Metallic glasses

C SURYANARAYANA

Centre of Advanced Study in Metallurgy, Department of Metallurgical Engineering, Banaras Hindu University, Varanasi 221 005, India

Abstract. Metallic glasses are a new class of materials produced by rapidly quenching the melts at rates often exceeding a million deg/sec. These have been found to display an optimum combination of properties such as high strength, good bend ductility, improved corrosion resistance and excellent soft magnetic properties. Thus, metallic glasses are emerging as economically viable competitors to conventional engineering materials.

A clear understanding of the atomic structure of metallic glasses and its change during annealing are of prime importance. Although techniques such as field-ion microscopy (FIM) x-ray diffraction and small angle x-ray scattering have been employed for this purpose, high resolution electron microscopic (HREM) investigations conducted during the last few years aided greatly in deriving information on the atomic scale. Availability of high-voltage high-resolution electron microscopes has been mainly responsible for this happy situation.

Studies on several metallic glasses have revealed that HREM images contain well-defined pattern of fringes over local regions, even though the diffraction pattern is that of a typical amorphous structure. The details of structure in the early stages of crystallization derived through HREM, FIM and analytical microscopic techniques are presented and discussed.

Keywords. Metallic glasses; glass-forming ability; melt quenching; rapid solidification techniques; crystallization behaviour; high-resolution microscopy; analytical microscopy.

1. Introduction

Metallic glasses are a new class of potential engineering materials which have come into prominence during the 1970s (Anantharaman 1982; Gilman 1980; Chen 1980). These are glassy in the sense that the atomic arrangement is random (non-crystalline), but differ from the conventional glasses in that they are not transparent, are not brittle and do not contain borates, silicates etc. Although non-crystalline solids can be prepared by methods such as vapour deposition (Chopra 1969), sputtering (Dahlgren 1978), laser treatment (Poate and Brown 1982), electrodeposition (Brenner 1963; Simpson and Brambley 1971), ion implantation (Grant 1978; Borders 1979; Picraux and Choyke 1982) and rapid quenching from the liquid state (Duwez 1967, 1979; Cahn 1980), purists reserve the term '*metallic glasses*' only to those that are produced by rapid quenching from the melt. The present article deals with the high resolution and analytical microscopic studies of metallic glasses with a view to understand their structure and its effect on the properties.

2. Classification of metallic glasses

The first metallic glass was produced in 1960 by Professor Pol Duwez and his colleagues at the California Institute of Technology, Pasadena, USA (Klement *et al* 1960). A few milligrams of the Au-25 at. % Si eutectic alloy were rapidly quenched from

the molten state by the "gun" technique. In this method, a molten droplet is atomised and allowed to solidify instantaneously in the form of a *thin film* on a *good heat conducting substrate* such as copper so that heat is removed rapidly through the process of *conduction* (Duwez and Willens 1963). Since this pioneering effort, literally several thousands of alloy compositions have been quenched into the glassy state (Jones and Suryanarayana 1973; Takayama 1976; Suryanarayana 1980b). Even though it is a formidable task to classify these metallic glasses in a systematic way, traditionally they are broadly grouped under two categories *viz* (i) metal-metalloid and (ii) metal-metal.

The metal-metalloid category can be represented by the general formula $A_{75-85}B_{15-25}$, where A represents the metal and B the metalloid. The metal can be either an early transition metal (Ti, Zr, . . .), a late transition metal (Fe, Co, Ni, . . .) or a noble metal (Au, Pd, Pt, . . .) while the metalloid can be either B, C, P, Ge or Si. Combinations of metals constituting about 80 at.% and combinations of metalloids constituting about 20 at.% can also be used. Some of the famous and useful compositions are $Pd_{80}Si_{20}$, $Fe_{80}B_{20}$, $Fe_{40}Ni_{40}B_{20}$, $Fe_{40}Ni_{40}P_{14}B_6$, $Fe_{80}P_{13}C_7$, while an exotic composition is $W_{35}Mo_{20}Cr_{15}Fe_5Ni_5P_6B_6C_5Si_3$. In the above alloys and in many others, the ratio of metal to metalloid is almost always 80:20. Recently, however, metal-metalloid glasses with a metalloid content much higher than 20% have also been detected (Inoue *et al* 1979).

The metal-metal category, on the other hand, contains only metals. The metals can be either (a) transition metals, (b) rare-earth metals, (c) alkali-metals or (d) uranium, neptunium or plutonium (Suryanarayana 1980a). An important difference of this group from the commercially more useful metal-metalloid category is that glasses in the metal-metal category are formed in a wide composition range from as low as 10 at.% to as high as 50 at.%. Typical compositions of this category are $Co_{90}Zr_{10}$, $Hf_{80}Ni_{20}$, $La_{76}Au_{24}$, $Ca_{73}Zn_{27}$, $Zr_{64}Ni_{36}$, $U_{60}Cr_{40}$. Some well-investigated compositions include $Cu_{50}Zr_{50}$, $Mg_{70}Zn_{30}$ and $Ni_{60}Nb_{40}$.

3. Glass-forming ability

A pure metallic melt has not been so far quenched into the glassy state, even though hundreds of binary, ternary and more complex alloys could be made glassy. To form a glass, a metallic melt must be solidified sufficiently rapidly, exceeding a critical rate R_c, such that spontaneous crystallization is avoided. The value of R_c can vary from as low as 10^2 ksec^{-1} for $Pd_{40}Ni_{40}P_{20}$ to as high as 10^8 ksec^{-1} for $Fe_{90}B_{10}$. In principle, *any alloy* can be made glassy if the critical cooling rate is exceeded. However, with the presently available cooling rates, only some alloys could be quenched to form glasses.

