most critical engine components. Such constraints will promote the development of new material systems and processes. As design schemes for gas turbine components increase in sophistication, it seems clear that manufacturing innovations will play an increasingly important role.

Some anticipated changes are outlined below:

1) Low- to moderate-temperature static and rotating components will be manufactured from high-performance composite materials.

2) Near-final shape disks will be produced that are graded in composition, microstructure, and anisotropy to optimize mechanical properties.

3) New burner configurations will permit the use of new, improved sheet materials.

4) Multipiece construction of vanes and blades to provide highly efficient cooling will become common practice.

The emphasis in military engines will be on improving system reliability and performance. Higher turbine inlet temperatures will continue to be the primary goal, since this is the most effective way to increase power output. Commercial engines will be designed primarily for fuel efficiency, possibly even at the expense of some sacrifice in component durability. An important consideration will be the attainment of higher metal temperatures for turbine blades, to reduce cooling-air requirements. The achievement of higher design strengths for disks and higher resistance to environmental degradation for vanes will also be important goals, because of the benefits of reduced weight, lower engine cost, and increased operating life.

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Metallic Glasses

John J. Gilman

Summary. The novel internal structures of metallic glasses lead to exceptional strength, corrosion resistance, and ease of magnetization. Combined with low manufacturing costs, these properties make glassy ribbons attractive for many applications. These materials also have scientific fascination because their compositions, structures, and properties have unexpected features.

During almost all of the 8000 years that metals have been used by humans, their structures have consisted of aggregates of crystals. Therefore, the discovery by Klement *et al.* (*1*) that selected metal alloys can be quenched fast enough to circumvent crystallization caused considerable exictement among metallurgists. They showed that very fast cooling ($\sim 10^6$ °C per second) can yield metallic materials that are rigid and have liquid-like molecular structures.

By analogy with other supercooled 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 noncrystalline metals. Also, since associations of atoms often exist in liquids, they are not necessarily "amorphous," but instead may contain well-defined short-range order.

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 most 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. They can be made from the least expensive of all metallic raw materials, iron.

To make a thin strip of steel in the conventional way, an ingot is first cast; this is hot-rolled to form a billet, the billet is flattened by further rolling into a narrow plate, and 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.

In contrast, thin strips of metallic glass are cast in one step. An entire spool can be produced in a matter of a few minutes. It is estimated that about four to five times less energy is consumed in going from a liquid metal to a thin, metallic glass strip than would be consumed by

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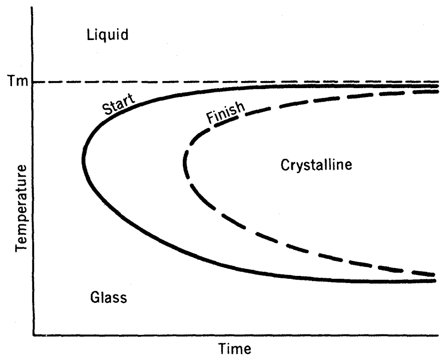

Fig. 1. Time-temperature-crystallization diagram. For a glass to be obtained, the cooling curve from the liquid state must avoid intersecting the crystallization "start" line.

conventional metallurgical processing.

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 of many of them (*2*). This is the basis of their interest for engineering uses because it makes them tough and easy to handle and increases their reliability markedly. It is exemplified by one of the first metallic glass products, nickel-base brazing foils (*3*). These were introduced to the marketplace in the spring of 1978, and their use for joining together parts of aircraft engines and other devices has grown since then. 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 these alloys are rapidly quenched to obtain glassy ribbons, they are ductile. Such ribbons can be more easily handled than conventional powders.

