalline alloy, there are microstructural features (such as grain boundaries and precipitate particles) that can inhibit the growth of fatigue cracks. In metallic glasses, the microstructure is completely featureless, and there is nothing to prevent fatigue cracks from growing once they have been initiated.

The poor fatigue resistance of metallic glasses is a critical limitation for structural applications in aerospace because it implies a need to overdesign components to keep the stresses far below the yield stress. Thus, much of the advantage of having a high-strength material in the first place is lost. The desire to improve metallic glasses' fatigue performance has led to the development of metallic-glass-matrix composites with outstanding properties, as discussed below.
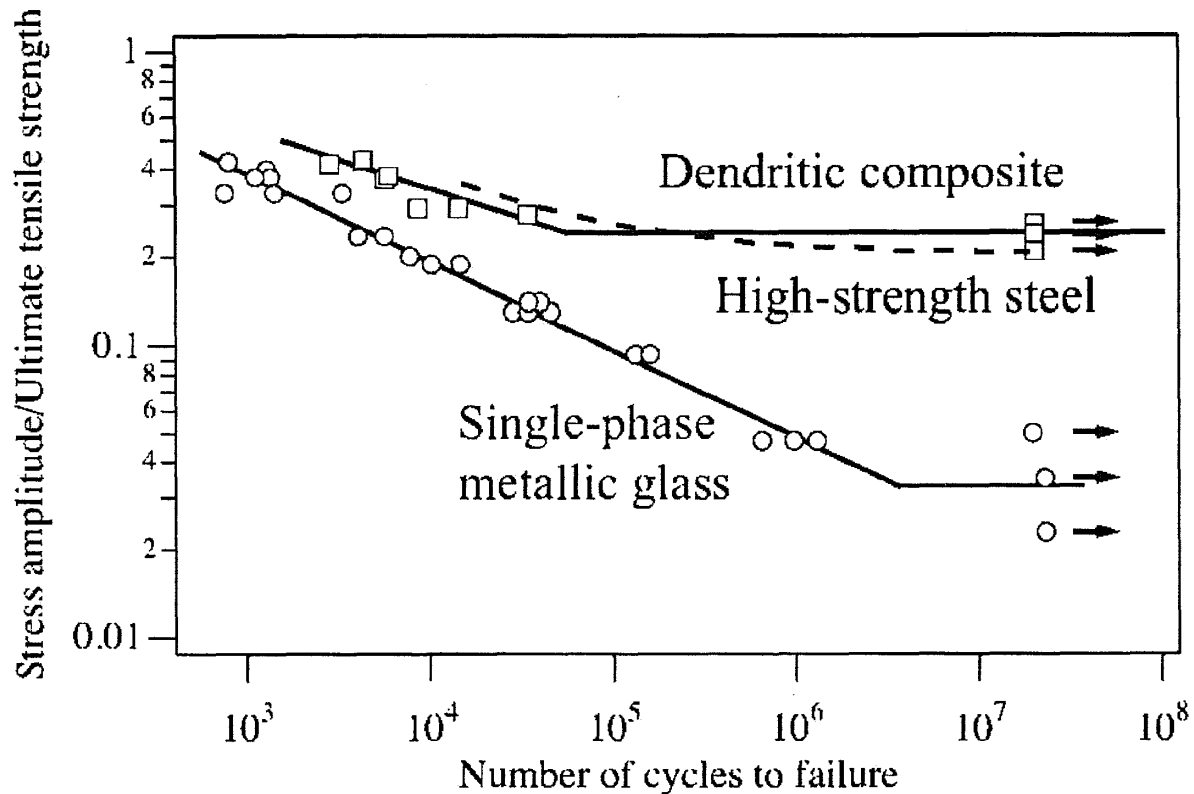
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Figure 5. Fatigue Limit of Metallic Glasses and Metallic-Glass-Matrix Composites. Fatigue life data for single-phase zirconium-based metallic glass (red) and a dendritic metallic glass matrix composite (blue). Representative data for steel (300-M) of similar tensile strength are shown for comparison.[17][18][19]

Wear Resistance

Because of their high yield strength, metallic glasses also have very high hardness. This, in turn, implies they might have good tribological behavior, which would be of particular interest when combined with the good corrosion resistance of some alloys (see below), opening up potential applications such as coatings on dry bearings for space applications.[20] However, the tendency of metallic glasses to form shear bands and (in some cases) partially crystallize owing to deformation means their wear resistance is perhaps not as good as their high hardness would suggest. Nevertheless, the wear resistance of metallic glasses can still be quite good, and in fact one of the principal current markets for amorphous alloys is as wear- and corrosion-resistant coatings for tools such as drill bits.

Corrosion and Stress-Corrosion Cracking

It is frequently stated that metallic glasses have excellent corrosion resistance, but this is not always true. The lack of grain boundaries and second-phase particles makes some metallic glasses extremely resistant to corrosion, but this is not true of all alloys (some of which oxidize rapidly in air). Broadly speaking, the corrosion resistance of nickel- and iron-based metallic glasses is better than that of alloys based on zirconium, titanium, and copper (particularly in environments containing chloride ions).[21] Some alloys are susceptible to localized pitting corrosion, probably facilitated by the presence of crystalline inclusions.