Based on the experimental observations, several criteria have been suggested to indicate easy glass formation. The most used criterion is the reduced glass temperature, T_{gr} representing the ratio of the glass transition temperature T_g to the melting point of the alloy T_m. The higher the value of T_{gr} the easier it is for the alloy to form a glass. Since T_g varies much less rapidly with composition than T_m, alloys at the eutectic composition will have very low T_m and consequently very high T_{gr}. The observation that several alloy compositions around deep eutectics can be easily made glassy lends support to this criterion (Nielsen 1979). Other criteria proposed include (i) a minimum disparity of atomic sizes between the two constituents (more applicable to metal-metalloid glasses);

the ratio of atomic radii should be in the range of 0·59–0·88, (ii) a high hole formation enthalpy (Buschow 1982), (iii) chemical short-range order in the melt such that the local composition in the melt differs substantially from any stable crystalline species (Sommer 1982). In addition, an electronic criterion that $2k_F = K_p$ where k_F is the Fermi energy wave vector and K_p is the position of the first peak in the diffuse x-ray scattering curve, has been proposed by Nagel and Tauc (1977). In spite of these several criteria, it has not been possible to explain the glass-forming ability of the various alloy systems. It appears that different criteria may apply to different systems. Cahn (1983) has recently published a review on this aspect.

4. Methods of production

The gun technique referred to earlier (Duwez and Willens 1963) gives the highest cooling rates attainable amongst the melt-quenching techniques. However, this method suffers from the disadvantage that it produces porous foils of irregular cross-section. As such these products are not amenable to property studies. Furthermore, only small quantities can be produced at a time (in other words, this is a batch process) and thus industrial applications cannot be visualised for these products. The piston-and-anvil technique (Pietrokowsky 1963), though again produces *only small quantities* at a time, yields large foils of uniform cross-section and has been used quite extensively. These limitations prompted the development of methods for *continuous production* of foils, tapes and wires of uniform cross-section. The popular methods of today include the twin-roller (Chen and Miller 1970), melt spinning (Hubert *et al* 1973), melt extraction (Maringer and Mobley 1974) and planar flow casting (Narasimhan 1979). Figure 1 shows the principles of these four methods. In the twin-roller technique, a stream of
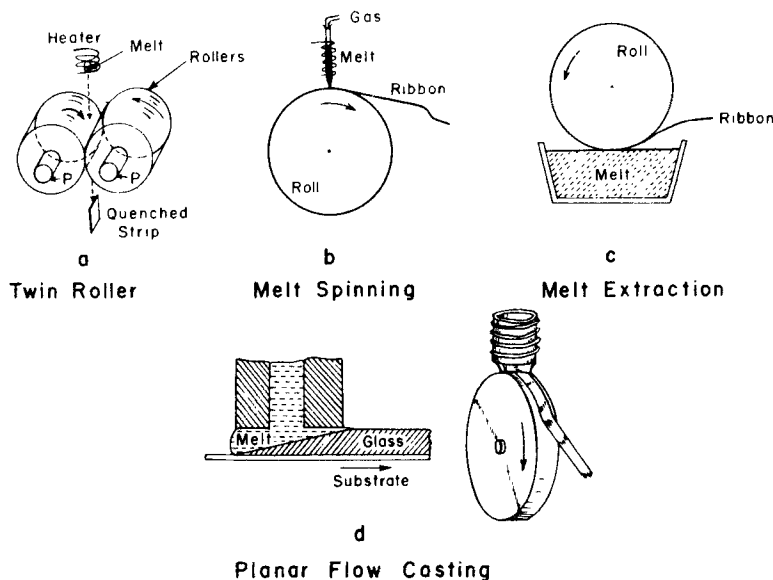

Figure 1. Diagrams showing the principles of the four common and popular melt-quenching techniques.

molten metal is rolled into a sheet or tape between two conducting rolls rotating in opposite directions. In melt spinning, by far the most popular of the rapid quenching methods of today, a stream of liquid metal is made to strike the outer rim of a fast-rotating disc. The centrifugal force acts to throw the ribbon off the disc. The tapes produced have a width of a few millimeters and a thickness of 50–100 μm. Melt extraction is slightly different from melt spinning in that the melt source is stationary, and the edge of a rotating disc or wheel picks up the melt to form filaments. The planar flow casting process employs a nozzle with a slotted orifice and positioned to be almost in contact with the surface of the rotating disc. Ribbons up to 15 cm in width have already been produced by this technique and it is claimed that ribbons with 30 cm width will be produced in the near future.

Since the thickness of the tapes produced by all the above methods is at least about 50 μm, these have to be electrolytically thinned for TEM investigations.

5. Properties of metallic glasses

The main reason for intensive worldwide activity in the field of metallic glasses is that these materials have the best combination of physical, chemical and mechanical properties.