The ductilities of glasses pose an interesting scientific question: For the same alloy composition, why is the crystalline form brittle but the glass 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 they are emphasized in this article. However, metallic glasses have been made in many alloy systems, using elements from all parts of the periodic table including the precious metals (for example, $Pd_{80}Si_{20}$), transition metal pairs ($Cu_{60}Zr_{40}$), low-density metals ($Ti_{60}Be_{40}$), metal-metalloids ($Fe_{80}B_{20}$), alkali metals ($Rb_{85}O_{15}$), alkaline earth metals ($Ca_{70}Mg_{30}$), rare earth metals ($La_{76}Au_{24}$), and actinides ($U_{70}Cr_{30}$). These many alloys and their properties have been reviewed 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 its atoms (or molecules) begin to move so sluggishly that the structure within it becomes "frozen." This may be understood by considering Fig. 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 lower 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 and thereby obtain a glass, 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 position of the nose may lie at hours or days. This makes it easy to bypass crystallization in these materials. For pure metals, because of their simple atomic structures, it may take less than a microsecond for crystallization to begin at the nose temperature. However, for the selected alloys that form interesting metallic glasses, the nose lies at a few milliseconds. Thus cooling rates of 10^5° to 10^6 °C per second are adequate.

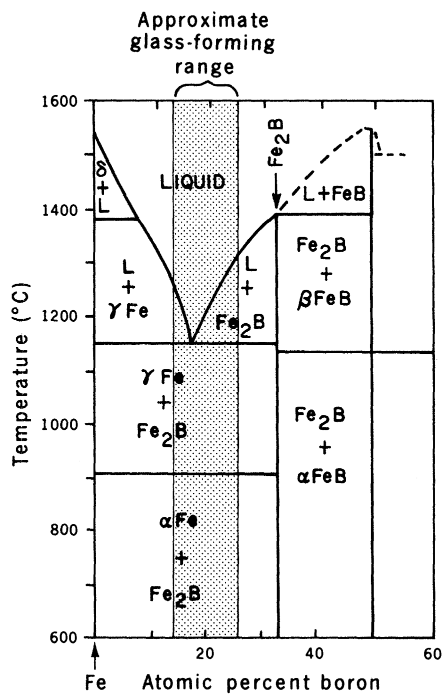

Fig. 2. Portion of the iron-boron phase diagram. The glass-forming region spanning the deep eutectic composition at 17 atomic percent boron is stippled.

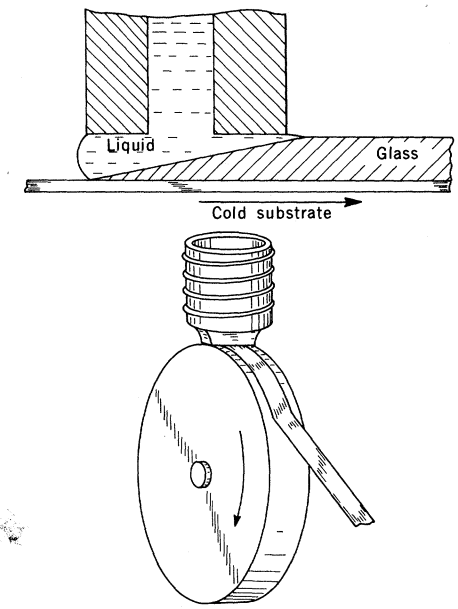

Fig. 3. Schematic diagram of the planar-flow-casting process, in which a slotted nozzle is brought very close to the surface of a rapidly moving cold substrate.

The alloys that can most easily be obtained in glassy form are usually eutectic compositions (*6*). The phase diagram of Fig. 2 illustrates this for the practically important Fe-B system. At a eutectic composition, the melting temperature is a minimum, but this is not the most important feature of a eutectic liquid for easy glass formation. What appears to be most important is the large structural change that must occur between the liquid just above and the two solid phases just below the eutectic temperature. If the atoms in the liquid are associated into quasi-molecules (as they often are), this increases the amount of change that must occur.

Complex structural changes during crystallization take time because much diffusion must occur and often the atomic movements must occur in specific sequences. Thus the nose of the C-curve is moved toward longer times.

In order to form useful materials, selected alloys must be quenched not only rapidly but also in a continuous way, so that useful filaments can be obtained. This can be done by "jet-casting" or by "planar-flow-casting." In jet-casting a thin stream of liquid metal is ejected from a laminar flow nozzle and then quenched. A cold liquid such as brine that flows cocurrently with the liquid metal may be used to quench the stream into a wire [the Kavesh process (*7*)], or the stream may be impinged onto a revolving piece of cold metal such as copper, thereby producing a flat ribbon [the Pond process (*8*)].