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The subject of stress-corrosion cracking of metallic glasses, despite its obvious importance for structural applications, has received scant attention in the literature. What little work that has been done has focused on zirconium-based glasses, with the observation that these alloys are very susceptible to stress-corrosion cracking in aqueous environments containing chloride ions, likely owing to the fact that they do not form protective oxide surface layers.[22]

Mechanical Behavior at Elevated Temperature

The discussion above relates to mechanical behavior at temperatures well below the glass transition temperature. At elevated temperatures, the strength drops and plastic deformation transitions to a homogeneous mode, occurring throughout the specimen instead of being localized into shear bands (Figure 6). Above the glass transition temperature, the alloy becomes a fluid, with a viscosity that drops exponentially with increasing temperature. Because the strength of the material is low, temperatures either above or below the glass transition may be useful for processing, as discussed above. However, the decrease in strength and the tendency for crystallization at elevated temperatures preclude use of metallic glasses from structural applications at temperatures approaching the glass transition temperature.
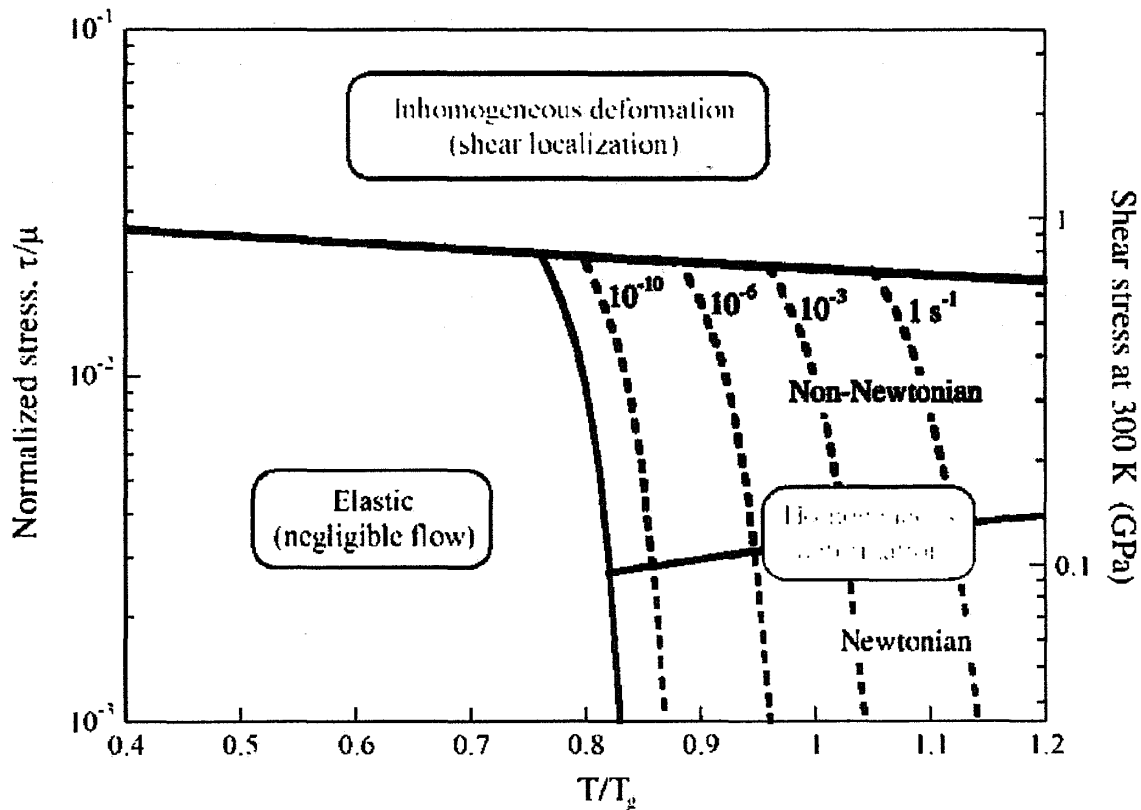
Figure 6. Deformation Map for Metallic Glasses. As a function of temperature (normalized to the glass transition temperature) and applied shear stress τ (normalized to the shear modulus, μ). At high stresses, plastic deformation occurs inhomogeneously, being localized into shear bands. At high temperatures, plastic deformation becomes homogeneous. The dashed lines represent different strain rates. The absolute stresses given are representative of the well-studied bulk metallic glass Zr41.2Ti13.8Cu12.5Ni10Be22.5, but the general features of the map are expected to apply to all metallic glasses.[73]

Other Properties: Magnetic, Electrical, Optical, Thermal, and Acoustic

Although most of the current interest in metallic glasses centers on their mechanical properties, it is appropriate to consider other properties of potential utility. Of these, the magnetic properties of ferromagnetic metallic glasses stand out.[24] A variety of ferromagnetic glass-forming alloys exist, mostly based on transition metals (iron, nickel, and cobalt). The presence of alloying elements (necessary to make the material glass-forming) means the saturation magnetization of metallic glasses is not as large as that of the pure elements. However, some amorphous alloys have very low coercivity (a measure of how strong a magnetic field must be to change the direction of magnetization of the material) owing to the lack of crystalline defects (such as grain boundaries) and magnetocrystalline anisotropy. In addition, the relatively high electrical resistivity of amorphous alloys (see below) minimizes eddy current losses caused by high-frequency magnetization/demagnetization. Some amorphous alloys also have strong magnetoelastic effects (coupling between magnetic properties such as susceptibility or magnetization and elastic strain). Current and potential future applications of these magnetic properties are discussed below.

