Rapidly Solidified Materials [and Discussion]

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Rapidly solidified materials

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Although rapid solidification has been used for generations to refine the grain sizes of materials, its effects are most significant when it succeeds in converting the liquid state into a glass. This is because homogeneous materials can be made in this way that have distinctly different compositions, as well as different molecular structures, from traditional materials. The liquids of interest are alloys, in the widest sense. These may consist of two or more metals, two or more polymers, two or more ceramic compounds, or other combinations. When they have been converted into glasses they may be useful in that form, or the glass may be the precursor to devitrified forms that cannot be created in any other way. Such materials often have unusual combinations of chemical and physical properties including strength, magnetic hardness or softness, electric response, catalytic ability and corrosion resistance.

INTRODUCTION

Metallurgists have known for a long time that metals become harder when they are quenched from the melt rather than slowly cooled. Usually this has been associated with grain-size refinement, but it is now known to involve metastable solute concentrations as well. Similarly, the properties of highly polymerized materials can be changed markedly by quenching them fast enough to suppress crystallization. This sometimes makes them transparent, and often stiffer. The effects are most dramatic for liquids that would ordinarily separate into two or more phases if they were more slowly cooled. Through fast cooling they are suspended in metastable states.

The metastability that follows fast cooling is associated with high concentrations of structural defects such as grain boundaries, or of chemical or structural states that are maintained metastably by the sluggishness of the kinetic processes in the materials. For the materials engineer it is the physical and chemical properties of these metastable structures that are of primary interest. 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 it may determine the relative manufacturing costs; and the faster the process the lower the cost, other factors being equal.

Observations of the distinct effects of rapid against slow solidification were made in ancient times. However, the range of rates has been extended in recent times, particularly at the high end. Rates less than about 10^{-5} K s^{-1} are impractical for experimental work. Until about 1960, rates above 10^{5} K s^{-1} were rarely observed. Then, following the early work on splat cooling (Klement *et al.* 1960), there were concerted efforts to increase the maximum rates. Currently, by heating surfaces with picosecond pulses of light followed by self-quenching, rates as high as 10^{12} K s^{-1} have been achieved (Lin & Spaepen 1984). At very low cooling rates liquids tend to transform into solids across a single interface, and single crystals result. At higher rates, while one crystal is growing, others become nucleated, and polycrystals result: the higher the rate, the more nucleation occurs and the smaller the grain size of the resulting polycrystal. At very high rates, there is insufficient time for crystals to nucleate and grow so the structure of the liquid is retained, and the substance is called a glass.

Glasses are often said to be 'amorphous', which in Greek means 'without form' (or by implication, 'without structure'), but this is misleading because they usually contain short-range order. They inherit this from their mother liquids, which usually contain associations of atoms or molecules. Even one-component liquids are often polymerized. As solidification rates have increased, grain sizes have decreased and maximum attainable metastable solute concentrations have increased. These trends have been evolutionary. For example, chill blocks have been used in the manufacture of railway wheels from cast iron for over a century in order to refine the microstructure and improve toughness: this represents a primitive form of rapid quenching.

However, when alloys were quenched by Klement *et al.* at rates that completely suppressed crystallization, 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, Chen & Polk (1973) spun the first ductile ferrous glasses at the laboratory that I organized for the Allied Chemical Corporation (now the Allied Signal Corporation). Their process, 'melt-spinning', essentially involves the projection of a liquid alloy jet against a rapidly spinning copper wheel. In a later version, the cylindrical nozzle is replaced by a more elaborate device, which allows wide sheets to be made.

A photograph of Chen's first specimen is shown in figure 1. Its composition in atomic per cent is 39Fe, 38Ni, 14P, 6B, 3Al; and it weighed about 5 g. At the time of writing, the specimen remains ductile. At present, thousands of metallic glasses have been made. In production lines, ribbons are made at linear speeds up to 30 m s^{-1} and in continuous lengths many miles long from tonne-sized heats of metal.

It should be noticed that this revolution has been based on the confluence of several elements, not just one. 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 many potential applications for it.

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 structural materials (Ray *et al.* 1983) and to exceptional Fe–Nd–B permanent magnets (Croat *et al.* 1984). Thus glasses are not only of interest for themselves, but also as precursors for special kinds of polycrystals.

Some people think that this subject has been exhausted by the hundreds, if not thousands, of projects that have been undertaken by people interested in it. I think that this is pessimistic. The subject has so many variations and ramifications that I think continued work will lead to many new scientific insights and technological opportunities.