If wide strips are desired, the metal can be passed through a nozzle with a thin slit in it that lies in close proximity to a cold rotating metal wheel (Fig. 3). As the metal flows from the slit it is very quickly quenched into a glass [the Narasimhan process (*9*)]. Since the geometry of this process is planar, it can produce strips of any desired width (ignoring practical problems that intensify as the width increases).

From a practical viewpoint, the production of metallic glass filaments has several advantages when compared with conventional metallurgy. Being a direct casting process, it eliminates a number of forging, rolling, annealing, and drawing steps. Since the alloys are eutectics, the maximum process temperatures are lower than those for pure metals or dilute alloys. Also, the shaping of the metal occurs in the liquid state so the forces needed for shaping are very small, leading to lightweight equipment. Finally, the processing is intrinsically fast (up to 2 kilometers per minute, 6000 feet per minute) because of the rapid quenching involved.

Some disadvantages are that heat must be extracted from the system very rapidly in order to achieve continuous operation. And heat must flow out of the material in a short time, so at least one dimension of the glassy product must be small. This limits feasible shapes to powders, wires, ribbons, and thin shells. Typical ribbons are 0.05 millimeter thick and 50 millimeters wide.

Another disadvantage of metallic glasses is that they have limited thermal stability. As they are heated, atomic motion occurs in them at temperatures of a few hundred degrees Celsius. At slightly higher temperatures they devitrify into one or more crystalline phases.

Compositions and Atomic Structures

The search for alloys that readily yield metallic glasses is aided by the fact that eutectic compositions are favored (*10*). This also provides clues about the structures of glasses because the structure of the eutectic liquid must anticipate the structure of the glass. When a pure metal cools through its melting temperature, it crystallizes into a solid of the same composition. But a eutectic alloy is converted into two solids just below its melting point, time permitting. If time does not permit, it is supercooled and eventually becomes a glass. Thus it is apparent that solids of eutectic compositions have

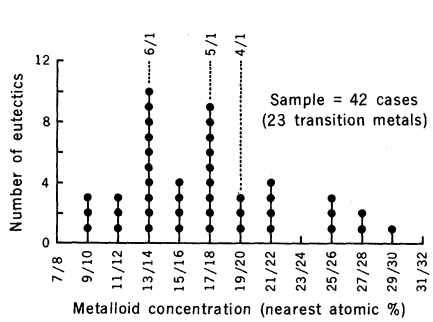

Fig. 4. Distribution of eutectic compositions for pairs consisting of a transition metal plus B, C, or P. All known cases are shown.

markedly different structures depending on the cooling rates at which they are formed. This is a key to the unusual properties of metallic glasses, whose compositions are often ones that metallurgists have discarded as worthless for centuries. These compositions are brittle in their conventional polycrystalline forms, but not when they are glassy.

A second important clue to the structures of metallic glasses is provided by the observation 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 Fig. 4. If arbitrary compositions yielded eutectics, the distribution would be flat. Instead, it has two strong peaks: one at the ratio 5/1, the other at 6/1.

Table 1. Yield strengths of iron-based glasses compared with some conventional polycrystalline steels.

Material	Yield strength (kpsi)	Yield strength (MPa)
Glasses		
$Fe_{40}Ni_{40}P_{14}B_6$	350	2400
$Fe_{80}B_{20}$	525	3600
$Fe_{60}Cr_6Mo_6B_{28}$	650	4500
Steels		
Type 302 (cold-worked)	200	1400
AISI 4340	240	1600
Ausformed	290	2000
Tire cord (0.8 percent C)	400	2800

Table 2. Toughnesses (tearing energies) of some metallic glasses compared with other materials. Note that about 10,000 times more energy is needed to tear the iron-based glass than ordinary silicate glass.

