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This has been a landmark year for metallic glasses as a new class of materials. More than 1000 large power-distribution transformers with glassy cores have been sold by the General Electric Company into the commercial marketplace. Also, the rate at which glasses have been produced has exceeded one million pounds per year (450,000 kg/yr). Thus, in the 13-14 years that have passed since the first ductile, ferrous glass was invented, the growth in production-rate has averaged about 90 per cent per year. Since there is no reason to expect that this growth-rate will drop in the near future, it is easy to see that metallic glasses have become an important new branch of metallurgy.

In order to make metallic glasses, appropriate alloys must be cooled rapidly enough to avoid crystallization. The appropriate alloys are typically eutectic compositions and they must be cooled at rates greater than about 10 exp(+5) deg/sec. Furthermore, in order to obtain useful shapes the rapid cooling must be done continuously to yield long wires or ribbons.

At very high cooling-rates, there is insufficient time for crystals to nucleate and grow, so the structure of the eutectic liquid is retained after the cooling process, and the substance is called a glass.

For the materials engineer it is the physical and chemical properties of these glasses that are of primary interest. The fact that they may have been produced by means of rapid solidification is secondary. On the other hand, for the businessman, the production process is of key interest because because it may determine the relative manufacturing cost; and the faster the process the lower the cost, other factors being equal.

Glasses are often said to be "amorphous" which means without structure in Greek, but this is misleading because glasses usually contain short-range-order. They inherit this from their mother liquids which contain associations of atoms or molecules. Even one-component liquids often contain polymer like associations.

There has been much work in recent years on rapid solidification. In the course of this work grain-sizes have decreased and metastable solute concentrations have increased. These trends have been evolutionary over a long period of time. For example, chill blocks have been used in the manufacture of cast-iron railway wheels for over a century.

However in 1960, when eutectic alloys were quenched by Klement, Willens, and Duwez at rates that completely suppressed crystallization in them, a revolution began. At first this involved scientific studies of metastable alloy phases including glasses. The specimens that were produced had little or no technological interest because they were misshapen, often brittle, and often composed of costly raw materials. Then, in 1972, H. Chen and D. Polk made the first ductile ferrous-glasses at the laboratory that I had organized for the Allied Chemical Corporation (now the Allied Signal Corporation). These were the first glasses with promise as engineering materials.

A photograph of Chen's first specimen is shown in **SLIDE 1**. Its composition in atomic per cent is 39Fe, 38Ni, 14P, 6B, 3Al; and it weighed about five grams. Up to the present, thousands of compositions of metallic glasses have been made; some in quite large quantities. Production ribbons are made at lineal casting speeds up to 6000 ft/min. and in continuous lengths many miles long from ton-sized heats of metal. Thus the process has been scaled up by a factor of about 100,000.

It should be noticed that this revolutionary advance resulted from the confluence of several factors, not just from one influence. In order to introduce a new material to the world of metallurgy it was necessary to invent not just any glass, but a glass with a relatively inexpensive composition combined with an inexpensive method for producing it. Furthermore, it was critical that it have ductility, and that there be a multitude of potential applications for it. Without these conditions, no one would have been willing to invest the time and money needed to develop the invention to the product level.

The revolution has been markedly strengthened by the fact that in the early stages of devitrification, glasses transform into microstructures that cannot be realized in any other way (or at least not easily realized). This has led to remarkable new structural materials; and to exceptional iron-neodynium-boron permanent magnets. Thus glasses are not only of interest for themselves, but also as precursors for special kinds of polycrystals.

Glasses have many variations and ramifications. So many in fact, that I think continued work in this field will lead to many new scientific insights and technological opportunities. Good examples are the icosohedral structural models of glasses that have been of intense interest in recent years.

While preparing for this lecture, I reviewed some of the many writings about the rapid solidification of metals. Through a series of evolutionary advances solidification studies have led to development of fine-grained, non-equilibrium, materials. They have also improved the compositions and grain-structures of the powders that are consolidated to make tools, jet-engine disks, and other structural parts. This has made very substantial improvements in the performances of these components, but it has not added a new revolutionary branch to the field of metallurgy as has the technology of metallic glasses.

Basis of the Novelty of Metallic Glass Materials

The novelty of metallic glass technology is based primarily on three factors: composition; molecular structure; and fast processing. These factors are not independent of one another, but they can be discussed separately.

Consider composition first. The compositions that form glasses readily have rarely been used in the past because relatively slow cooling of them usually leads to brittle substances. One class of examples that illustrates this point is the transition metal-boron alloys. In these alloys relatively small concentrations of boron lead to brittleness if the alloy is cooled slowly. But if the alloy is quenched to the glassy state, ductility exists at atomic concentrations of boron that are 10 to 100 times as great as in boron-containing compositions from the alloys of the past.