While preparing this paper, I reviewed some of the many writings about the rapid solidification of metals, and tried to find information about this process in the fields of ceramics and polymers. I could find very little in these latter fields although I did learn that a major

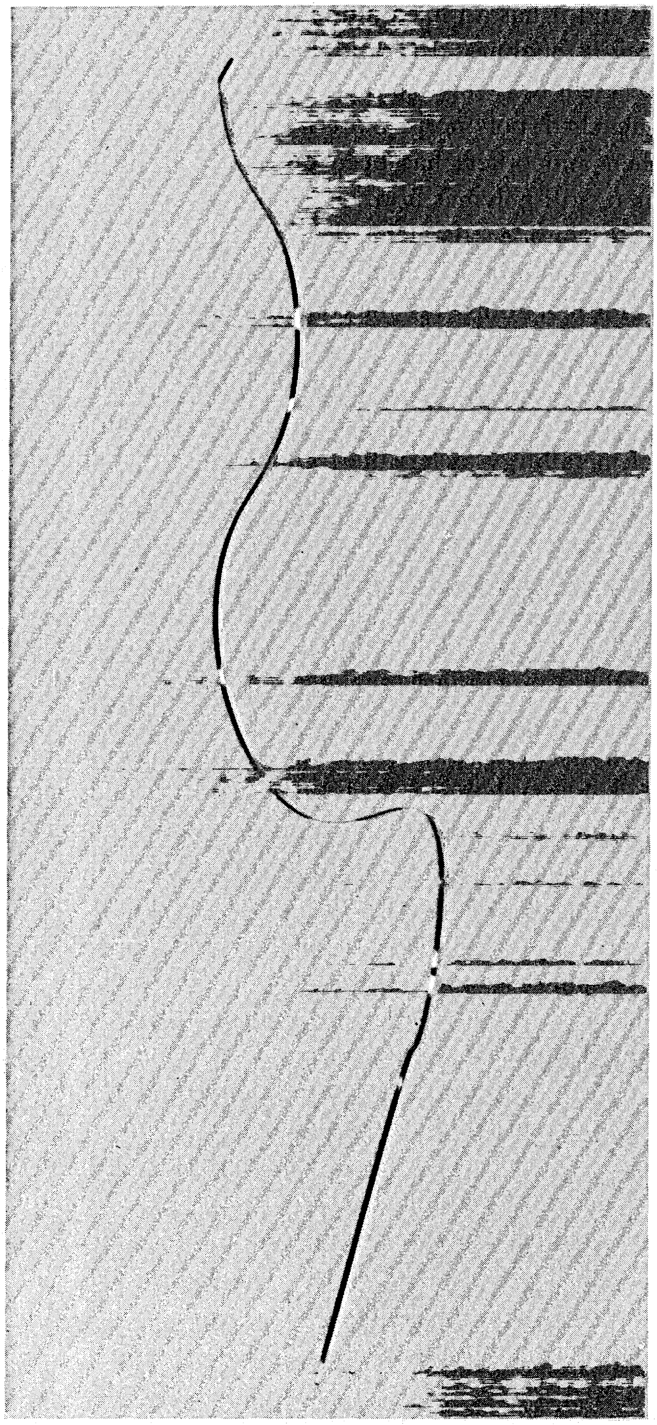

Figure 1. Piece of the first ductile, ferrous glass made by H. S. Chen. The composition is 39Fe–38Ni–14P–6B–3Al.

abrasive is rapidly cooled from its liquid to refine its grain size. One of its manufacturers is the Norton Company and it has a mixed aluminum oxide–zirconium oxide composition. Its fine grain-size enhances its toughness. In addition, laboratory studies of ceramic materials have been pursued (Revcolevschi & Livage 1981).

Applications of quenched polymeric materials have escaped me, although laboratory research by H. S. Chen and others has been done. A variant of melt-spinning is used to produce highly oriented, stiff polymer fibres.

As already stated, I consider that the development of fine-grained, non-equilibrium, metallurgical materials through rapid solidification has been an evolutionary process. In recent times, it has taken the form of improving the compositions and grain structures of the powders that are consolidated to make tools, jet-engine discs, and other structural parts. An excellent volume of reviews is Das *et al.* (1985). Rapidly solidified crystalline alloys have contributed very substantial improvements in performance, but they have not added a new, revolutionary branch to the field of metallurgy as has the technology of metallic glasses. I shall therefore concentrate on the latter in the remainder of this paper.

BASIS OF THE NOVELTY OF METALLIC GLASSES

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

Consider composition first. The compositions that form glasses readily had rarely been used in the past because if they are relatively slowly cooled, brittle solids generally result. 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 steels. Thus glassy alloys can have dramatically different compositions from the crystalline 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. This has been demonstrated by examining 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 (Gilman 1978), which suggests that the short-range order in a glass is characteristic of the mother liquid.

The characteristic structure of a liquid is different in most cases from the short-range structure that would be found in other antecedents of ‘amorphous’ alloys, such as: gases before condensation; plasmas during deposition; electrochemical solutions before plating. 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 (i.e. quench-casting) processing. A ribbon that is 3 mil (0.07 mm) thick and 4 in (98 mm) wide being cast at 3000 ft min^{-1} (165 m s^{-1}) corresponds to a casting rate of 3.3 ton h^{-1} (3353 kg h^{-1}). When one considers that the product is in its final form (and has gone from liquid metal to final form in one step), and 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 revolutionary process.

In this process – called planar flow-casting – the liquid alloy is first melted in a large crucible and then poured into a tundish that delivers it to a specially shaped nozzle (figure 2). The nozzle deposits the liquid onto a rapidly rotating water-cooled wheel that it partly 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.