Material	Tearing energy (J/cm^2)
$Fe_{80}P_{13}C_7$ glass	11
$Pd_{80}Si_{20}$ glass	4
$Cu_{57}Zr_{43}$ glass	6
Steel	2
Aluminum alloy	1
Elastomeric glass	< 0.1
Polymeric glass	< 0.1
Silicate glass	< 0.001

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, and so on. However, these compounds are brittle, whereas the glasses tend to be ductile. In order to account for these and other facts, it may be postulated that the eutectic liquids consist of randomly packed clusters or quasi-molecules, rather than 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 stereoregular *d*-orbital bonds, while the clusters are held together by a Fermi gas of *s* electrons. In a glass derived from such a liquid, ductility is possible through gliding of dislocations between the clusters without a need for disrupting *d* bonds. On the other hand, the local short-range order within the clusters allows *d*-orbital symmetry to be partially preserved.

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. Absence of long-range order has been amply confirmed by x-ray, electron, and neutron spectroscopy (*15*).

Properties

Some of the properties of metallic glasses are outstanding, such as the ease with which they can be magnetized and their mechanical toughness. Selected alloys also have very 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 phenonomena occur in them such as the propagation of spin waves (*20*). There is too little space here to discuss the many properties that have been measured. Only the strengths, corrosion resistances, and magnetizabilities will be described. The reviews already mentioned contain a wealth of further information.

Strength. Metallic glasses have good elastic stiffness, and some of them resist plastic deformation better than the strongest steels, such as those used in aircraft landing gear. They also resist cracking very effectively, which is especially interesting when their high strengths are considered, because crack resistance tends to decrease markedly as strength increases.

No other ferrous materials have as high yield stresses as the best metallic glasses, although some steels have comparable breaking strengths (Table 1). Ductile iron-based compositions were first discovered by Chen and Polk (*21*). An example of one of their compositions is the multicomponent alloy $Ni_{39}Fe_{38}P_{14}B_6Al_3$. A much simpler composition is the binary alloy $Fe_{80}B_{20}$ discovered by Ray and Kavesh (*22*), which has a yield strength of 525,000 pounds per square inch (3600 megapascals). It has a correspondingly high hardness [1100 DPH (diamond pyramid hardness)] and a good abrasion resistance. The strongest composition to date is one found by Ray (*23*), $Fe_{60}Cr_6Mo_6B_{28}$, which has a yield strength of 650,000 psi (4500 MPa).

After plastic flow begins, glasses show little strain-hardening. Therefore, they are plastically unstable in tension, but they can sustain very large plastic strains when they are loaded in bending, torsion, and compression. Their yield stresses are essentially independent of temperature below about 0.7 of their glass transition temperatures. This is reflected in the small dependence of their yield stresses on applied strain rates.

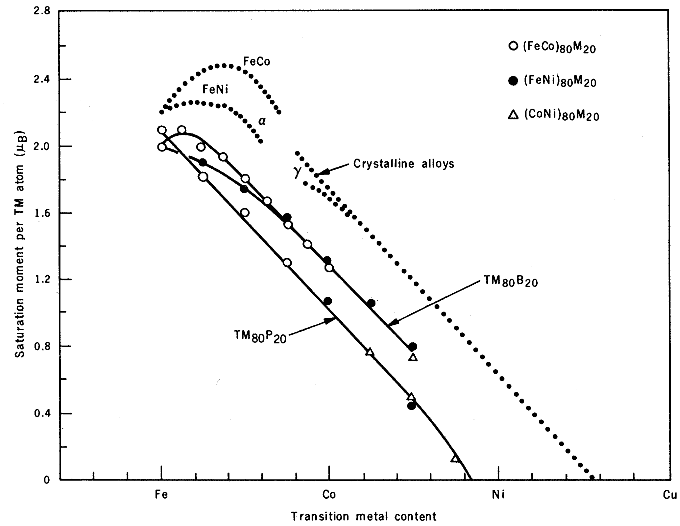

Fig. 6. Dependence of magnetic moments for glasses on alloy composition. Note that phosphorus depresses the magnetic moment more than does boron. Abbreviations: *TM*, transition metal; *M*, metalloid.