Next, consider molecular structures. As I mentioned earlier, the liquids from which glasses are formed contain well-defined short-range-order. A simple way to demonstrate this is to examine the distribution of eutectic (glass-forming) compositions in a large number of binary systems. It is found that eutectics are clustered at specific integral atomic ratios. Thus the short-range-order is characteristic of the mother liquid.

The short-range structure of a liquid is different in most cases from the structure that would be found in other antecedents of glassy alloys, such as: gases prior to condensation; plasmas during deposition; electrochemical solutions prior to plating; and so forth. Thus the short-range molecular structures that metallic glasses inherit from their mother liquids are unique. They may well result in unique physical properties, although this does not necessarily follow.

Finally, consider fast-processing. A ribbon that is 3 mils (0.074 mm.) thick and 4 in. (98 mm.) wide and is being cast at 3000 ft./min. (882 m./min.) corresponds to a weight rate of 3.6 tons/hr. (3300 kg./hr.). When one considers that the product is in its final form (and has gone from liquid metal to it in one step); plus the fact that lightweight equipment is used (because the resistance to the shape change is only the low viscosity of the liquid metal); this is indeed a unique, revolutionary process.

In this process, the liquid alloy is first melted in a large crucible and then poured into a tundish which delivers it to a specially shaped nozzle. **SLIDE 2.** The nozzle lays it onto a rapidly-rotating water-cooled wheel which it partially wets. As it travels with the wheel it loses heat quickly and solidifies into the glassy state. Then the solidified ribbon leaves the wheel, passes through guides and monitoring sensors, and then onto a windup sheave. If the operating mode is quasi-continuous, an automatic mechanism changes sheaves as they become full, and a sequence of melting crucibles replenishes the tundish. Signals from the monitoring sensors provide the means for feedback control of the process.

This fast-casting technology (developed at Allied Signal) for producing metallic glass ribbons can be applied to other materials. For example, it has been applied to the manufacture of polycrystalline brazing tapes.

Development of a satisfactory quasi-continuous process required many inventions and new engineering elements. These include: planar-flow casting nozzles; cooling systems for intensely heated quenching wheels; mechanical mechanisms for catching ribbons moving at high velocities and threading them into rotating sheaves and "doffing" the sheaves as they become full; sensors and systems for feedback control; and methods for handling and metering liquid alloys.

The importance of fast processing can be appreciated by considering a demand chart for metals. The demand (#/yr.) for metals is strongly correlated with their unit prices ($/#) as indicated in **SLIDE 3.** This means that the annual revenues that are generated by the sales of any given metal are strongly dependent on the unit price as indicated by the dashed revenue lines in the slide.

This may be clarified by replotting the data to show the dependence of revenues on prices as in **SLIDE 4.** This graph illustrates the powerful effect of price on the dollar volume of metal consumption. This provides a forceful motivation for seeking low manufacturing costs.

It is not a secret, of course, that fast processing tends to minimize manufacturing costs. But the magnitude of the effect does not appear to be widely appreciated, so it may be useful to consider some numbers. Suppose that a quench-casting unit produces one-inch ribbon at a rate of one ton/hr. and costs $100,000 at a time when the interest rate is 8 per cent. Further suppose that the unit is leased (in order to minimize the arithmetic). Then the direct rental charge for a one-shift operation and a 40% duty-cycle is about 0.01 $/#. Compare this with a hot-pressing unit that costs the same amount and produces about 10# of product per shift. In this latter case, the rental charge will be about 10 $/#, or about 1000 times greater.

In the first case, the capital rent per unit of product is a small fraction of the raw materials cost. In the second, it is a multiplier of the raw materials cost. It seems clear then which process is more likely to be of long-range general importance.

The other primary manufacturing costs are: energy, labor, and equipment expendables such as nozzles. They act to reinforce the conclusion above. The efficient use of capital equipment in most processes is a dominant factor in determining costs.

Translation of Novel Properties into Applications

New materials find their way into applications either by substituting for older materials in established applications, or by allowing devices to be invented that exploit their properties. Then these new devices substitute for older ones.

Fast processing combined with some unusual combinations of properties is what has made metallic glasses so attractive for a for several applications. For example, they combine extreme hardness with high corrosion resistance. This makes them attractive for cutting devices such as razor blades and scalpels. Also, they combine magnetic softness with mechanical hardness. This is an excellent combination for tape-recording heads. Some alloys combine high magnetostriction with high strength so they make excellent transducers. And so on. So many actual and potential applications have been reported that it is difficult to summarize them succinctly, but an attempt will be made here.