Like crystalline alloys, metallic glasses have conduction electrons that make them both electrically and thermally conductive,[25] although their structural disorder and high alloy content make them poor conductors. In addition, in a behavior that is useful in some applications, the conductivity of metallic glasses is not very sensitive to temperature; an exception is near absolute zero, where some amorphous alloys become superconducting.

Another consequence of the amorphous structure of metallic glasses is that they tend to have very low acoustic damping. This may be useful in applications such as vibrating-structure gyroscopes for vehicle orientation.[26]

A common misperception among those hearing about metallic glasses for the first time is to think they are transparent. This is not the case; amorphous alloys are highly reflective, with a shiny luster similar to that of other metals (Figure 7). This is a result of the presence of the conduction electrons, which scatter and absorb incident light.
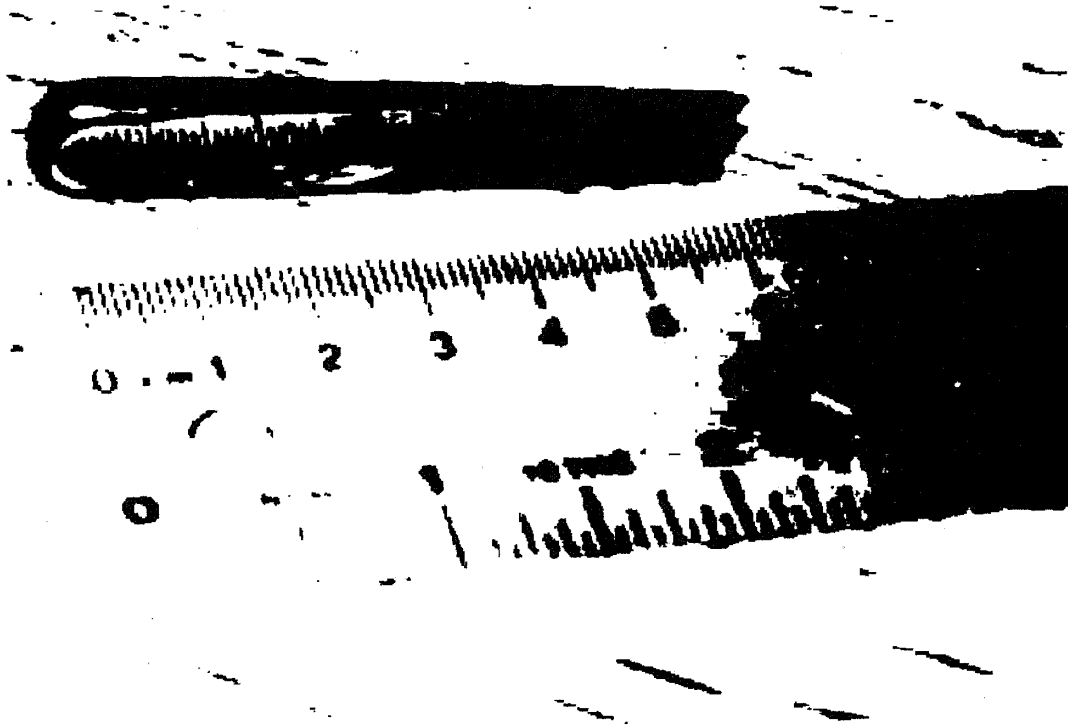
Figure 7. Cast Metallic Glass Wedge. Wedge of a zirconium-based bulk metallic glass produced by casting. Note the shiny metallic luster, typical of metallic glasses.[2]

Metallic Glass Matrix Composites

As discussed above, the lack of crystalline defects gives metallic glasses high strength but compromises their ductility and fracture toughness. In particular, the tendency for plastic deformation to localize into shear bands prevents the material from deforming in a "graceful" manner. So it should not be surprising that there have been many attempts to control shear band initiation and propagation by making composite materials consisting of particles or fibers of some other material (most commonly a ductile crystalline metal) in a metallic glass matrix. The idea is to produce a material with improved ductility, fracture toughness, and fatigue properties while (hopefully) not sacrificing the qualities—especially strength and processing flexibility—that make metallic glasses interesting in the first place.