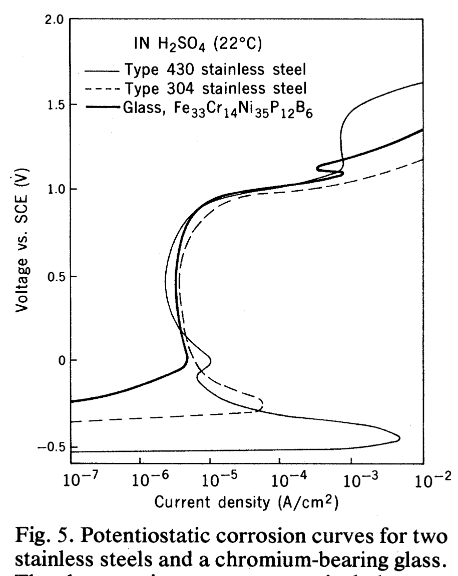

Fig. 5. Potentiostatic corrosion curves for two stainless steels and a chromium-bearing glass. The glass passivates at comparatively low potentials. Abbreviation: *SCE*, standard calomel electrode.

Since they yield abruptly when an applied shear stress reaches a critical value, and the yield stress depends little on temperature, it is apparent that metallic glasses do not exhibit Newtonian viscosity. Instead, they approximate an ideal elastic-plastic material. In several ways their plastic behavior resembles that of a crystalline metal that has been heavily strain-hardened.

Plastic flow in metallic glasses occurs very heterogeneously at low temperatures and high strain rates. This is readily confirmed by polishing a flat surface on a specimen and then observing it with a microscope after the specimen has been deformed. It will show a broad spectrum of steps on the surface that have resulted from localized plastic shearing; that is, from the motion of dislocations through the structure.

In pure crystalline metals the dislocations that create plastic flow are very mobile because of the periodic atomic structure. But in glasses they have very low mobilities because the structure is not periodic. Low dislocation mobility requires a high driving stress for plastic flow; hence the yield stress is high. Its magnitude can be accounted for quantitatively by means of a very simple theory (*24*).

One consequence of plastic flow is good resistance to crack propagation. This makes a material resistant to impact and insensitive to surface defects such as scratches. It is measured by a fracture toughness parameter. This parameter is one feature that differentiates metallic glasses from silicate glasses; the latter can be quite strong, but they have very little resistance to cracking. Metallic glasses have fracture toughness parameters much larger than those of silicate glasses (*25*). Their resistance to tearing is especially high. Measurements by Kimura and Masumoto (*26*) are shown in Table 2.

A unique mechanical feature of metallic glass strips is that they are not only strong in the longitudinal direction, but just as strong in the transverse direction. This biaxiality of strength makes such strips attractive for reinforcing compliant materials such as rubber and for constructing composites. More discussion is given elsewhere (*27*).

Corrosion resistance. All metals oxidize readily in aqueous electrolytes. But some become "passivated" by the formation of a protective oxide film on their surfaces. An example is the case of iron, which rusts readily because simple iron oxide is porous and hence not protective. If several percent chromium is added to the iron, a protective chromate film forms on the surface and stainless steel results.

On the surfaces of iron-chromium glasses extremely protective films form

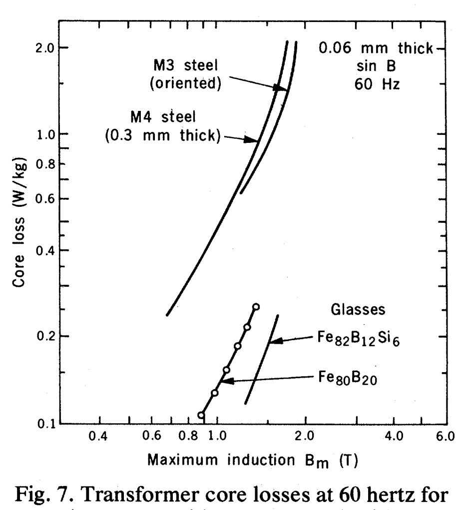

Fig. 7. Transformer core losses at 60 hertz for two glass compositions compared with conventional magnetic steel. Note the loss reduction of nearly an order of magnitude.

Table 3. Characteristics of two 15-kVA transformers. The total loss for the conventional transformer is 322 watts, compared with 180 watts for the transformer having a Metglas magnetic ribbon core. Note also the large differences in operating temperature and exciting current.