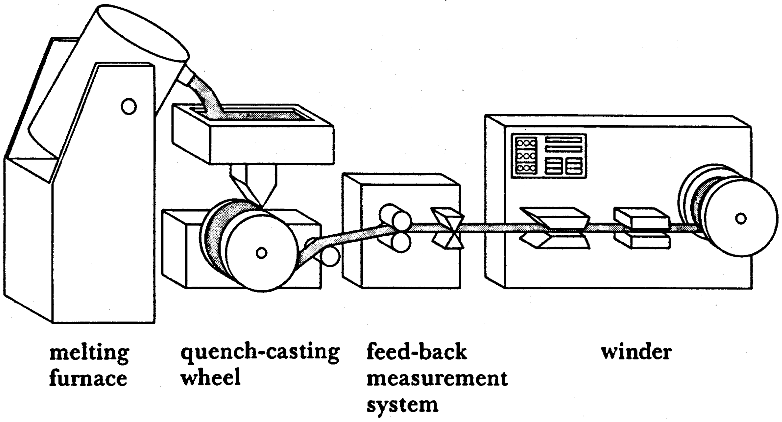

FIGURE 2. Quasi-continuous quench-casting manufacturing line. Note wrapping of ribbon on casting wheel for traction. Flow is controlled through combination of liquid head and gas pressure in tundish (details not shown).

This fast-casting technology (developed at Allied Signal) for producing metallic glass ribbons can be applied to other materials, of course. For example, it has already been applied to polycrystalline brazing tapes (see DeCristofaro & Datta 1985).

Development of a satisfactory quasi-continuous process required many inventions of new engineering elements. These include: planar-flow casting nozzles; cooling systems for intensely heated quenching wheels; mechanisms for catching ribbons moving at high velocities, threading them into rotating sheaves and 'doffing' the sheaves as they become full; sensors and systems for feedback control; methods for handling and metering liquid alloys. The importance of fast processing can be appreciated by considering a demand chart for metals. The annual demand (dollars) for metals is strongly correlated with their unit prices ($\$\,\mathrm{lb}^{-1}$†) as indicated in figure 3. 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 lines in the figure.

This may be clarified by replotting the data to show the dependence of revenues on prices as in figure 4. The powerful effect of price on dollar volume that this figure indicates provides a forceful motivation for seeking low manufacturing costs.

It is not a secret, of course, that fast processing tends to minimize manufacturing cost. But the magnitude of the effect in this particular case does not appear to be widely appreciated so it may be useful to consider some numbers. Suppose that a quench-casting unit produces ribbon 1 inch (2.54 cm) wide at a rate of 1 ton (1.0161 t) per hour and the unit costs $100000

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† 1 lb = 0.4536 kg.

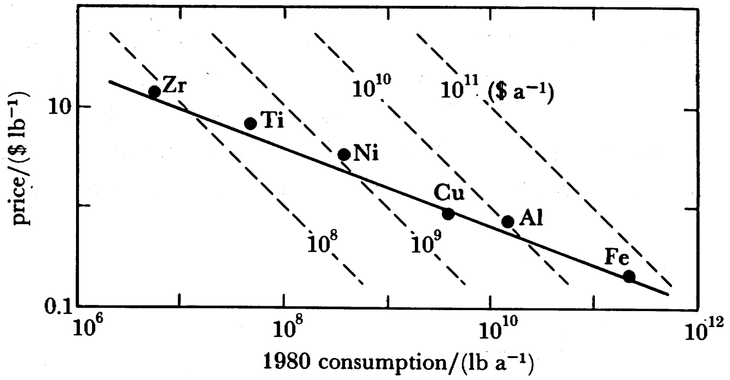


FIGURE 3. Demand chart for structural metals.

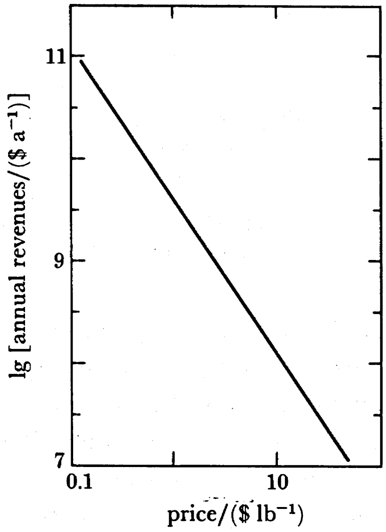


FIGURE 4. Dependence of revenues on price for structural metals (data from figure 3).

at a time when the interest rate is 8%. Further suppose that the unit is leased (to simplify the arithmetic). Then the direct rental charge for a one-shift operation and a 40% duty-cycle is about \$0.01 lb^{-1}. Compare this with a hot-pressing unit that costs the same amount and produces 10 lb of product per shift. Then the rental charge is \$10 lb^{-1}, 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 desirable.

The other primary manufacturing costs are: energy, labour, 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, and quench-casting uses it very efficiently.

TRANSLATION OF NOVEL PROPERTIES INTO APPLICATIONS

New materials find their way into applications either by being substituted for older materials in established applications, or by allowing devices to be invented that exploit their properties. Then these new devices are substituted for older ones. In either type of substitution, the new must have more utility than the old (that is, be more cost effective), otherwise there is no driving force for the substitution and it will not occur.