PROCESSING AND STRUCTURE OF COMPOSITES

Broadly speaking, there are two kinds of metallic glass matrix composites: ex situ and in situ. In ex situ composites, the metallic glass and the crystalline phase (be it in the form of particles or fibers) are physically combined, for instance by adding particles to the melt before casting. In situ composites are different in that the crystalline phase is produced directly from the melt (by precipitation) during processing. This fundamental difference in processing leads to significant differences in structure and therefore in properties.

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EX SITU COMPOSITES

There are two basic ways of making ex situ composites, in which the metallic glass matrix and the crystalline phase are combined physically, without a chemical reaction:

- Add crystalline particles to a melt of a glass-forming alloy and then cast under conditions that allow the matrix to form a metallic glass.

- Make a preform of a crystalline phase (by packing fibers into a mold, for instance) and then cast the glass-forming alloy around the preform.

Both approaches have limitations. In the first, the addition of particles to the melt increases the viscosity (which is already quite high relative to non-glass-forming alloys) considerably, ultimately to a point where casting becomes impossible. This limits the volume fraction of particles that can be added, which in turn limits the control one has over the microstructure and, in particular, the spacing of the particles. With a perform, the volume fraction of the crystalline phase can be much higher (up to about 80 percent by volume), but the problem then is how to infiltrate the high-viscosity melt into the preform without leaving voids and while still ensuring sufficiently rapid cooling to form a glassy matrix. With both approaches, interfacial reactions between the crystalline phase and the melt can cause partial or complete crystallization of the matrix, degrading the mechanical properties.

IN SITU COMPOSITES

The difficulty of making satisfactory ex situ composites has led to the development of a new approach in which the crystalline phase is precipitated directly from the melt, either during casting[28] or in a separate step prior to casting.[29] [30] Precipitation during casting, although easier, is problematic from a practical standpoint because variations in the cooling rate (from the surface to the center of a casting, for instance) lead to significant variations in structure and, hence, in properties.

One of the most promising recent advances in the metallic glass field is the development of in situ composites in which the crystalline phase is precipitated as dendrites, either during casting (Figure 8) or by holding the alloy at an elevated temperature prior to casting.[31] By suitably choosing alloy composition, holding time, and temperature, the volume fraction, size, and spacing of the dendritic phase can be controlled. This control provides great flexibility in determining the mechanical properties of the resulting material. Because the crystalline phase is produced prior to casting, variation in the cooling rate across the casting is much less important, though the cooling rate must still be sufficiently high to ensure the matrix forms a glass during cooling. Once the glassy matrix is formed, the composite can be reheated above the glass transition temperature, allowing for thermoplastic forming in a manner similar to single-phase metallic glasses (as described above). Finally, the presence of the dendritic second phase allows for deformation processes (for example, by cold rolling or forging), similar to crystalline alloys.[32]
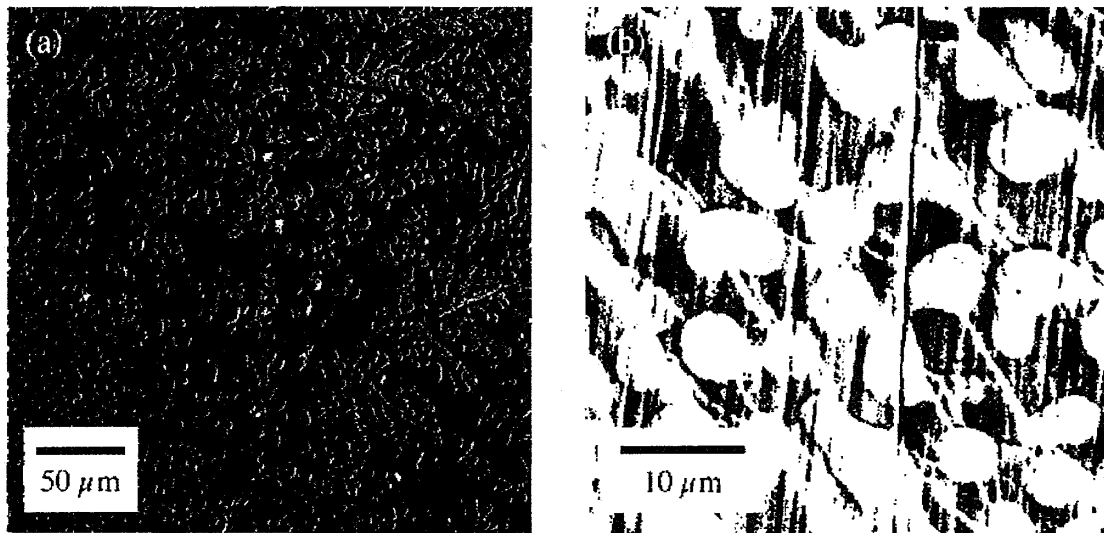
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Figure 8. Microstructure of In Situ Metallic Glass Matrix Composite. With ductile crystalline dendrites.
(a) Scanning electron micrograph showing the dendrites (light gray) in the glassy matrix (dark gray).
(b) Composite after plastic deformation; note the multiplicity of slip steps, indicating extensive
interaction of shear bands with the dendrites.[33]

The key limitation of these in situ composites is that not every alloy system is capable of forming them. While any alloy will form crystalline phases at elevated temperatures, usually the crystalline phases that form are brittle intermetallics that degrade rather than enhance the mechanical properties. To be effective in controlling shear bands, the precipitated phase needs to be ductile, have a shear modulus lower than that of the glassy matrix, and (preferably) form as dendrites. To date, the only published reports of systems that satisfy these criteria concern alloys based on early transition metals, notably zirconium and titanium. Whether in situ composites can be developed in other alloy systems remains to be seen.