Ferromagnetic glasses are very easily magnetized because magnetic domain-walls move through them with extraordinary ease. The domain-wall mobilities for some typical materials are listed in **SLIDE 5**. The mobility for the glass is 500 times greater than for the standard Fe-Si material. This is why these glasses represent the greatest advance in the field of soft magnetic materials that has occurred in 50 years.

a. Transformers

When the domain-wall mobility described above is combined with the other properties of magnetic glasses and made into an electric power transformer, the core losses are markedly reduced. Data for a variety of prototypes made by five different manufacturers and in five different sizes are shown in **SLIDE 6**. For small sizes, the difference between the standard material and glass is a factor of four, while at large sizes (say 100 kVA) it becomes a factor of ten.

Since there are nearly 40,000,000 power distribution transformers in the USA, the total losses are about 35 billion KWH annually. Glass cores could save 23 billion KWH. At an average cost of $0.05/KWH this is 1.2 billion dollars per year. In other countries where the cost of electric energy is higher, the savings would be comparable or greater. Naturally, this has generated intense interest on the part of the electric utility industry, and has led to the development of commercial transformers.

The largest single transformer made to date is a 500 KVA unit made by the Westinghouse Electric Corporation. Its reported core losses are 200 W, as compared with 1000W for a similar unit with a conventional steel core.

For frequencies up to about 100 kHz, metallic glasses also make superior small transformers. This has led to their use in switching-mode power-supplies, tape-recording heads, aircraft transformers, pulse-suppression-chokes, current-metering transformers, ground-fault interrupters, transformer turns-ratio testers, high-speed welders, and a variety of other small transformers.

In 1979 it was shown by C. Cline and coworkers that if very intense magnetic pulses are applied to selected metallic glasses, their magnetizations can be reversed in as little as 25 nano-sec. Thus glasses are useful as the cores of pulse transformers and magnetic switches. These can be very large (up to several tons in weight) and are used in ion accelerators, ultra-violet lasers (excimers), and radar modulators. They have been be used to switch pulses in the multi-terawatt range of power; that is, to switch one million amperes at two million volts.

b. Surveillance monitors

The magnetization loop for an easily magnetized metallic glass is quite "square". That is, under the influence of a small applied field the magnetization rises rapidly to nearly its saturation level and then is nearly constant. In other words the magnetic response of the material is highly non-linear. A result is that if the material is exposed to electro-magnetic radiation of a particular frequency, it reradiates at several harmonics in addition to the fundamental frequency. This makes it useful for surveillance devices because the distribution of harmonics that is reradiated provides a "signature" that is relatively easy to detect.

An additional feature can be used to advantage in surveillance devices. This is the mechanical hardness which has very low acoustic-attenuation as a corollary. In other words, the glass "rings" for a long time after it is set into mechanical vibration. Thus outstanding mechanical oscillators can be made from it. These oscillators allow its response to incident electro-magnetic radiation to be sharply tuned. Through tuning then, its reradiation signature can be designed, and the sensitivity of a surveillance device markedly increased.

c. Magnetic Shielding

The high magnetic permeability of metallic glass is the basis of this application. Cobalt-bearing alloys of low magnetostriction are particularly effective. Shields may be constructed by weaving ribbons into a fabric, or by wrapping cables with ribbon in a helical configuration, or by other methods. Shielding ratios (field outside/field inside) of 100 are achieved with double helical windings on cable at a frequency of 60 Htz. For the same amount of shielding this is about 8 times better than previous materials.

d. Transducers/Sensors

Various combinations of the electrical, magnetic, and mechanical properties of metallic glasses have been used as the bases of transducers. There is no time here for a review of them, but a listing (no doubt incomplete) is given in **SLIDE 7.**

e. Joint Formation (brazing)

One of the earliest applications of metallic glasses was the manufacture of brazing tapes for making strong joints in jet-engine components. The basis of this application is that the glassy forms of the brazing alloys are ductile, unlike the crystalline forms which are very brittle. Ductile tapes are much easier to manipulate, and make superior joints, than the powders that were used previously.

The scope of this application area has been expanded by the development of ductile polycrystalline tapes of a variety of compositions, and it will probably continue to expand as the quench-casting technology is developed to include still more alloys. At present at least twenty-five compositions are offered commercially. They are grouped into families. One of these is nickel-based tapes for brazing high-temperature alloys to make engine components such as vanes in a shroud. **SLIDE 8.** Heat exchangers and food processing equipment are also made with this tape. A second family is glassy nickel-palladium tapes which can replace conventional gold-based alloys in aerospace and power electronics. **(SLIDE 9)**. A third family is copper-based alloys to replace "silver-solders" for the joining of copper- and iron-based alloys. The glassy tapes use lower cost components, and they melt and flow more uniformly than the materials they replace.