Metallic glasses are very hard (with a hardness value as high as 1300 kg/mm^2 for $Fe_{75}B_{25}$ and 1700 kg/mm^2 for $Fe_{55}Mo_{40}B_5$) and very strong. For example, the tensile strength of $Fe_{60}Cr_6Mo_6B_{28}$ glass is 4800 MPa while that of an ausformed crystalline 18 % Ni steel is only 2000 MPa. The bend ductility is fairly high, although in tension, they withstand only about 1 % strain. This high bend ductility is maintained almost up to the crystallization temperature in many glasses. Since alloys containing light metals such as Ti and Be can also be made strong glasses, the strength to weight ratio is much higher than is possible in crystalline alloys (for a comprehensive recent review on mechanical properties of metallic glasses please see Li 1981).

Because of the random atomic arrangements, metallic glasses have electrical resistivity 2–3 times higher than their crystalline counterparts. In addition, the temperature coefficient of resistivity is small and often negative (Cote and Meisel 1981). The phenomenon of superconductivity is also observed in metallic glasses; the highest transition temperature recorded is only about 9 K. But, they have a high critical field and their properties can be modified by suitable heat treatment (Johnson 1981; Inoue and Masumoto 1981; Suryanarayana 1983).

Another interesting feature of metallic glasses is their high corrosion resistance. Alloys containing additions of Cr and P have been found to have better corrosion resistance than even stainless steels (Masumoto and Hashimoto 1980; Waseda and Aust 1981). Certain glasses can also act like selective catalysts (Brower *et al* 1983).

Metallic glasses have outstanding magnetic properties. They are magnetically soft, have a reasonably high saturation magnetization, very low coercivity, zero magnetostriction and high electrical resistivity. Further, because of the absence of crystallinity, metallic glasses are magnetically isotropic. In view of this excellent combination of properties, applications for these materials in transformer cores, tape recorder heads, magnetic shielding, motors, transducers, amplifiers, etc are being seriously considered (Luborsky 1980; Masumoto and Egami 1981).

In spite of the superior properties achieved in metallic glasses, during annealing they

undergo drastic changes. For example, after crystallization (sometimes even before) they are very brittle. The magnetic and electrical properties also show substantial changes even before the onset of crystallization. All these are expected to be related to the modifications in the glassy structure of the alloy and thus high resolution electron and field-ion microscopic studies will aid in understanding these changes due to low temperature annealing.

6. Structure

A crystalline solid is characterised by a periodic distribution of the constituent atoms in three dimensions. The diffraction patterns from crystals consist of a series of sharp spots (single crystals) or rings (polycrystalline samples). While the positions of these spots/rings give an idea of the dimensions and angular relations of the unit cell, the intensities help in determining the precise locations of the constituent atoms. Metallic glasses, on the other hand, possess a disordered structure and their diffraction patterns show two or three broad diffuse rings. From these, it becomes experimentally impossible to derive complete information regarding the atomic arrangements in metallic glasses.

From the intensity data, one can, however, calculate the radial distribution function (RDF), which is equal to $4\pi r^2 \rho(r)$, where $\rho(r)$ is the average number density of atoms at a distance r from any atom chosen as the origin. The RDF provides an *average* structure and indicates the approximate distance r (peak positions) and numbers (peak areas) of first, second, etc nearest neighbours. It does not, however, indicate the angular positions of the neighbours, wherein lies the lack of detail (Cargill 1975).

An alternative representation of the structure is provided by the reduced RDF, $G(r)$ $= 4\pi r [\rho(r) - \rho_0]$, where ρ_0 is the density of the glass. Figure 2 shows this function for a variety of metal-metalloid glasses. Analysis of the first peak indicates that the number of first nearest neighbours is of the order of 11·5 to 13 and that the near neighbour distance is about 2% greater than the respective 12-coordinated Goldschmidt diameter of the metal species. From these results it appears that metallic glasses are close-packed materials. Figure 2 further shows that the relative positions and heights of higher order peaks are approximately the same and that the second peak is *always* split, with the higher spacing peak diminished relative to the first. The split in the second peak distinguishes the RDF's of metallic glasses from those of liquids, where the split is absent. It is important to note here that the curves do not provide any information concerning the environment of a metalloid atom. Thus, in order to more fully characterise an n-component glass, one must perform separate scattering experiments utilising $n(n + 1)/2$ different wavelength radiations. This has been done only in a few cases (see for example, Waseda 1980, 1981) and the results clearly indicate that no two metalloid atoms can be nearest neighbours.

The next step in the analysis of the structure is to start with a model, calculate the theoretical RDF from this (with the help of a computer) and compare it with the experimental RDF. Recently, Livesey and Gaskell (1982) introduced the concept of a figure of merit for evaluating the accuracy of RDF's.

The concept of dense random packing of hard spheres (DRPHS) introduced by Bernal and developed by Finney (1979), originally to explain the structure of liquid metals, has found favour for the structure of metallic glasses as well. This is natural because metallic

glasses can be considered as frozen-in liquids and so their structures are expected to be similar. Figure 3 shows the remarkable agreement between the experimental and calculated RDF's for $Ni_{76}P_{24}$. In spite of this, the model takes into account the presence of only the metal atoms in the alloy and the packing fraction is only about 0.63, which is about 10% less than the value computed from measured densities. To overcome this limitation Polk (1972) proposed that the metal atoms form essentially a DRPHS structure and the metalloid atoms occupy the larger holes characteristic of the DRPHS structure, which was contested by Gaskell (1979) on the ground that to accommodate, *without*
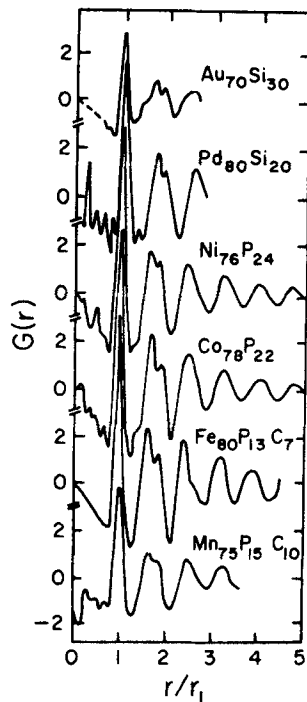

