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Properties of Amorphous Metals

Overview of the Technology and Significance of Metallic Glasses

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Abstract. - Metallic glasses have exceptional strength, corrosion resistance, and ease of magnetization as a result of their novel internal structures. Combined with low manufacturing costs, these properties make these materials attractive for many applications. Metallic glasses also have scientific fascination because their compositions, structures, and properties have unexpected features.

Introduction

Liquid metals crystallize with great rapidity. As a result, solid metals have been used from antiquity up to nearly the present in polycrystalline forms. Therefore, when Klement, Willens, and Duwez (1) discovered that selected metal alloys can be quenched fast enough to circumvent crystallization, considerable excitement was created among metallurgists. Metallic materials that are rigid, and which have liquid-like molecular structures result if very fast cooling (-10⁶°C/sec) successfully circumvents crystallization.

By analogy with other super-cooled liquids, quenched metallic alloys are called glasses. Since they are derived from liquids rather than gases or plasmas, they do not necessarily have the same structures as other non-crystalline metals. Also, since associations of atoms often exist in the liquids from which they form, they are not necessarily "amorphous," but instead may contain well-defined short-range ordering of atoms.

Perhaps the prime virtue of metallic glasses is that they can be produced in useful forms economically. As a result, on a comparative cost basis, they are potentially the strongest, toughest, most corrosion resistant, and easily magnetized materials known to man. Their costs are very low because they are formed directly from the liquid without passing through the many steps that are used in conventional metallurgy. Also, they can be made from the least expensive of metals; namely, iron.

To make a thin strip of steel in the conventional way, an ingot is first cast; this is then hot-rolled to form a billet; further rolling flattens the billet into a narrow plate; then a series of cold-rolling and annealing steps is used to reduce the plate to thin strip-stock. In all, six or eight steps are needed.

By contrast, thin strips of metallic glass are quickly cast in one step. More than a kilometer of strip can be produced in one minute. It is estimated that about four to five times less energy is consumed in going from liquid metal to a thin, metallic glass strip than would be consumed by conventional metallurgical processing of an ingot into thin strip.

Supercooled liquid alloys have remarkable combinations of properties as a result of their unusual molecular structures. Of all their physical properties, perhaps the
most remarkable is the ductility that many of them have (2). This is the basis of their interest for engineering uses because it provides the toughness that makes them easy to handle and markedly increases their reliability. It is exemplified by one of the first commercial products; nickel-base, glassy brazing-foils (3). These were introduced to the market place in the spring of 1978, and their use for joining together parts of aircraft engines and other devices has grown since. Their utility comes from the fact that nickel-base brazing alloys are brittle when they are crystalline; so the conventional form is powder. But when such alloys are rapidly quenched to obtain glassy ribbons, these are ductile. Ribbons can be more easily handled by users than powders.

The ductilities of glasses pose an interesting scientific question: for the same alloy composition, why is the crystalline form brittle, while the glass is ductile? The answer lies in subtleties of the atomic arrangements and the nature of chemical bonding in metals.

Because iron is the least expensive metal, ferrous glasses have the greatest commercial value and are emphasized here. However, metallic glasses have been made in many alloy systems using elements from all parts of the periodic table including the precious metals (e.g., Pd86Si14), transition metal pairs (e.g., Cu66Zr34), low density metals (e.g., Ti60B40), metal-metalloids (e.g., Fe95B5), alkali metals (e.g., Rb85S015), alkaline earth metals (e.g., Ca76Mg24), rare earth metals (e.g., La76Au24), and actinides (e.g., U70Cr30). Recent reviews of these many alloys and their properties have been given by Waseda and Toguri (4), and by Chen (5).

**FORMATION**

In principle, any liquid can be quenched so rapidly that it does not have enough time to crystallize before the atoms (or molecules) within it begin to move so sluggishly that the structure within it becomes "frozen." This may be clarified by considering Figure 1, a time-temperature-crystallization diagram.

Here the "C"-shaped curves indicate the times at which crystallization will start and finish if a liquid is quickly cooled below its melting point to a particular temperature level. The "nose" of the C-curve indicates the minimum time for crystallization to start. The higher the temperature is above the nose, the smaller the supercooling, and therefore the longer it takes to start crystallization. The further the temperature is below the nose, the higher the viscosity of the liquid and therefore the longer it takes for crystallization to start.
To avoid crystallization, the time taken to cool below the C-Curve's nose must be less than the time at which the nose is positioned. For silicates and many organic polymers, the nose may lie at hours or days. This makes glass formation easy in these materials. For pure metals, the nose may lie at less than a micro-second. For selected glass-forming alloys, the nose lies at a few milliseconds. Thus cooling rates of $10^5-10^6 \degree C/sec$ are adequate to bypass crystallization.