Some unusual combinations of properties, combined with fast processing, are what have made metallic glasses very attractive for a variety of 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 that they make effective transducers.

In fact, so many actual and potential applications have been reported that it is difficult to summarize them succinctly, but an attempt will be made here, starting with magnetic devices.

Ferromagnetic glasses are very easily magnetized because magnetic domain walls move through them with extraordinary ease as shown by the listing of mobilities for some typical materials in table 1. The mobility for the glass is 500 times greater than for the standard Fe–Si material. This is why these glasses are such an extraordinary advance in the field of soft magnetic materials.

TABLE 1. COMPARISON OF MAGNETIC DOMAIN-WALL MOBILITIES IN VARIOUS MATERIALS

material	domain-wall mobility / $10^3\ \mathrm{cm}^3\ \mathrm{s}^{-1}$
Fe–Si crystal	4
Ni–Fe wire	6
Fe crystal	40
Ni–Fe glass	2000

(*a*) *Transformers*

When the 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 figure 5. For the small sizes, the difference between the standard material and the glass is a factor of four, whereas for large sizes (say 100 kV A) it becomes a factor of ten (figure 6).

Because there are nearly 40000000 power distribution transformers in the U.S.A., the total losses are about 35×10^9 kW h annually. Glass cores could save 23×10^9 kW h of this. At an average cost of \$0.05 $(\mathrm{kW\ h})^{-1}$ this is \$$1.2 \times 10^9$ 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. Numerous test transformers have already been placed at field locations and are being observed. For a set of 25 distribution transformers, no significant aging effects were observed over two years (Bailey *et al.* 1986).

In the second generation of field testing, the (U.S.) Electric Power Research Institute (EPRI) commissioned the (U.S.) General Electric Company to manufacture 1000 distribution transformers (25 kV A size) made with ferrous glass manufactured by the Allied Signal

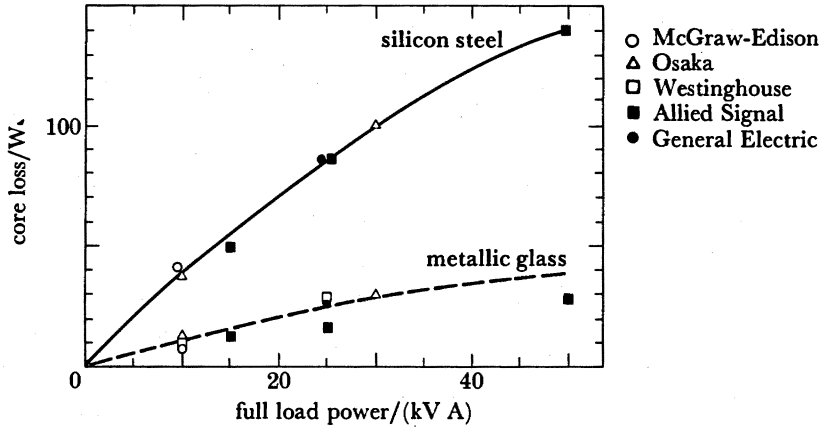


FIGURE 5. Energy losses in transformers of various sizes made by various companies. The decreases achieved by using metallic glass cores is dramatic.

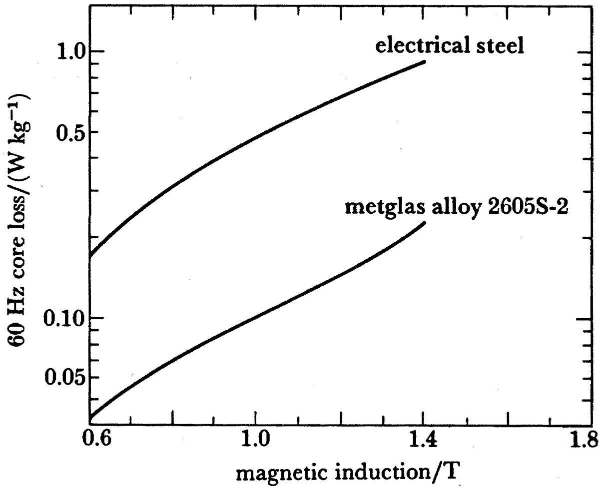


FIGURE 6. Comparison of intrinsic core losses between standard magnetic steel and metallic glass.

Company. These are being distributed to the utility companies that support EPRI for two-year field tests (Smith 1985).

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

The magnetic cores of electric motors also convert large amounts of their input energy into heat. It has been shown that this could be substantially reduced if metallic glass cores were used in them (Raskin 1983). However, this will not happen unless some difficult fabrication problems are overcome.

For power frequencies up to about 100 kHz, metallic glasses make superior small transformers. This has led to their use in switching-mode power-supplies (Coutant Electronics, Toshiba), tape-recording heads (Sony, Kenwood), aircraft transformers (Allied Signal), pulse suppression chokes (Toshiba), current-metering transformers, ground-fault interrupters, transformer turns-radio tester (Biddle Instruments), high-speed welder (Mitsubishi) and a variety of other small transformers (Raskin 1983).