Figure 2.   Reduced radial distribution functions for several metal-metalloid glasses (Cargill 1975). Here r_1 is the position of the first peak maximum.
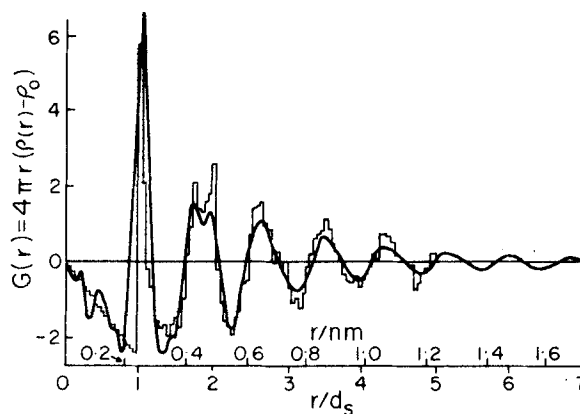

Figure 3.   Comparison of reduced radial distribution functions $G(r)$ for Finney's DRPHS structure and for amorphous $Ni_{76}P_{24}$ (Cargill 1975).

distortion, 20% of metalloid atoms even in the largest holes, the diameter of the metalloid atom must be ≤ 0.48 of the metal atom diameter. And this is true of only boron and carbon and not of other metalloids. Turnbull (1981) points out that the size of the metalloid is reduced to fit the available interstitial space. In other words, the metalloid atoms adjust to the environment. Modifications to the DRPHS model include relaxation (Boudreaux and Gregor 1977) of *soft* spheres, which gives a packing factor of 0·69–0·7, in agreement with values deduced from density measurements.

Fujita (1982) proposes intermediate-range ordering in amorphous solids and works out the diffraction theory for $Fe_{80}B_{20}$ (Hamada and Fujita 1982) and shows that there is excellent agreement between the model and the experiment.

Another model which finds favour at present seems to be the one proposed by Gaskell (1979). The origin of this model lies in the observation that during HREM of amorphous alloys, structural units as large as 1·5–2 nm are observed (Gaskell *et al* 1979). The 'microcrystalline' model will be insufficient to explain this. Further, this would require a large amount of boundary volume and an accompanying density deficit larger than the 1–2% observed (Cargill 1970, 1981). Thus, Gaskell (1979, 1982) proposes the existence of structural units (containing 200–400 atoms) in which the atoms are *crystallographically* defined and twinning planes, in three dimensions, comprise the interface. These units are packed to give essentially *random* long-range structures. These structural units have been identified to be trigonal prisms, which can be dissected (distorted) into tetrahedra and octahedra similar to those existing in crystalline interstitial phases. Thus, the local and, perhaps, medium-range structure of metallic glasses resemble *in detail* the structure of the corresponding crystalline phase. Experimental confirmation of this model is provided by Mehra *et al* (1983) from their studies on Ru-Zr-B alloys, where they show that irregular prismatic packing based on Ru_2B crystal gives good fit of the observed RDF's, while the DRPHS model cannot give even a moderate agreement.

All the above models have been proposed specifically for the metal-metalloid glasses. The Polk model ably explains the 80:20 ratio of metal to metalloid atoms based on DRPHS model. The model of Gaskell also is in a position to explain the composition ranges of 15–25 at. % metalloid on the basis of the existence of crystalline compounds of the type A_3B and A_4B. However, very few models have been proposed for metal-metal glasses. These pose more problems in view of the wide range of compositions where glasses form. Wang (1979) proposed a model, involving random stacking of interpenetrating Kasper polyhedra, which successfully explained the observations made on sputtered W-Fe, Ni-Nb, etc amorphous alloys produced at equiatomic compositions. Finney (1979) raised doubts about its applicability in three dimensions.

It must be emphasised, however, that the problem of the structure of metallic glasses is far from solved. Other techniques such as small-angle x-ray scattering (Osamura *et al* 1979, 1981, 1982) Mössbauer spectroscopy (Fujita 1981), nuclear magnetic resonance (Durand 1981), extended x-ray absorption fine structure studies (Hayes *et al* 1978) and HREM techniques can also aid in determining the structure of metallic glasses and efforts are being made in this direction.

7. Crystallization behaviour

Since the crystalline form of alloys is the lowest energy configuration, metallic glasses can be considered metastable. On continuous heating, metallic glasses will first lower

their energy by relaxing to a more stable glassy state and then at still higher temperatures (above the crystallization temperature), they crystallize into the most stable phases (Scott 1980). The crystallization temperature depends on the alloy system under consideration and can vary from as low as 380 K (for $Mg_{70}Zn_{30}$) to as high as 1225 K (for a complex tungsten-base alloy). The crystallisation temperatures can be determined with the aid of a differential scanning calorimeter. Irrespective of whether it is a metal-metalloid or a metal-metal glass, the decomposition behaviour can be represented by the general sequence (Masumoto and Maddin 1971; Suryanarayana 1980a).