Operating parameter	Core material	
	Silicon steel	Metallic glass
Exciting current, amperes	2.5	0.12
Core loss, watts	112	14
Copper loss (15-kVA), watts	210	166
Total loss (15-kVA), watts	322	180
Energy saving, kilowatt-hours per year	0	1250
Temperature, °C	100	70

that consist of hydrated chromium oxyhydroxides, and "super-stainless steels" result (*28*). Such glasses are particularly resistant to chlorides (seawater) and sulfate environments. For example, in a standard ferric chloride solution conventional stainless steels are severely attacked, whereas an appropriate iron-chromium glass is barely touched.

A more general indication of the superior corrosion resistance of metallic glasses is provided by polarization curves (Fig. 5)—plots of the currents flowing through specimens at various constant applied potentials. The current is proportional to the rate of corrosive attack. Note that the metallic glass specimen is passivated at much lower potentials than either of the stainless steels. Also, its maximum corrosion rate is 1000 times smaller than that of type 430 and 10 times smaller than that of type 304 stainless steel.

Not just the transition metal content but also the metalloid content is important in determining the corrosion resistance of a glass. Naka *et al.* (*28*) have shown that ferrous glasses containing 5 to 10 percent chromium are most corrosion-resistant if they contain several percent phosphorus in addition to other metalloids. Silicon is least effective, while boron and carbon lie between phosphorus and silicon in effectiveness.

Ease of magnetization. Strong steels are usually relatively difficult to magnetize, but ferrous glasses are among the most easily magnetized of all ferromagnetic materials. Some can be magnetized by the application of fields in the millioersted range; that is, fields 100 times smaller than the earth's field. Previously, only nickel-iron alloys such as Permalloy could be so easily magnetized. But conventional, easily magnetized materials differ from metallic glasses in being annealed, and therefore mechanically soft, whereas the glasses are mechanically hard. Also, they are more difficult to manufacture.

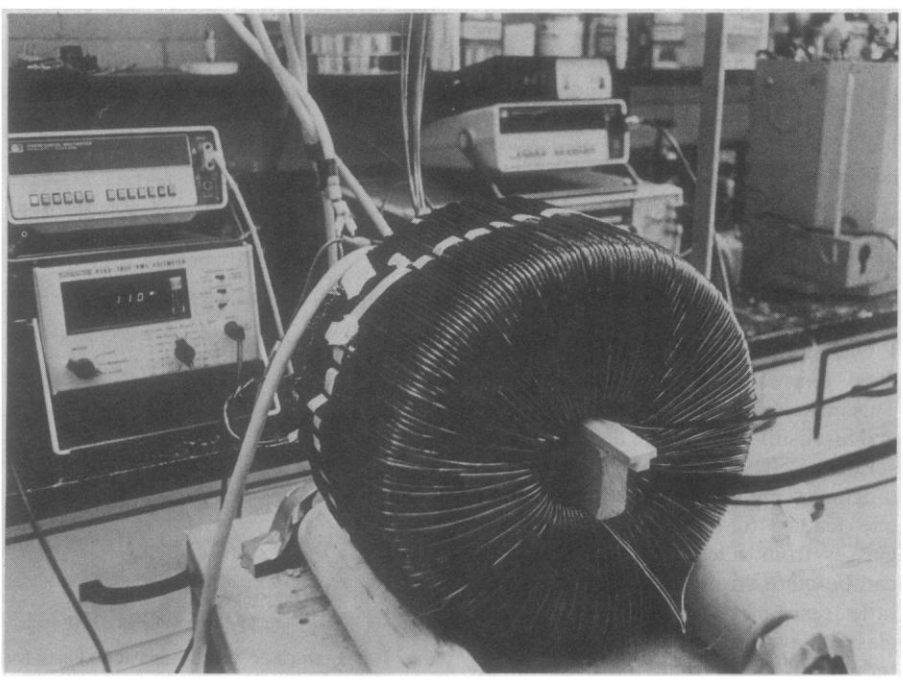

Fig. 8. Photograph of a 15-kVA transformer being tested. This transformer has a toroidal metallic glass core.