If very high magnetic fields are applied to selected metallic glasses, their magnetizations can be reversed in as little as 100 ns. Thus, they are useful as the cores of pulse transformers and magnetic switches. These can be very large (up to several tonnes in mass) and are used in ion accelerators, ultraviolet lasers (excimers), and radar modulators. They can be used to switch pulses in the multiterawatt range of power, that is, to switch 10^6 A at 2×10^6 V (Smith 1985). A new particle accelerator called Hermes IV that will be built at the Sandia National Laboratory is scheduled to have 110 saturable reactor cores made of metallic glass. Because each will have mass of about 300 kg, this machine will use about 33 t of metallic glass.

The magnetization loop for an easily magnetized metallic glass is quite 'square'. That is, under the influence of a small applied field the magnetization rate rises rapidly to nearly its saturation level and then remains nearly constant. In other words, the magnetic response of the material is highly nonlinear. A result is that if the material is exposed to electromagnetic 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 of the material which gives it low acoustic attenuation as a corollary. In other words, the glass 'rings' for a long time after it is set into mechanical vibration. Thus excellent mechanical oscillators can be made from it, and this allows its response to incident electromagnetic radiation to be sharply tuned. Through tuning, its reradiation signature can be designed, and the sensitivity of a device markedly increased (Anderson *et al.* 1985).

(*b*) *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 a cable (60 H). For the same amount of shielding this is about eight times better than previous materials (Hilzinger 1985).

(*c*) *Transducers: sensors*

Various combinations of the electrical, magnetic and mechanical properties of metallic glasses have been used as the bases of transducers. There is insufficient space here for a review of them, but a listing (no doubt incomplete) will be made to indicate the large scope of applications (Mohri 1984, 1985; Makino 1985; Matsuki & Murakami 1985):

1. high-output tape-heads (both audio and video);
2. photocartridges;
3. fast-response magnetometers;
4. delay lines;
5. displacement, force, or torque transducers;
6. strain gauges;
7. rotational speed sensors;
8. fuel-injector controls;
9. temperature sensors;
10. vibration sensors;
11. electromagnetic radiation meters;
12. height gauges;
13. microphones
14. data tablets;
15. cloth inductors.

(*d*) *Joint formation* (*brazing*)

One of the earliest applications of metallic glasses was the manufacture of brazing tapes for joining parts of jet-engine components. The basis of the application is that the new glassy forms of the alloys that are used for this purpose are ductile, unlike the previous crystalline forms, which are very brittle. Ductile tapes are much easier to manipulate, and they make superior joints, compared with 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 25 compositions are offered commercially. They are grouped into families. One of these families comprises nickel-based tapes for brazing high temperature alloys to make engine components, heat exchangers, and food processing equipment. Another comprises nickel palladium tapes to replace gold-based alloys in aerospace and power-electronics brazing. A third 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 (De Cristofaro & Datta 1985).

Even ordinary solder benefits from the quench-casting process. The joints made using quenched solders have finer grains, better homogeneity, and smaller shrinkage voids than ones made with conventional solder.

(*e*) *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 (Gilman 1984). Also, as a result of their homogeneity, 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. The principal reason may be fabrication difficulties, for example, such things as the hardness of the glass, which rapidly wears stamping dies, and finding compatible adhesives for making composites that can withstand cyclic loadings, etc. It is very encouraging for the future of these applications that excellent fatigue resistance of the glasses themselves has been reported recently (Hagiwara *et al.* 1985).

(*f*) *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 that are otherwise discoloured by them.

Applications such as the use of 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 (Cocke 1986).

Crystalline descendants of glasses

Two new branches of the metallurgist's art have descended from the early work on metallic 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 because I have already presented some of the arguments in its favour.

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. In various practical situations the results may be virtually indistinguishable, but not always.

The first work, to my knowledge, in which exciting new materials were derived from glasses was that of Ranjan Ray 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 fragmented to form a coarse powder that was consolidated into cylinders by hot-pressing, or hot-extrusion.

These devitrified materials were strong, tough, and heat-resistant. They are quite remarkable (Ray *et al.* 1983). Their microstructures consist of tiny grains about 10^{-1} μm in size, stabilized by very small borides about 10^{-2} μm in size at the grain boundaries. They led to the development of Ni–Mo–Cr–B materials with attractive properties for die-casting moulds and hot-working dies (Chang *et al.* 1985).

Even more exciting was the discovery by Croat and Herbst at the General Motors Research Laboratories of a new class of permanent magnet materials, based on Fe–Nd–B alloys (Croat *et al.* 1984). 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 additives improved the hard magnetism, and that alignment of the devitrification products by hot-working further improved the properties.

Parallel work at 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.

A figure of merit for hard magnets is the energy product. Values as high as 50 MOe have now been achieved for Fe–Nd–B magnets. This may be compared with 40 for the best previous material, Sm–Co alloy. The new material is already in production for use in the small electric motors used for actuators in automobiles.