Amorphous → amorphous' → MS I → MS II → stable phases where amorphous' represents the relaxed amorphous structure and MS I and MS II represent metastable phases. While the Japanese workers prefer the above representation, Köster and Herold (1981) proposed that crystallization reactions can be classified into three groups:

(i) *Polymorphous crystallization* in which the metallic glass crystallizes without any change in composition into a supersaturated solid solution or a metastable or stable crystalline compound; (ii) *Primary crystallization*, in which the first crystals to form will have a composition different from that of the glass; and (iii) *Eutectic crystallization* where simultaneous crystallization of two crystalline phases occurs by a discontinuous reaction.

It is possible to relate these two classifications. Polymorphous crystallization is rare, but can be considered as equivalent to the formation of MS I or directly the stable phase. This is possible only in concentration ranges encompassing a stable compound in the equilibrium diagram. Primary crystallization is equivalent to the formation of MS I followed by MS II containing higher solute contents. Eutectic crystallization is equivalent to simultaneous formation of MS I and MS II from the amorphous matrix.

8. High-resolution and analytical studies

HREM, field-ion microscopy and analytical microscopic techniques are helpful to determine the structure of metallic glasses (so far, this had only limited success) and to characterize the products of early stages of decomposition.

8.1 *As-quenched structure*

Electron micrographs recorded from metallic glasses at 100 kV do not show any contrast at normal resolution level (figure 4). The selected area diffraction pattern shows only a diffuse halo. This observation brings out the limitation, that even if microcrystals were to be present, the resolution limit of 100 kV instruments is insufficient to bring these out (Gaskell *et al* 1979). Observations made with a 500 kV electron microscope reveal a 'droplet' structure for the as-quenched amorphous Pd-Si alloy (Gaskell and Smith 1980), even though the diffraction pattern continues to show only diffuse haloes. High-resolution micrographs of these droplets reveal fringe patterns with a spacing of about 0·23 nm. While the fringes are very clear in thin films, only edges show the fringe pattern in thicker foils. This is a reflection of the decreased probability of overlap with disordered regions or with ordered domains not at the Bragg angle. Further, the fringes have only a low contrast (even though higher than that observed in amorphous semiconductors, which have a low intensity first peak in the
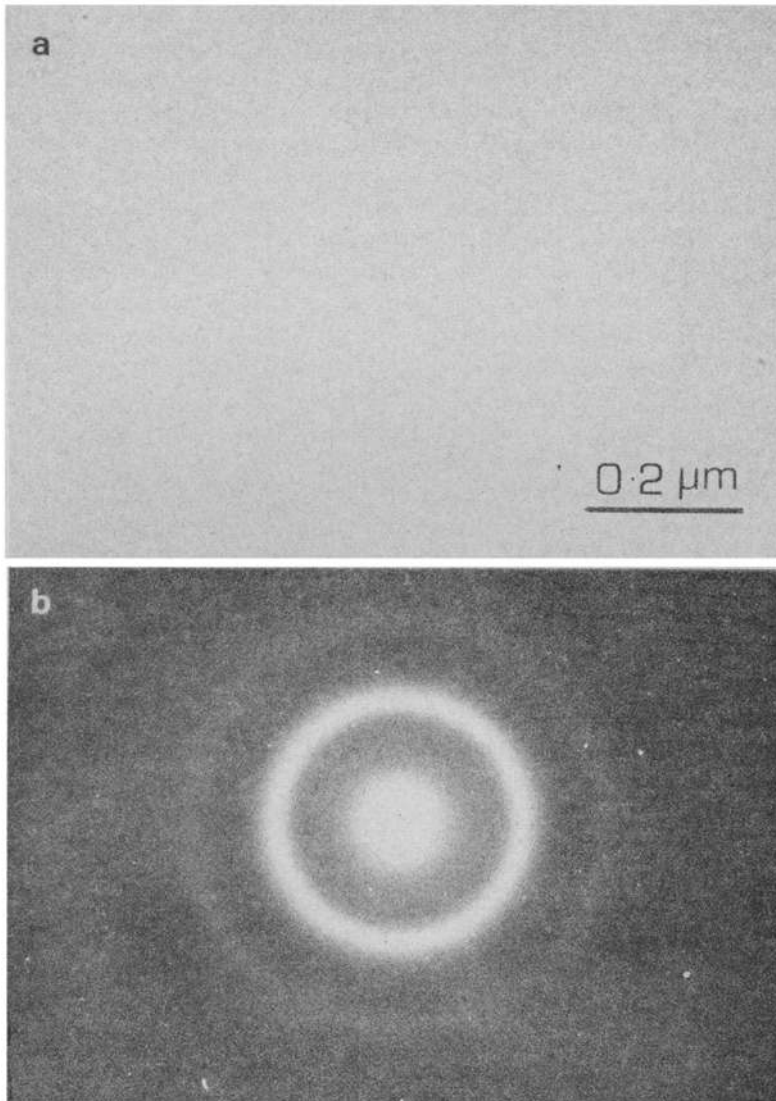
Figure 4. **a.** An electron micrograph representing a typical as-quenched glassy structure. No contrast can be observed. The selected area diffraction pattern showing a broad diffuse halo is shown in **b**.

structure factor curve) and there are several apparently independent fringe systems per particle. Gaskell and Smith (1980) claim that these particles are characteristic of the glassy structure and suggest that the diffuse interface present distinguishes them from crystalline particles nucleated during annealing. (Fujita *et al* 1980, however, show that low temperature annealing at 563 K of an $Fe_{83}B_{17}$ alloy, precipitates α-Fe crystals having a diffuse interface with the matrix). Apart from the nature of the interface, the size of the crystal formed during thermal decomposition is larger. These fringe patterns in the droplets (particles) have been shown to conform to the polytetrahedral packing mentioned earlier in §6.