MECHANICAL PROPERTIES OF COMPOSITES

The ability to produce mixed amorphous-crystalline microstructure provides the ability to control the formation and propagation of shear bands. The resulting materials can have good fracture and fatigue resistance while retaining the high strength and processing flexibility associated with metallic glasses.

The origin of these effects is related to the development of a region of plastic deformation at the tip of an advancing crack. For a crack opening under tensile loading, the size of the plastic region is approximately given by:

$$R_p \approx \frac{1}{2\pi}\left(\frac{K_{Ic}}{\sigma_y}\right)^2 ,$$
(Equation 1)

where K_{Ic} is the plane-strain fracture toughness (mentioned above) and σ_y is the yield strength. The size of the plastic zone varies from ~ 1 μm for "intrinsically brittle" metallic glasses to ~ 1 mm for glasses capable of some plastic deformation.[34] If the material has structure on this length scale (or if the sample itself is of this size), then

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deformation can proceed in a stable manner by generation and subsequent arrest of shear bands. The key to composite design is to produce a microstructure with the correct length scale to prevent propagating shear bands from becoming catastrophic cracks. This turns out to be relatively difficult with ex situ composites, for reasons of processing described above. As a result, the recently developed dendritic in situ composites have the most promising properties, and we focus the remainder of our discussion on them.

STRENGTH AND DUCTILITY: PLASTIC DEFORMATION

As with other composite materials, the yield strength of metallic glass matrix composites can be approximated as a simple rule of mixtures based on the volume fraction of the two phases. Because the ductile crystalline phases useful for limiting shear band propagation are weaker than the amorphous matrix, in producing a composite, some sacrifice in strength is inevitable. However, the gains in tensile ductility can be significant. For instance, monolithic titanium-based metallic glasses (like all metallic glasses) have essentially zero tensile ductility, but in situ composites based on titanium have been reported with tensile elongation as large as 12 percent.[35] This is comparable to the ductility of Ti-6Al-4V (the most common conventional titanium alloy), but in a material with about 30 percent greater strength. The properties of metallic glass matrix composites and more conventional materials are further compared below.

FRACTURE AND FATIGUE

The development of a stable plastic zone means additional energy is required for crack propagation, making in situ composites much more resistant to fracture and fatigue than are single-phase glasses. For instance, the plane-strain fracture toughness of some zirconium-based in situ composites can exceed 170 MPa $m^{1/2}$—7 times greater than that of single-phase glasses and greater than that of virtually any other metallic alloy.[36] This resistance to crack propagation is also manifested as improved fatigue performance. The fatigue strength of the zirconium-based in situ composites is 20-30 percent of the tensile strength; in comparison, monolithic metallic glasses have a fatigue strength of only ~ 5 percent of the tensile strength.[37] The fatigue strength of the in situ composites is thus comparable to that of conventional structural alloys.

Aerospace Applications of Metallic Glasses

STRUCTURAL APPLICATIONS

The key properties of materials for structural applications in aerospace are:

- Strength.

- Stiffness (Young's modulus).

- Density (weight).

- Fracture toughness (damage tolerance).

- Fatigue resistance (including resistance to both fatigue crack initiation and fatigue crack growth).

- Corrosion resistance (including stress-corrosion cracking).

- Cost (including raw materials, shaping, and assembly).

Figure 9 illustrates the mechanical properties of metallic glasses and metallic glass matrix composites compared with other structural materials. Since weight is a particular concern in aerospace applications, in Figure 9(a) we normalize both yield strength (σy) and stiffness (E) to density (ρ); two materials with the same specific strength ($\sigma y / \rho$) or specific stiffness (E/ρ) could be used to produce a component with the same overall strength or stiffness, respectively, at the same weight. Materials in the upper-right corner of the plot have the best combination of strength and stiffness for a given weight. Notice that the metallic glasses (and dendritic composites) can be stronger than virtually all crystalline metals, although the stiffness of metallic glasses tends to be somewhat smaller than that of crystalline alloys of similar composition.

Figure 9(b) illustrates the damage tolerance of metallic glasses compared with other materials. By plotting the fracture toughness (KIc) against modulus (E), we can also compare the fracture energy (GIc $\approx$ (KIc)2/E) of the materials; the dashed diagonal lines are lines of constant fracture energy. Figure 9(b) reveals several interesting aspects of the damage tolerance of metallic glasses. First, although the fracture toughness of some metallic glasses is comparable to that of crystalline metals, some metallic glasses—most notably those based on iron (Fe) and magnesium (Mg)—are as brittle as any ceramic. Second, both the fracture toughness and the fracture energy of the dendritic metallic glass matrix composites can be superior to those of all but the most fracture-resistant metals.