The alloys that can most easily be obtained in glassy form are usually eutectic compositions (6) as illustrated in Figure 2 for the practically important Fe-B system.

![Graph showing approximate glass-forming range](image)

At a eutectic composition, the melting temperature is a minimum but this is not the most important feature for easy glass formation. More important is the large structural change that must occur between the single phase liquid just above, and the two solid phases just below the eutectic temperature; especially if the atoms in the liquid are associated into quasi-molecules.

During eutectic crystallization, diffusion must occur over many atomic distances in order to nucleate more than one solid phase. Thus the nose of the C-curve lies at longer times.

In order to form useful materials, rapid quenching must be done continuously to obtain long filaments. This can be done by "jet-casting," or by "planar-flow-casting:

In jet-casting, a thin stream is ejected from a laminar-flow nozzle and then quenched. A cold liquid that flows co-currently with the liquid metal quenches the stream into a wire (the Kavesh process), (7); or the stream may impinge on a revolving copper wheel, thereby producing a flat ribbon (the Pond process), (8).

If wide strips are desired, a slitlike nozzle can be used that lies in close proximity to a rotating wheel (Figure 3).

![Diagram of jet-casting process](image)

Alloy coming from the slit is quickly quenched into a glass (the Narasimhan process), (9). This process can produce strips of any desired width.

The production of metallic glass filaments has several advantages when compared with conventional metallurgical pro-
cessing. Being direct, it eliminates a number of forging, rolling, annealing, and drawing steps. Since the alloys are eutectics, the maximum process temperature is lower than for dilute alloys. Since the metal is shaped in the liquid state, only small forces are needed. Finally, the processing is intrinsically fast (up to 2 km/min or 6000 ft/min). A disadvantage is that heat must be extracted from the metal very rapidly so at least one dimension of the product must be small. Typical ribbons are 0.05mm thick.

Another disadvantage is that metallic glasses have limited thermal stability. At a few hundred degrees Centigrade, they devitrify into one or more crystalline phases, and drastically change their properties.

COMPOSITIONS AND ATOMIC STRUCTURES

In searching for glass-forming alloys, eutectic compositions are favored (10). This provides structural clues about glasses because the structure of the eutectic liquid anticipates the structure of the glass. A eutectic alloy converts into two solids just below its melting point, time permitting. Otherwise, it becomes supercooled and eventually a glass. Thus eutectic compositions have markedly different structures depending on how fast they are cooled, and their properties vary accordingly. For example, eutectic compositions are often brittle as polycrystals, but not when they are glassy.

A second structural clue is the fact that eutectic compositions tend to lie at simple atomic ratios (11). Many important glass-forming alloys consist of transition metals plus metalloids (B, C, N, Si, or P). The frequencies with which eutectics of transition metals plus B, C, or P lie at particular compositions are plotted in Figure 4. If arbitrary compositions yielded eutectics, the distribution would be flat. Instead, it has two strong peaks: one at the ration 5/1; the other at 6/1.

The presence of specific compositional ratios suggests specific chemical bonding. This is consistent with the strong interactions between transition metal atoms and metalloids which lead to refractory borides, carbides, silicides, etc. However, these compounds are brittle, whereas the glasses tend to be ductile. In order to account for these facts, it may be postulated that the eutectic liquids consist of randomly-packed atoms. Each cluster tends to be made up of a metalloid atom surrounded by five (or six) transition metal atoms. The clusters are bound internally primarily by stereo-regular d-orbital bonds, while the clusters are held together by a Fermi gas of s-electrons.

Clear evidence of the existence of
short-range-order within metallic glasses has been provided by anelastic relaxation studies (12): magnetic textures and annealing phenomena (13); and Mössbauer spectroscopy (14). Other types of studies have also provided evidence of short-range-order; but not necessarily of the molecular clusters hypothesized above. An absence of long-range-order has been amply confirmed by X-ray, electron, and neutron spectroscopy (15).