A point of caution here is that the above results refer to flash-evaporated or sputtered films, and similar results are not reported in many melt-quenched glasses so far. In fact, through-focal series on several melt-quenched metallic glasses do not show any fringe patterns (Fujita *et al* 1980; Imura *et al* 1982; Fukamichi *et al* 1979, 1982), but only the presence of coherently scattering domains 0·5–2 nm in size (probably due to limitations of resolution). High-voltage electron microscopy studies of these alloys have been carried out by Ishida *et al* (1982). They find that the as-quenched structure varies depending on the composition, quenching method and quenching conditions. Figure 5(a) shows an electron micrograph of a sputter-deposited $Co_{94}Zr_6$ alloy indicating that it is microcrystalline. Even though the diameter of the crystals is only 10–20 atomic diameters, the density of microcrystals increases with the thickness of the foil. However, when the Zr content is increased to 11 at. % a truly random structure without the presence of any fringe structure is produced (figure 5b). It is interesting to note here that the $Co_{94}Zr_6$ alloy has the best magnetic properties (better than even $Co_{89}Zr_{11}$) even though it contains some microcrystallites.

High-resolution electron micrographs of *melt-quenched* $Fe_{40}Ni_{40}P_{14}B_6$ (METGLAS 2826) and wide $Pd_{80}Si_{20}$ ribbon specimens are shown in figure 6(a) and (b), respectively. Although the selected area diffraction patterns from both the samples show only diffuse rings, the $Fe_{40}Ni_{40}P_{14}B_6$ alloy has a true amorphous structure, while the $Pd_{80}Si_{20}$ alloy shows some lattice fringes. It is suggested that these fringes may arise due to the lower cooling rate (specimen width $\sim$ 15 mm). From these results, Ishida *et al* (1982) conclude that the details of the structure of the amorphous phase may differ from system to system.

It was pointed out earlier (Ranganathan and Suryanarayana 1972) that field-ion microscopy can play an important role in understanding the structure of metallic glasses. Cotterill and Kragh (1977) observed a $Pd_{80}Si_{20}$ glassy sample in a field-ion microscope at 78 K and reported the absence of any wide-spread crystallinity. They reported that in some regions they could detect small clusters of atoms that are suggestively regular. However, other recent investigations (Jacobaeus *et al* 1980; Inal *et al* 1980, 1981; Arise *et al* 1982) clearly indicate a random distribution of atoms in the as-quenched state. The interpretation of field-ion images is made difficult due to the fact that only one species of atoms is visible. There are additional problems in concentrated alloys (Müller and Tsong 1969).

Jacobaeus *et al* (1980) imaged specimens of $Fe_{80}B_{20}$ and $Fe_{78}Mo_2B_{20}$ (METGLAS 2605 and 2605A, respectively) in a field-ion microscope and found no dissimilarities in configurations in the as-quenched state. By careful plotting of the co-ordinates of the image points (representing the iron atoms), the triplet correlation of atomic positions was produced. This may represent the first step in the quest to remove the ambiguities inherent in the exclusive use of pair distribution functions in the study of the non-crystalline state. It is also possible that this type of approach will help to shed some light on the question of the microstructure of metallic glasses.

8.2 *Early stages of crystallization*

High-resolution and analytical microscopic investigations have been more useful in understanding the intricacies of the early stages of crystallization. Quite a few detailed studies have been undertaken in this direction in recent times.

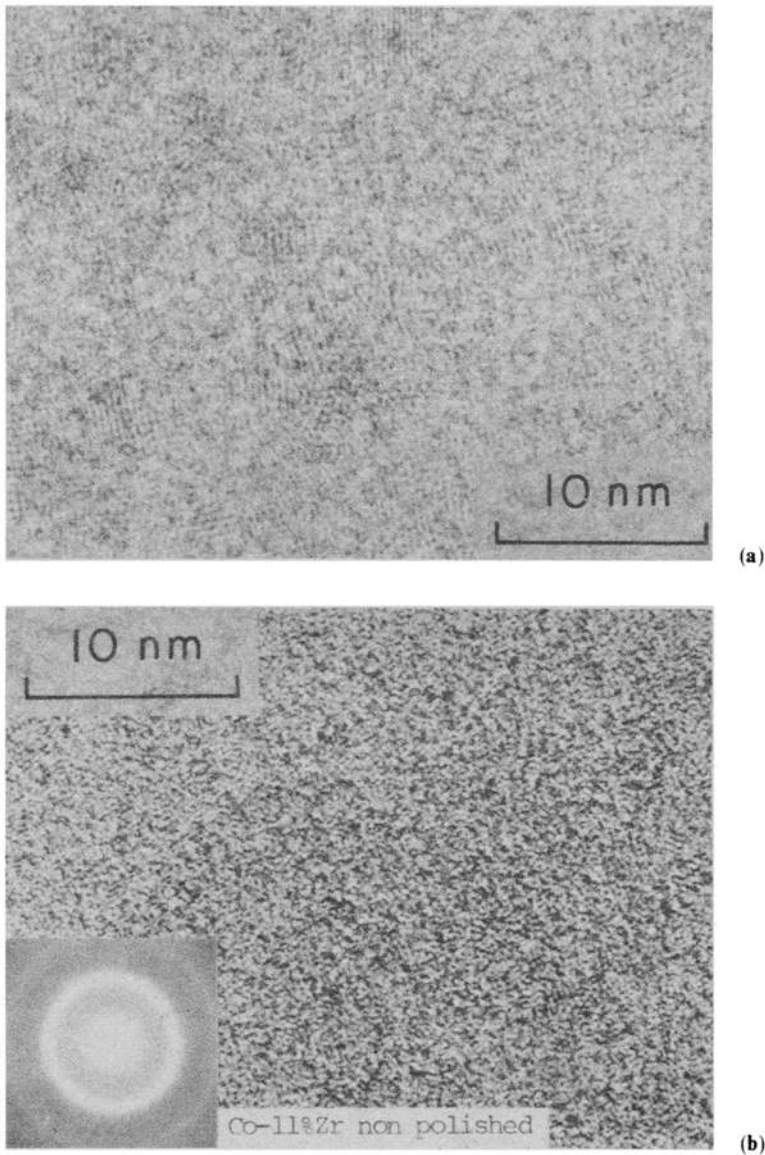One of the detailed investigations concerns the crystallization behaviour of Fe-B and