Various crystalline descendants have followed these early ones. They include:

1. Al–Fe alloys for use at high temperatures (Skinner *et al.* 1985);
2. Mg–RE (rare earth) corrosion-resistant alloys (Chang *et al.* 1985);
3. W and U alloys for ballistics (L. A. Davis, personal communication);
4. Ti alloys (Kubel 1986);
5. shape-memory alloys (Li 1985; Eucken 1985);
6. precipitation-hardened stainless steels (Ray 1986);
7. Fe–Si transformer steels (Warlimont 1985);
8. Nickel aluminide with B (Taub 1985).

In all of these, benefits occur as a result of grain refinement and fine-scale homogeneity and increased solute concentrations. From these, 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 although some strong themes were established early in the development period.

First, relatively little is known about the structures of glass-forming liquids before the time of quenching. It is to be expected that their structures will vary with temperature above the liquidus, sometimes sluggishly. Also, it is known empirically that relatively small additions of specific elements can change the liquid behaviour observably.

Through adjustment of the liquid composition relative to the phase diagram, heterogeneous structures can be generated. An example, first shown by D. Narasimhan, was 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 hard particles embedded in a ductile glass. This technique has not been fully exploited.

Composition itself has a primary influence on properties. So many compositions have been tested for their glass-forming propensities and subsequent properties that it seems at first sight that there is little room in which to explore further. This may be true for most of the potentially interesting binary systems, but it is certainly not true of ternary, quaternary, and higher-order systems. Therefore, searches for important new compositions should continue to be rewarding.

There are various opportunities for the development of new, or improved, processes. Quench-casting itself can be further improved, and better methods for consolidating ribbons are needed. Coating techniques, shell-casting, and other processes can be improved. Perhaps the most promising area of all for the future is that of the use of glasses as precursors for fine-grained polycrystalline materials. These may have unusual compositions, microstructures and properties. They already form the bases 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 influences other than temperature. For example, stresses and magnetic fields. Gradients may also induce new microstructures. Thus directional devitrification may put a strong texture into the product and this may enhance desired properties in some cases.

In the 13–14 years since the first ductile ferrous glass was invented, the annual production rate has increased from about 1 kg per year to 10^5–10^6 kg per year. This corresponds to a growth rate of 85–100 % per year. Because there is no reason to expect that this growth rate will drop soon, it is easy to see that this technology indeed represents an important new branch of metallurgy.

L. A. Davis, M. C. Flemings, R. I. Jaffe, R. W. Lee, Y. Makino, I. Ogasawara, T. Sato, C. H. Smith, D. R. Uhlmann and H. Warlimont (listed in alphabetical order) provided their opinions of the status of the field and copies of many preprints and reprints. This work was supported in part by the U.S. Department of Energy under contract no. DE-AC03-76SF00098.

REFERENCES

Anderson, P. M., Bretts, G. R. & Kearney, J. E. 1985 Surveillance system having magnetomechanical marker. U.S. Patent nos. 4510489 and 4510490.

Bailey, L. A., Lowdermilk, L. A. & Lee, A. C. 1986 Field performance of amorphous metal core distribution transformers. *J. Magn. magn. Mater.* **54–57**, 1618.

Chang, C. F., Das, S. K. & Raybould, D. 1985 Rapid solidification of Mg-Al-Zn-RE alloys. In *rapidly solidified materials* (ed. P. W. Lee & R. S. Carbonna), p. 129. Metals Park, Ohio: American Society of Metals.

Chen, H. S. & Polk, D. E. 1973 U.S. Patent no. 3845805 (Also reported in *Chem. Engng. News* **51**, 24.)

Cocke, D. L. 1986 Heterogeneous catalysis by amorphous materials. *J. Metals* **38**, 70–74.

Croat, J. J., Herbst, R. W., Lee, R. W. & Pinkerton, F. E. 1984 Pr–Fe and Nd–Fe-based materials: a new class of high-performance permanent magnets. *J. appl. Phys.* **55**, 2078.

Das, S. K., Kear, B. H. & Adam, C. M. (eds) 1985 *Rapidly solidified crystalline alloys*. Warrendale, Pennsylvania: Metall. Society of AIME.

Das, S. K. & Raybould, D. 1985 The effect of microstructure on the mechanical properties and wear resistances of Ni–Mo–Cr–B alloys. In *Proc. 5th Int. Conf. Rapidly Quenched Metals* (ed. S. Steeb & H. Warlimont), vol. 2, pp. 1787–1790. Amsterdam: North-Holland.

De Cristofaro, N. J. & Datta, A. 1985 Rapidly solidified filler metals in brazing and soldering applications. In *Proc. 5th Int. Conf. Rapidly Quenched Metals* (ed. S. Steeb & H. Warlimont), vol. 2, pp. 1715–1722. Amsterdam: North-Holland.

De Cristofaro, N. J. & Datta, A. 1985 *Rapidly solidified crystalline alloys* (ed. S. K. Das, B. H. Kear & C. M. Adam), p. 263. Warradale, Pennsylvania: Metal Society of AIME.

Eucken, S. & Hornbogen, E. 1985 Rapidly quenched shape memory alloys. In *Proc. 5th Int. Conf. Rapidly Quenched Metals* (ed. S. Steeb & H. Warlimont), vol. 2, pp. 1429–1434. Amsterdam: North-Holland.

Gilman, J. J. 1978 Structures of ferrous eutectic liquids. *Phil. Mag.* B **37**, 577.