**Properties**

Some properties of metallic glasses are outstanding. For example, their magnetizabilities, and their mechanical toughness. Some also have small temperature coefficients of electrical resistivity (16), and of lineal expansion (17). And acoustic waves can propagate through them for remarkably long distances (18). At low temperatures, some become superconductors (19), and other interesting electronic phenomena occur in them such as the propagation of spin waves (20). Only the strengths, corrosion resistances, and magnetizabilities will be described here.

**Strength.** Metallic glasses have good elastic stiffnesses. Some of them resist plastic deformation better than the strongest steels. Also, they resist cracking very effectively, especially when their high strengths are considered.

No other ferrous materials have such high yield stresses as the best metallic glasses, although some steels have comparable breaking strengths (Figure 5). Ductile iron-based compositions were first discovered by H. S. Chen and D. Polk (21). An example of one of their compositions is the multi-component alloy, Ni$_3$Fe$_2$P$_{14}$B$_6$A1$_3$. A much simpler composition is the binary alloy, Fe$_8$B$_{28}$, discovered later by Ray and Kavesh (22), which has a yield strength of 525,000 psi (3600 MPa). The strongest composition has been found by Ray (23), Fe$_6$Cr$_6$Mo$_6$B$_28$, which has a yield strength of 650,000 psi (4500 MPa).

Since metallic glasses yield abruptly at a critical applied shear stress which depends very little on temperature, they do not exhibit Newtonian viscosity. Instead, they approximate an ideal elastic-plastic material. Their behavior resembles that of a heavily strain-hardened crystalline metal.

Plastic flow in metallic glasses occurs very heterogeneously at low temperatures and high strain-rates. This is consistent with the motion of dislocations through the structure.

In crystalline metals, dislocations are very mobile because of the periodic
atomic structure. In glasses they have very low mobilities because the structure is not periodic. The magnitude of the consequently high yield stress can be calculated by means of a very simple theory (24).

Plastic flow provides good resistance to crack propagation. This makes a material resistance to impact, and insensitive to surface defects. This differentiates metallic glasses from silicate glasses which can be quite strong, but brittle. Metallic glasses have much greater fracture toughnesses than silicate glasses (25). Measurements (Figure 6) of their resistance to tearing were made by Kimura and Masumoto (26).

<table>
<thead>
<tr>
<th>GLASS</th>
<th>TEARING ENERGY (J/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₈₀P₁₀C₇</td>
<td>11</td>
</tr>
<tr>
<td>P₄O₁₀S₁₀O</td>
<td>4</td>
</tr>
<tr>
<td>Cu₉₁Z₄₉</td>
<td>6</td>
</tr>
<tr>
<td>STEEL</td>
<td>2</td>
</tr>
<tr>
<td>AL-ALLOY</td>
<td>1</td>
</tr>
<tr>
<td>ELASTOMERIC</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>POLYMERIC</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>SILICATE</td>
<td>&lt;0.001</td>
</tr>
</tbody>
</table>

A unique mechanical feature of metallic glass strips is that they are strong in both the longitudinal and the transverse directions. This biaxiality of strength makes them attractive for constructing composites (27).

Corrosion Resistance. All metals oxidize readily in aqueous electrolytes. But some become "passivated" by a protective surface oxide. For example, iron rusts readily because simple iron oxide is porous and hence not protective. If several percent of chromium is added to the iron, a protective chromate film forms on the surface.

Iron-chromium glasses form extremely protective films and "super-stainless-steels" result (28). Such glasses are particularly resistant to chlorides (sea-water), and sulfates. In a standard ferric chloride solution conventional stainless steels are severely attacked whereas an appropriate iron-chromium glass is barely touched.

The metalloid as well as the transition metal contents determines the corrosion resistance of a glass. Naka, Hashimoto, and Masimoto have shown that ferrous glasses containing 5-10 percent chromium are most corrosion resistant if they contain several percent of phosphorous in addition to other metalloids (28). Silicon is least effective while boron and carbon lie between P and Si in effectiveness.

Ease of Magnetization. Ferrous glasses are among the most easily magnetized of all materials. Some need only fields in the milli-Oersted range; that is, fields 100X smaller than the Earth's field. Previously, only special nickel-iron alloys could be so easily magnetized. But conventional soft magnetic materials are mechanically soft, whereas glasses are very hard.

Despite their irregular atomic structures, ferrous glasses exhibit high saturation magnetizations. The magnetic moment per transition metal atom is decreased in the glasses by the irregular structure,
and by the presence of the metalloid atoms. Boron decreases the moment less than phosphorus does.