Figure 5. **a.** An axial HREM of sputter-deposited $Co_{94}Zr_6$ alloy. Microcrystals are seen, **b.** Micrograph of the $Co_{89}Zr_{11}$ alloy. No lattice fringe is seen (Courtesy: Yoichi Ishida).

Ni-B glasses (Fujita *et al* 1980). Crystallization starts with the precipitation of α-Fe microcrystals (primary crystallization) which have a diffuse interface with the matrix. These microcrystals contain further fine structures several nanometres in size. These crystals have a rhombic shape whose diagonal axes are parallel to the $\langle 110 \rangle_{Fe}$ direction. Lattice imaging of the crystals confirmed that they are α-Fe and that they contain fine crystallites as evidenced by the presence of boundaries and Moiré patterns. The microcrystals were found to grow only when the interface became sharp. Annealing at higher temperatures resulted in the formation of the Fe_3B crystals.
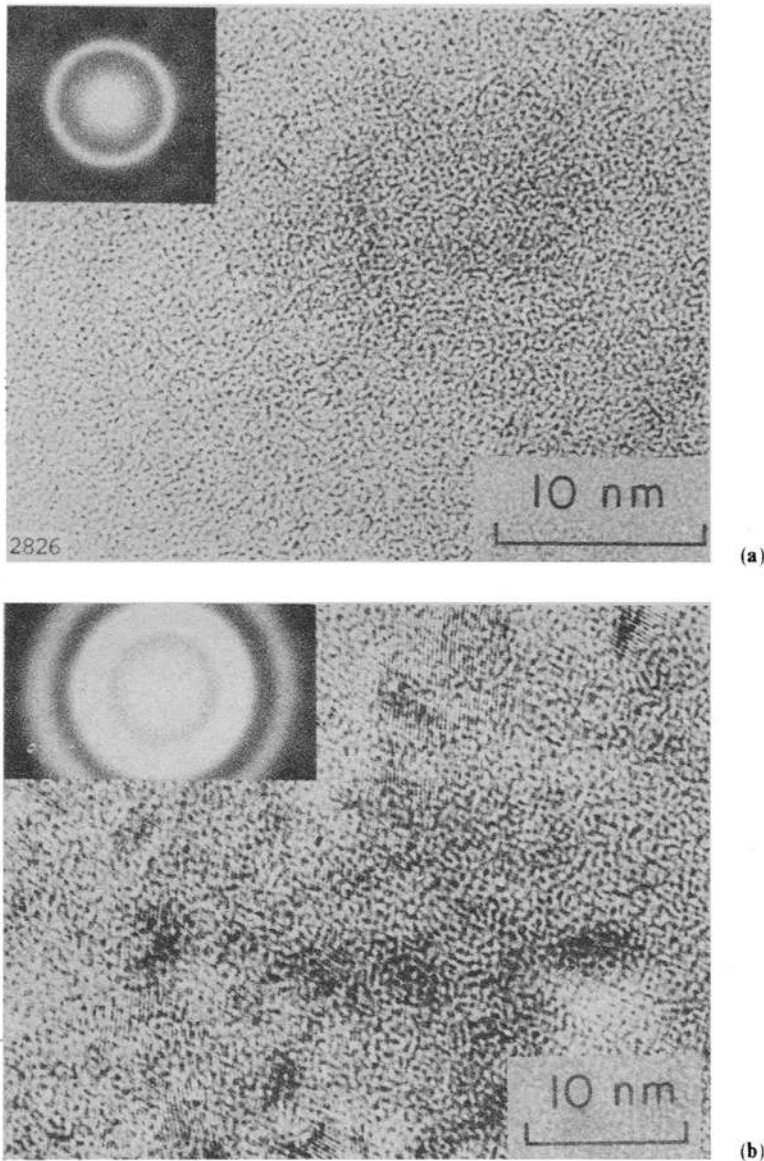
Figure 6. **a.** HREM of a melt-quenched $Fe_{40}Ni_{40}P_{14}B_6$ sample. Notice the true amorphous nature. **b.** Micrograph from melt-quenched $Pd_{80}Si_{20}$ wide ribbon. Lattice fringes can be seen in some areas (Courtesy: Yoichi Ishida).