These considerations suggest the dendritic metallic glass matrix composites might indeed find applications as structural materials in aircraft and/or spacecraft. The most obvious applications would be to replace steel in certain components where strength is critical but space is limited. These might include pylon structures and landing gear,38 although it has yet to be demonstrated that the composites can be fabricated in the sizes necessary. Furthermore, the corrosion and stress-corrosion cracking resistance of these materials has not been fully evaluated.

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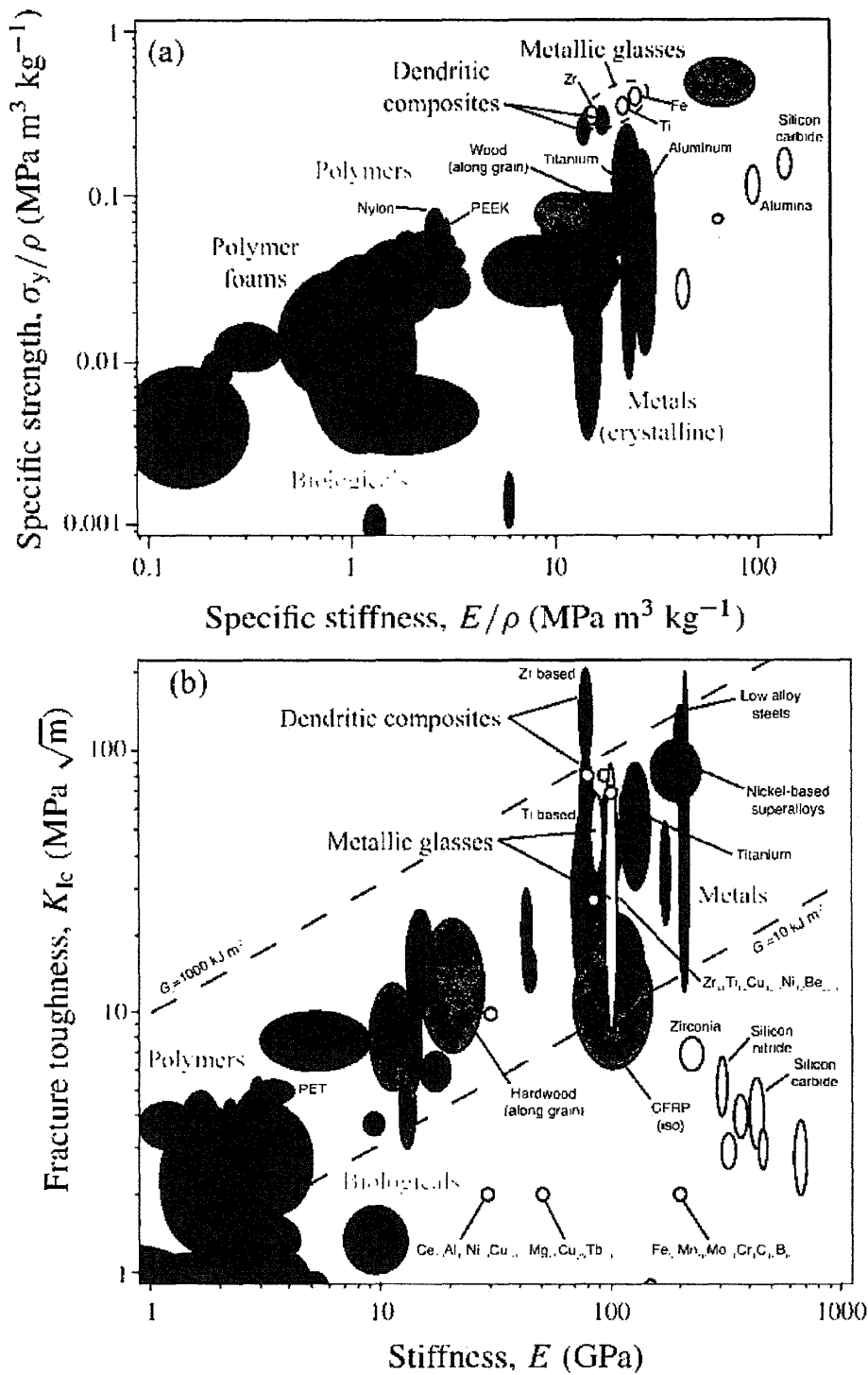
Figure 9. Materials Property Charts. (a) Strength and stiffness (both normalized to density) of metallic glasses (yellow) and dendritic metallic glass matrix composites (red) compared with other materials. (b) Damage tolerance. On this plot, the dashed lines represent contours of equal fracture energy. In both plots, polymer composites (CFRP and GFRP) are represented by isotropic averages; continuous fiber composites can have greater strength and stiffness in a direction parallel to the fibers.[39]

Metallic glass foams (see above) also provide intriguing possibilities for structural applications. It has recently been shown that metallic glass foams with outstanding strength can be formed by controlling the size of the ligaments between pores.[40] This is a new development, and these foams have not been fully characterized, but it seems likely that optimized foams will have a specific stiffness (E/ρ) superior to that of polymer foams, along with high strength and acoustic damping. Such structural foams could be useful in applications requiring strength and stiffness under compressive loads, such as structural panels for extraterrestrial buildings. Conceivably, such structural foams might even be produced on site (from raw feedstock), reducing the volume of material that needs to be launched.