Gilman, J. J. 1984 Metallic glass materials. In *Industrial materials science and engineering* (ed. L. E. Murr), pp. 1–27. New York: Marcel Dekker.

Hagiwara, M., Inoue, A. & Masumoto, T. 1985 Iron-based amorphous wires with high fatigue strength. In *Proc 5th Int. Conf. Rapidly Quenched Metals* (ed. S. Steeb & H. Warlimont), vol. 2, pp. 1779–1782. Amsterdam: North-Holland.

Hilzinger, H. R. 1985 Design aspects for the use of amorphous alloys in electronics. In *Proc. 5th Int. Conf. Rapidly Quenched Metals* (ed. S. Steeb & H. Warlimont), vol. 2, pp. 1695–1698. Amsterdam: North-Holland.

Klement, W., Willens, R. H. & Duwez, P. 1960 Non-crystalline structure in solidified gold–silicon alloys. *Nature, Lond.* **187**, 869.

Kubel, E. J. 1986 All eyes on metallic glasses. *Metal Prog.* **129**, 61–70.

Li, D.-S., Rong, Q.-G. & Zhu, Y. 1985 The shape memory effect (SME) of liquid rapidly quenched (LRC) Cu–Sn alloys. In *Proc 5th Int. Conf. Rapidly Quenched Metals* (ed. S. Steeb & H. Warlimont), vol. 2, pp. 1425–1428. Amsterdam: North-Holland.

Lin, C. J. & Spaepen, F. 1984 Metallic glasses and metastable crystalline phases produced by picosecond pulsed-laser quenching. In *Rapidly solidifed metastable materials* (ed. B. H. Kear & B. C. Giessen), pp. 75–80. New York: Elsevier Science Publishing.

Makino, Y. 1985 Amorphous materials for magnetic heads. In *Proc. 5th Int. Conf. Rapidly Quenched Metals* (ed. S. Steeb & H. Warlimont), vol. 2, pp. 1699–1706. Amsterdam: North-Holland.

Matsuki, H. & Murakami, K. 1985 A new cloth inductor using amorphous fiber. *IEEE Trans. Mag.* MAG-**21**, 1738–1740.

Mohri, K. 1984 Review on recent advances in the field of amorphous-metal sensors and transducers. *IEEE Trans. Mag.* MAG-**20**, 942–947.

Mohri, K. 1985 Application of amorphous alloys to sensors and transducers. In *Proc. 5th Int. Conf. Rapidly Quenched Metals* (ed. S. Steeb & H. Warlimont), vol. 2, pp. 1687–1690. Amsterdam: North-Holland.

Raskin, D. 1983 'Glass' motor cores will cut loses, save energy. *Power Transm. Des.* **25**, 153–155.

Raskin, D. & Smith, C. H. 1983 Applications of amorphous metals: progress and prospects. In *Amorphous metallic alloys* (ed. F. E. Luborsky), pp. 381–400. London: Butterworths.

Ray, R., Jain, S. & Isserow, S. 1986 Borides boost strength of precipitation hardening stainless steels. *Metal. Prog.* **129**, 43–47.

Ray, R., Panchanathan, V. & Isserow, S. 1983 Microcrystalline iron-based alloys made using a rapid solidification technology. *J. Met.* **35**, 30.

Revcolevschi, A. & Livage, J. 1981 Rapid solidification of non-metals. In *Treatise on materials science and technology*, vol. 20, pp. 73–116. New York: Academic Press.

Skinner, D., Adam, C. & Okazaki, K. 1985 Enhancement of high temperature strength of aluminum alloys by rapid quenching from the melt. *Mod. developments in powder metallurgy* **15–17**, 427–435.

Smith, C. H. 1985 Metallic glasses in high-energy pulsed-power systems. In *Glass . . . current issues* (ed. A. F. Wright & J. Dupuy), pp. 188–199. Dordrecht: Martinus Nijhoff Publishers.

Smith, C. H. & Nathasingh, D. M. 1985 Recent developments in amorphous alloys. Presented at SMM7, Blackpool, U.K. In *Soft magnetic materials 7* (ed. J. Thompson), p. 300. Cardiff: University College.

Taub, A. I. 1985 Mechanical properties and potential applications of rapidly solidified alloys. In *Proc. 5th Int. Conf. Rapidly Quenched Metals* (ed. S. Steeb & H. Warlimont), vol. 2, pp. 1611–1618. Amsterdam: North-Holland.

Warlimont, H. 1985 New magnetic materials by rapid solidification. In *Proc. 5th Int. Conf. Rapidly Quenched Metals* (ed. by S. Steeb & H. Warlimont), vol. 2, pp. 1599–1609. Amsterdam: North-Holland.