In a very interesting and thought-provoking paper, Piller and Haasen (1982) reported results on an atom-probe field-ion microscopic study of a $Fe_{40}Ni_{40}B_{20}$ glass and observed that the glass on annealing at 643 K decomposes into two amorphous phases $(FeNi)_3B$ and FeNiB of low boron content. (It was indicated that the formation of the $(FeNi)_3B$ supports the glass model of Gaskell 1979). Another interesting observation made by them was that $70 \pm 10\%$ of the image spots are due to boron atoms (while

Jacobaeus *et al* (1980) assumed that only iron atoms were imaged!). Piller and Haasen (1982) had also analysed the kinetics of decomposition and concluded that kinetics seem to be governed by long-range diffusion of boron in the glassy state. A glass containing more than 18 % boron was found to be brittle.

Inal *et al* (1980) investigated the crystallization behaviour of glassy $Fe_{80}B_{20}$ by combined x-ray diffraction and field-ion microscopy (FIM) techniques. They showed that FIM was more potent in revealing the presence and distribution of crystalline particles in the early stages of decomposition. As an example, they observe that while a sample annealed at 1053 K for 15 min shows the presence of only Fe_3B compound in the x-ray patterns, FIM investigations show the presence of α-Fe particles and Fe_3B even on annealing for 45 sec at 1053 K. This is understandable because x-ray patterns show the average picture and may not show the presence of a phase present in very small quantities, while FIM can show the presence of even very small volume fractions of a phase. However, the usefulness of FIM in the last stages of crystallization is limited owing to the large size of the crystalline particles. An FIM study of laser-induced phase transformations in $Fe_{80}B_{20}$ also revealed features similar to the above with the proviso that the laser beam impingement area corresponded to longer periods of anneal, and the regions removed from this zone show the same phase structure obtained with shorter periods of annealing (Inal *et al* 1981).

Vitek *et al* (1975) report the high-resolution electron microscopic study of the crystallization of a metal-metal glass ($Cu_{60}Zr_{40}$). In the early stages of crystallization, small crystals of a $Cu_{10}Zr_7$ phase were detected which consisted of subgrains 30–50 nm in size. Since lattice fringes were not terminating inside a subgrain, it was concluded that the subgrains were free from dislocation arrays.

Only a few analytical microscopic investigations have been reported in the literature so far. It is needless to emphasise that HREM coupled with analytical techniques can give a wealth of information which can resolve many of the controversies existing today.

As mentioned earlier, precipitation of an MS I phase takes place on annealing the glass at the crystallization temperature. This MS I phase may have a composition which is the same or different from the glass composition. Diffraction patterns recorded from the crystals were used to measure the lattice parameter (accuracy is not very high) and estimate the solute content of the crystal. This can decide whether the crystallization is of the primary type or polymorphous type. However, energy dispersive spectroscopy (EDS) techniques, now-a-days commonly available as attachment to transmission electron microscopes, can readily evaluate the composition of the crystal and decide the type of crystallization. Such a type of investigation was reported by Heimendahl and Oppolzer (1978) on $Fe_{32}Ni_{36}Cr_{14}P_{12}B_6$ (METGLAS 2826A). They showed that this glass undergoes a primary crystallization, since the crystal to form first had much less Cr and P and higher Fe content than the glass (B could not be analysed). A similar investigation was undertaken on $Fe_{40}Ni_{40}P_{14}B_6$ (METGLAS 2826) and the results showed that the phase first precipitating was $(FeNi)_3PB$ (Tiwari and Heimendahl 1981).

Since metallic glasses are non-crystalline, formation of voids is difficult to understand. Free volume exists in metallic glasses, but aggregation of this to form voids is again doubtful. However, Morris (1980) reports the observation of voids in METGLAS 2826 ribbons annealed at 653 K. This was questioned by Tiwari and Heimendahl (1981), but Morris (1981) insists that under suitable kinetic conditions the formation of such metastable aggregates might occur. He supports the observation by the fact that the voids (very small, round, featureless objects) (i) show an orientation-dependent

contrast and (ii) show through-focus contrast variations similar to those expected of small voids.

9. Concluding remarks

It has been shown that metallic glasses have outstanding physical, chemical and magnetic properties. In fact, the combination of properties is so excellent that it is difficult to think of a better engineering material. In addition, metallic glasses are produced directly from the liquid state into the net shape in a *single step* and thus the process is much cheaper than the conventional methods and so economically viable. These factors are responsible for the intensive activity throughout the world to see that metallic glasses replace the existing crystalline materials at least in some spheres. Some progress has already been made in this direction in Japan.

The nature of the metallic glasses, their structure and its influence on the properties (the so-called structure property correlations) are beginning to be understood only now. The difficulties being encountered are enumerated in the preceding sections; but it is hoped that the advent of new techniques and sophistication of the existing techniques and methods will aid in overcoming the difficulties. Urgent attention is required to be focussed on resolving the many *different results* obtained on the *same alloy*. This may be due to changes in quenching methods, quenching conditions (thickness of specimen, cooling rate, atmosphere) or even local changes in composition. Thus, it will be fruitful if investigations are carried out by producing the glassy structure in *one alloy* under controlled conditions by *different methods* and correlate the structure with the properties. Until this is done we will continue to have a large body of unrelated results on various alloys.

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