A final possibility is that metallic glasses might be combined with polymer composites into metal-fiber laminate materials. Similar laminates (with crystalline aluminum alloys) are being employed in large quantities on the new Airbus 380 and are likely to find increased application in the future.[41] The use of metallic glasses in these laminates is appealing because of their high specific strength (although the specific stiffness is lower than that of aluminum). Furthermore, the individual layers in the laminate are sufficiently thin that a wide range of glass-forming alloys might be considered (in contrast to thicker structural sections, which will be limited by the glass-forming ability of the alloy).

OTHER APPLICATIONS

Monolithic metallic glasses are unique among metallic materials in having no microstructure at length scales of more than a few atomic spacings. In principle then, metallic glasses should be capable of replicating features down to this scale. This possibility is facilitated by the ability of metallic glasses to be formed in the supercooled liquid temperature range with controllable viscosity. Indeed, superplastic forming of metallic glass surfaces with features as small as 13 nanometers has been demonstrated.[42] This ability could be exploited for direct embossing of nanostructures in polymers or other materials. Structures on this length scale are also potentially useful as diffraction gratings for ultraviolet and soft x-ray radiation.

In a related area, metallic glasses have a variety of useful properties for application in micro-electromechanical system (MEMS) actuators, including large elastic strains and high resilience (elastic strain energy storage), good corrosion and wear resistance, and an excellent surface finish.[43] The scale of these devices is smaller than the plastic zone size (Equation 1 above), making brittle fracture unlikely. Furthermore, a much wider variety of amorphous alloys can be made in thin film form (by vapor deposition) than is possible by casting.

Finally, the magnetic properties of certain amorphous alloys have long been exploited. For instance, their low coercivity and high electrical resistivity make ferromagnetic amorphous alloys attractive as high-efficiency electrical transformers, particularly at high frequencies. Such applications are likely to continue well into the future.

Current Challenges and Prospects for the Future

ALLOY DESIGN

A critical limitation of existing metallic glass technology (and related composites) is the relative dearth of alloys with good glass-forming ability. The best glass-forming alloys are either based on expensive elements (for example, palladium) or contain toxic elements (for example, beryllium in the best zirconium- and titanium-based alloys). For aerospace applications, the most glaring lack is that, despite significant alloy design efforts in the United States (through the DARPA Structural Amorphous Metals program), Japan, China, and elsewhere, there are no good glass-forming alloys based on aluminum. Attempts to make aluminum-based metallic glass components by consolidating amorphous powders have met with limited success. Similarly, all of the good iron-based metallic glasses contain considerable amounts of nonmetallic elements (notably carbon, boron, silicon, and/or phosphorus), which are thought to contribute to the very low fracture toughness of these alloys (Figure 9(b)).

However, there is reason to expect that further progress is possible. Recent experimental results have shown that some of the empirical "rules" of glass-forming ability[44] are actually quite flexible, and that glass-forming ability is much more sensitive to composition than had been previously appreciated.[45] So it is highly probable that some excellent glass-forming alloys compositions remain to be discovered, possibly including some low-density glasses based on aluminum.

Identifying these good glass-forming alloys will be a challenge. Most alloy development to date has been done with a brute-force approach, but combinatorial techniques[46]re likely to enable much more rapid screening. One issue is identification of suitable metrics for glass-forming ability, since the combinatorial approaches use vapor-deposited thin films, and it is not clear what characteristics of such a film correlate with glass-forming ability in the bulk. Similarly, continued development of ab initio molecular dynamics techniques should enable identification of candidate alloys from computer simulations, particularly as computers continue to increase in power.

One area that has received insufficient attention is the influence of processing conditions on glass-forming ability. For instance, application of electromagnetic vibrations during cooling reportedly significantly enhances the glass-forming ability of magnesium-based metallic glasses.[47] This approach could, in principle, be applied to other alloys, possibly greatly extending the range of alloys and compositions that can be produced as bulk metallic glasses.

THERMOPHYSICAL PROPERTIES AND THERMOPLASTIC PROCESSING

Most of the practical interest in single-phase (monolithic) metallic glasses centers on the potential for thermoplastic processing near to or above the glass transition temperature. However, the thermophysical properties and behavior of metallic glasses are not well understood. For instance, the viscosity of the metallic glass melt (or supercooled liquid) is of critical importance, but we do not know how and why alloy composition influences viscosity. From an engineering point of view, the practical aspects of molding of metallic glasses are just beginning to be explored. Certainly many

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parallels can be drawn with thermoplastic forming of polymers, but there are certain to be many differences as well.