Despite their irregular atomic structures, ferrous glasses exhibit high saturation magnetizations. This is illustrated by Fig. 6, which shows how the saturation magnetizations vary with composition in the series Fe, Co, and Ni. The magnetic moment per transition metal atom is decreased in the glasses by the irregular structure and by the presence of the metalloid atoms. The latter effect is clearly demonstrated by the fact that boron shifts the curve less than phosphorus does.

The easy magnetization in glasses implies that magnetic domain walls move through them easily. This was confirmed by O'Handley (*29*), who made direct measurements of domain wall velocities as a function of an applied magnetic field. Such measurements yield damping constants (viscous drag) for domain wall motion. Comparative data show that domain walls do indeed move through metallic glasses with exceptional ease. Some reasons for this are that obstacles such as grain boundaries are absent; glasses have high electrical resistivity, which damps eddy currents; and crystal anisotropy is absent (although some short-range-order anisotropy is present).

Domain wall mobility translates into excellent macroscopic magnetic properties. In particular, the loss factor is very low in comparison with conventional materials (Fig. 7). In addition, some glasses exhibit substantial changes in magnetization when stresses are applied to them (magnetostriction), and elastic waves propagate through them with exceptionally little attenuation because they have such high yield stresses. This combination gives them interesting magnetoacoustic properties. Reviews of the magnetic behavior of metallic glasses have been written by Luborsky *et al.* (*30*) and by Hilzinger *et al.* (*31*).

Role in Engineering

As a result of the invention of metallic glasses, metallurgical engineering has a new branch. Unlike science, engineering demands that economic considerations be applied to any material that attempts to compete with other materials. Thus the fundamental features of metallic glasses that become important are the ease and speed with which they can be manufactured, the facility with which they can be fabricated into product components, and their ability to reduce operating costs of devices in which they are incorporated.

To construct components, metallic glass ribbons can be woven to make fabrics, braided to make tubes, 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 biomedical uses. Products 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 attractive 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 they maximize acoustic wave propagation.

Because of their widespread use, transformers are particularly attractive. The core losses in transformers that one finds in every residential neighborhood for reducing high transmission voltages to lower household voltages waste approximately $500 million worth of electricity per year in the United States. Metallic glass transformer cores can potentially cut this waste in half. Much of the waste occurs because transformers are often operated continuously, whether any load is being placed on them or not. An extreme example is the doorbell transformer. The only time this transformer is used is when someone presses the doorbell button, but the transformer dissipates energy continuously. Transformers in the electricity distribution system are also not used continuously. Late at night, for example, the loads on them are small. On the other hand, they tend to be overloaded in the early evenings of hot summer days.

Some advantages of putting metallic glass cores into power transformers are illustrated by the data of Table 3, which compares some of the operating characteristics of two 15-kilovolt-ampere transformers: one with a conventional magnetic steel core, the other with a metallic glass core (Fig. 8). In the transformer with the metallic glass core the exciting current is reduced by a factor of 21 and the core loss by a factor of 8. The low core loss also allowed design improvements to be made which reduced the copper loss (Joule heating) and gave an overall loss improvement by a factor of 1.8 at full load. For electricity costing $0.05 per kilowatt-hour, the energy savings for this transformer correspond to about $63 a year. The total electric generating capacity of the United States is about 0.5 terawatt. If the rate of savings that these data indicate could be scaled up to include the whole system of generators, substations, and distribution transformers, the annual savings would be $2 billion to $3 billion.

Even larger energy savings can be realized if motors can be developed that use metallic glasses effectively.

Role in Science

Studies of metallic glasses are improving our understanding of the metallic state, both liquid and solid. More detailed knowledge of the short-range atomic structures of metallic glasses will lead to further insight, because the availability of glassy specimens allows measurements to be made of materials in composition regimes that were not accessible previously. These composition ranges together with novel atomic patterns lead to electronic structures that have not been studied in the past.

Structural defects such as vacancies, impurities, dislocations, and Bloch walls take on new meanings in these materials, as do excitations such as phonons and spin waves. Surfaces and their defect structures in metallic glasses need a great deal of definition and reference to surfaces on crystals.

As scientific knowledge of these glasses grows, there is every reason to expect that it will reinforce and accelerate their effect on technology. Just as recent technological advances have provided rich scientific opportunities in this field, so will scientific studies enrich the technology.

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