Easy magnetization implies easy domain-walls motion. This has been confirmed by O'Handley who measured wall velocities directly (29), and obtained drag constants. Comparative data show that domain-wall mobility is exceptionally high in glasses. This results because obstacles such as grain boundaries are absent; electrical resistivities are high which damps eddy-currents; and crystal anisotropy is absent.

Domain-wall mobility yields excellent macroscopic properties. The loss factor is very low (Figure 7).

In addition, some glasses have exceptionally high magnetostriction. Also, elastic waves propagate through them with exceptionally little attenuation. Thus their magneto-acoustic properties are unusual. Reviews have been written by Luborsky, Frischmann and Johnson (30); and by Hilzinger, Mager and Warlimont (31).

ROLE IN ENGINEERING

The invention of metallic glasses has given metallurgy a new branch. Unlike science, engineering imposes economic demands on any material that competes with other materials. Some features that become important are: the speed with which glasses can be manufactured; fabricability into product components; and ability to reduce the operating costs.

To construct components, glassy ribbons can be woven to make fabrics, or braided to make tubes, or helically wrapped to make cylinders, or laminated to make plates. Such components may be used in structures for their strength, in hostile environments because of their corrosion resistance, or in magnetic circuits to save energy and improve performance. Under some conditions, shock compression can be used to make objects from glassy powders (32).

Structural applications may include high-strength control cables, sheathing on electrical and optical cables, pressure vessels, flywheels for storing energy and power, mechanical transmission belts, torque transmission tubes, rocket casings, reinforcing belts in rubber tires, and more.

Because chromium-bearing glasses resist general corrosion and pitting so well in chlorides and sulfates, they may be attractive for marine, and bio-medical uses. These include naval aircraft cables, torpedo tubes, chemical filters and reaction vessels, electrodes, razor blades, scalpels, suture clips, and others.

Ease of magnetization combined with hardness makes metallic glasses very at-
tractive for carrying flux in a variety of magnetic devices including motors, generators, transformers, amplifiers, switches, memories, recording heads, delay lines, transducers, and shielding. Some of these applications take advantage of the mechanical hardnesses of glasses to minimize wear, or maximize acoustic wave propagation.

Because of their widespread use, transformers are particularly attractive. The core losses in transformers used for reducing high transmission voltages to lower household voltages dissipate roughly $5 \times 10^8$ dollars worth of electricity per year in the United States. Metallic glass transformer cores can potentially cut this in half. Although transformers are efficient devices when fully loaded, they are often not operated at full load and they use energy whether any load is being placed on them or not.

Some advantages of metallic glass cores in power transformers are illustrated in Figure 8 which compares two 15KVA transformers: one with a steel core; the other with a glass core.

Use of the glass reduces the exciting current by a factor of 21, and the core losses by a factor of 8. The low core losses also allowed design improvements to be made which reduced the copper losses (Joule heating), and gave an overall loss improvement by a factor of 1.8 at full load.

**ROLE IN SCIENCE**

Studies of metallic glasses are generating improved understanding of the metallic state; both liquid and solid. One reason is the availability of reproducible glassy specimens which allows physical measurements to be made of metals in composition regimes that were not accessible previously. These new composition ranges together with novel atomic patterns lead to electronic structures that have not been studied in the past. Interpretations of property observations are limited at present by the lack of precise knowledge of the short range order that exists in metallic glasses. This must be improved in order to significantly reduce ambiguity in the interpretation of the physical properties.

Structural defects such as vacancies, impurities, dislocations, Bloch walls, and others take on new meanings in these materials. As do excitations such as phonons, and spin waves.

Surfaces and their defect structures constitute still another aspect of metallic glasses that need a great deal of definition. Improved scientific knowledge of metallic glasses will reinforce their impact on technology. In turn, technological advances will provide new scientific opportunities.
REFERENCES

2. J. J. Gilman, Physics Today 28, 46 (1975)

CAPTIONS

FIGURE 1 - Time-temperature-crystallization diagram.
FIGURE 2 - Iron-boron phase diagram with glass-forming region cross-hatched.
FIGURE 3 - Diagram of the planar-flow-casting process.
FIGURE 4 - Distribution of eutectic compositions for transition metal-B, C, or P pairs.
FIGURE 5 - Yield strengths of glasses and steels.
FIGURE 6 - Toughnesses of metallic glasses compared with other materials.
FIGURE 7 - Transformer core losses.
FIGURE 8 - Characteristics of two 15KVA transformers.