Continued developments in this area are highly likely to result in the ability to produce complex net-shape parts in a single processing step. This ease of processing could offset the higher raw materials costs for metallic glasses, making them competitive in a much wider range of applications. Furthermore, as noted above, the ability to replicate extremely small features (< 20 nanometers) in metallic glasses is likely to be exploited in the manufacture of nanostructured devices.[48] [49]

Finally, development of metallic glass foams will continue and will be aided by improved understanding of thermophysical properties. It is highly likely that foams will be produced in a wide range of glass-forming alloys, and that techniques will be developed for precise control of the porosity, pore size, ligament size, and connectivity. This will allow the properties of these foams to be tailored to particular applications.

COMPOSITES AND THE QUEST FOR DUCTILITY

From the point of view of structural applications, localization of plastic deformation into shear bands is the single biggest challenge because this tendency limits the tensile ductility, fracture toughness, and fatigue crack resistance of metallic glasses. There may well be no solution to this problem for monolithic metallic glasses, for the simple reason that they lack any microstructure to interact with shear bands.

Progress is likely to occur on two fronts. First, it is now well established that some alloys are inherently brittle, in the sense that they experience very little plastic deformation around a crack tip, while other alloys show extensive plastic deformation (albeit localized into shear bands). The precise reason for this difference is not understood at present, but it seems likely that it will be resolved with continued work on fundamental aspects of plastic deformation and fracture. This is likely to lead to development of new alloys with reasonable fracture toughness, although not to tensile ductility. However, even this will be an important step if such alloys can be used as matrices for composites.

Second, in order to achieve tensile ductility, it appears to be necessary to have some microstructural features to interact with shear bands. Furthermore, the length scale of the microstructure is clearly a critical parameter in arresting shear band propagation. Again, the precise reasons for this are not known, but continued research quite likely will lead to an improved understanding of the interactions between second-phase particles and shear bands.

At present, the most promising approach to producing composite materials with the proper microstructural length scale is the formation of dendritic composites, as discussed above. A critical limitation is that this process has been demonstrated in only two, closely related alloys and does not appear to be a general phenomenon.

Unfortunately, our understanding of thermodynamics and phase formation in complex multicomponent alloys is not such that we can predict a priori which alloys are capable of producing ductile dendrites in a glass-forming matrix. Until that understanding is developed, discovery of new dendritic composite materials will remain a matter of trial

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and error. The potential benefits are significant, however, because there exists the possibility of making materials with exceptionally high strength, fracture toughness, and fatigue resistance.

Summary and Recommendations

Metallic glasses combine some of the advantageous mechanical properties of metals—strength, stiffness, and in some cases toughness—with the processing flexibility usually associated with thermoplastic polymers. The absence of crystalline defects allows metallic glasses to be much stronger than conventional alloys but also means they have near-zero tensile ductility and poor fatigue resistance. In structural applications, therefore, metallic glasses are most likely to be useful in the form of composites consisting of ductile crystalline dendrites in a metallic glass matrix. These dendritic composites sacrifice some strength but can have exceptionally high fracture toughness, as well as good fatigue resistance, and could replace high-strength steels in certain load-limited structural components in aerospace vehicles where space is limited.

Because they are true glasses, thermoplastic forming near the glass transition temperature affords metallic glasses tremendous flexibility in processing. For instance, metallic glass components can be formed in a single step (for example, by injection molding) in complex geometries that would be difficult or impossible to produce with conventional alloys. In addition, metallic glass foams can be made with relative ease, raising the possibility of making structural foams with high strength and stiffness. Finally, because they lack a crystalline grain structure, metallic glasses can be used to form nanoscale features with high fidelity. This may make metallic glasses useful in a variety of micro-electromechanical systems (MEMS) applications.

Metallic glasses also have significant limitations for aerospace applications, however. Foremost among these is a lack of good glass-forming alloys; in particular, there are no good aluminum-rich glass-forming alloys, the known titanium-based alloys are either relatively dense (owing to high concentrations of alloying elements) or contain beryllium, and the known magnesium- and iron-based alloys are all quite brittle, with low fracture toughness. Although metallic glass matrix composites can have outstanding properties (particularly strength and fracture toughness), the number of good composite systems known at present is also quite limited.

For metallic glasses (and their composites) to be of broad utility in aerospace structural applications, progress in the following areas is required:

- Development of new lightweight alloys and composite systems, preferably by computational and/or combinatorial approaches rather than by trial and error.

- Understanding of mechanical behavior, especially:

  - The effect of alloy composition and structure on plastic deformation.

  - Microstructural design of composites for optimal toughness.

- Development of processing techniques, including thermophysical processing of complex and/or nanoscale features as well as production of metallic glass foams.

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It is highly likely that continued work over the next 20-50 years will result in significant advances in all these areas, and that metallic glasses and metallic glass matrix composites will see increasing acceptance as structural materials. Whether or not they achieve widespread use in aerospace applications, however, depends critically on the development of new, lightweight alloys.

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