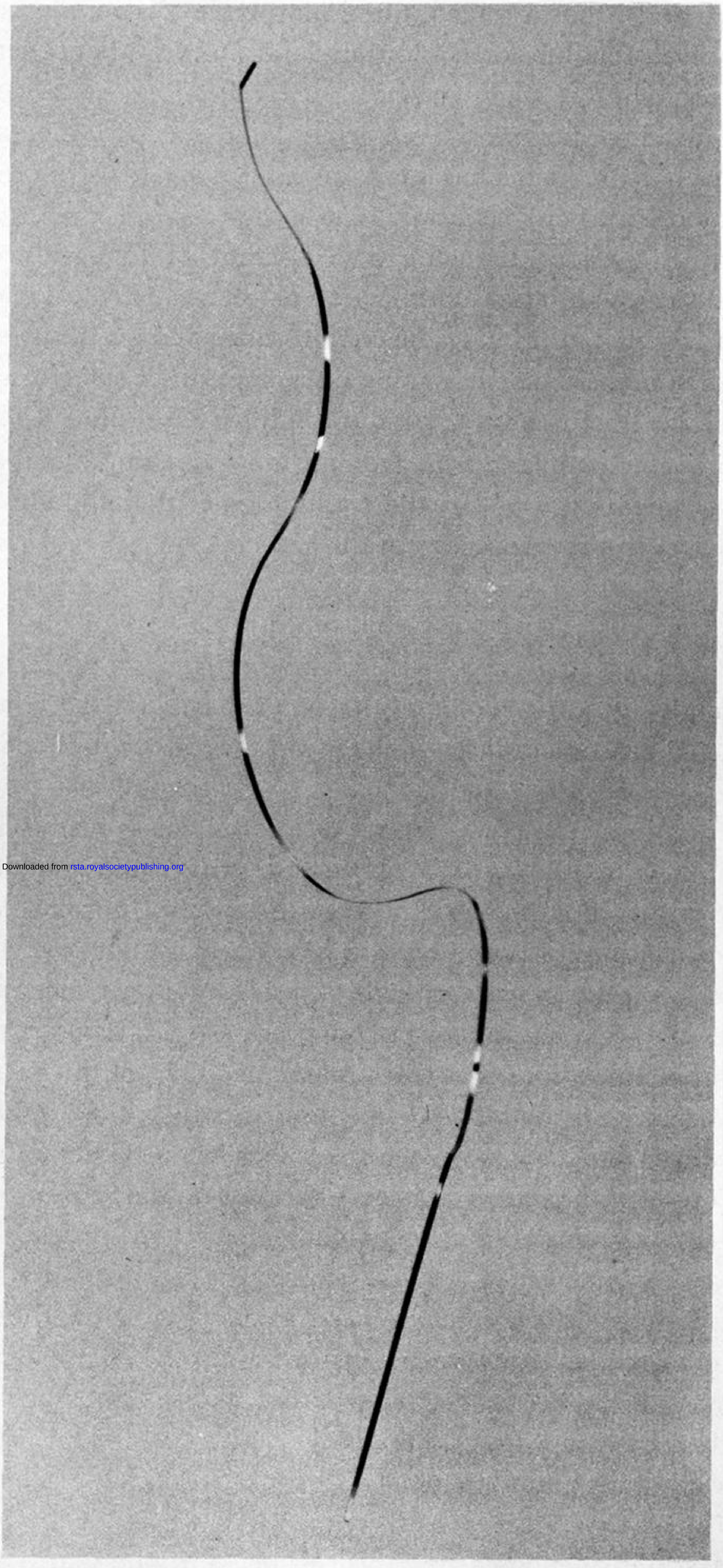
Discussion

J. A. Champion (*Division of Materials Applications, National Physics Laboratory, U.K.*). Dr Gilman's presentation was most interesting but he did not say much about the good corrosion resistance that some rapidly solidified materials show. Does he think that this is an area for application that will develop and become more important in the future?

J. J. Gilman. Dr Champion is quite justified in wondering when applications based on corrosion resistance might arise. Many workers, especially Hashimoto in Japan, have found that some metallic glasses have outstanding resistance to very corrosive chemicals; for example, to 10% sulphuric acid. In fact, in Japan they are called 'super stainless steels'. The barrier to applications on a significant scale in this area has been the lack of an economic and effective method for applying them to the surfaces of less resistant materials, or for making the glasses in bulk form.

R. W. Cahn (*Department of Metallurgy and Materials Science, University of Cambridge, U.K.*). Dr Gilman mentioned in passing the intrinsic suitability of metallic glasses for the construction of cutting edges. Although there has been a certain amount of indirect evidence for the interest of the makers of razor blades in such a possibility, there have been no published descriptions of metallic-glass cutting instruments and nothing of the sort has appeared on the market. Could Dr Gilman comment on this circumstance, particularly in view of the fact that the melt-spinning of a metallic glass ribbon is a single-stage process whereas the preparation of high-grade steel for razor blades involves many involved production stages? Would the grinding of a metallic glass ribbon to make a sharp edge be likely to devitrify the glass?

J. J. Gilman. Glassy ribbons are too thin to be used directly as cutting tools in most cases. They must be attached to, or embedded in, backing materials. This increases manufacturing costs. However, they can be honed to superior levels of sharpness because of the absence of a grain structure. Also, they retain sharpness well because of their hardnesses and corrosion resistances. Devitrification during grinding does not appear to occur.



IGURE 1. Piece of the first ductile, ferrous glass made by H. S. Chen. The composition is 39Fe–38Ni–14P–6B–3Al.