Even ordinary solder benefits from the quench-casting process. The joints it forms have finer-grains, better homogeneity, and smaller shrinkage-voids than conventional solder.

f. Mechanical components

Some of the mechanical properties of metallic glasses are outstanding. For example, they have the highest biaxial tensile strengths of any known material. So they should make useful composite structures. Also, as a result of their homogeneities, laboratory tests have demonstrated that they make superior cutting edges. And very strong wires can be made from them. Industrial applications based on these properties have been slow in developing, however. The principal reason may be fabrication difficulties. For example, the hardness of the glass rapidly wears stamping dies; and it is difficult to find compatible adhesives for making composites that can withstand cyclic loadings; and so on. It is very encouraging for the future of these applications that excellent fatigue resistance of the glasses themselves have been reported recently by Japanese workers at Unitika.

g. Chemical Components

One application of metallic glasses in chemical processing is for filters in high-field, high-gradient filtering systems. These are used to remove paramagnetic iron oxides from clays and waters which are otherwise discolored by them.

Other applications such as using glasses as catalysts, and as corrosion resistant coatings, have encountered fabrication difficulties much as the mechanical applications have. However, it appears that these are gradually being overcome.

Descendants of Glasses

Two new branches of the metallurgist's art have descended from the early work on glasses. One is the fast continuous direct-casting of ribbons and wires. The other is the use of glasses as precursors for fine-grained polycrystalline metals. I will not consider the first of these further since I have already presented some of the arguments in its favor. But I will consider the second.

In general the microstructural state that is reached by devitrifying a glass is not the same as the one that is reached by rapid solidification to a fine-grained polycrystal. In the latter case crystallization occurs in the presence of a large thermal gradient, whereas in the former case it may occur under nearly isothermal conditions. However, in various practical situations the results may be virtually indistinguishable.

The first work that I know of in which exciting new materials were derived from glasses is that of Ranjan Ray when he was at Allied Signal. He quenched ferrous alloys containing about half as much boron as usual into the glassy-state. The resulting ribbons were then warmed to embrittle them and they were fragmented to form a coarse powder which was consolidated into cylinders by hot-pressing, or hot-extrusion. These devitrified materials were strong, tough, and heat-resistant. They were, and are, quite remarkable. Their microstructures consist of tiny grains about one-tenth micron in size, stabilized by very small borides about one one-hundredth micron in size at the grain boundaries. This led to the development of Ni-Mo-Cr-B materials with attractive properties for die-casting molds and hot-working dies.

Even more exciting was the discovery by Croat and Herbst at the General Motors Research Laboratories of the new class of permanent magnet materials, based on Fe-Nd-B alloys. They initially discovered that quenching a 60Fe-40Nd alloy at an optimum intermediate rate yielded material with a coercive force of 7.5 kOe. Later it was found that a full quench to the glassy-state followed by tempering to initiate devitrification gave essentially the same result. Also, it was later found that boron additions improved the hard magnetism, and that alignment of the devitrification products by hot-working further improved the properties.

Parallel work at the Sumitomo Special Metals Company done by sintering appropriate powders produced similar high performance material. However, it appears that the quench-casting method is more cost-effective.

These materials for permanent magnets are already in production for use in the small electric motors used for actuators in automobiles.

A series of other descendants of glasses have followed these two early ones. They include:

1. Aluminum-iron alloys for use at high temperatures
2. Magnesium-RE corrosion resistant alloys
3. Tungsten and uranium alloys for ballistic penetrators
4 Titanium alloys
5. Shape-memory alloys
6. Precipitation-hardened stainless steels

In all of these beneficiation occurs as a result of grain refinement and fine-scale homogeneity. From these characteristics, higher strengths, toughnesses, increased thermal stability, and enhanced corrosion resistance follows.

FORECAST

The future of this field is likely to be just as exciting as the recent past. Much of the territory remains unexplored.

First, relatively little is known about the structures of glass-forming liquids prior to quenching. It is to be expected that their structures will vary with temperature, time and composition above the liquidus.

Second, through adjustment of the liquid composition heterogeneous structures can be generated. An example, first shown by Narasimhan , is obtained by cooling a nearly eutectic liquid below its liquidus causing small particles of precipitate to form, and then quenching to convert the remaining liquid into glass. The result is very hard particles embedded in a ductile glass.

Third, consider composition. So many compositions have been studied that it seems at first sight that there is little room in which to explore further. This may be true for binary systems, but it is certainly not true of ternary, quatenary, and higher order systems. Therefore, searches for important new compositions should continue to be rewarding.

Perhaps the most promising area of all for the future, is that of using glasses as precursors for fine-grained polycrystalline materials. As indicated above these may have unusual compositions, microstructures, and properties. They already form the basis of permanent magnet materials, as well as strong materials that are stable at high temperatures. However, only a relatively few compositions have been explored. Also, much more can be done to determine the effects of applied fields other than temperature. For example, stresses and magnetic fields. Gradients may also induce new microstructures. Thus directional devitrification will put a strong texture into the product and this may enhance desired properties in some cases.

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