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Review
Structure of metallic glasses

C. V. GOKULARATHNAM
Department of Metallurgy, Indian Institute of Technology, Madras, India

Metallic glasses or amorphous alloys have been produced by rapid quenching of alloys from the liquid or vapour phase.

This paper is a review of the studies on the structure of metallic glasses. The theory of diffraction by amorphous materials is dealt with at length followed by a description of the procedure of obtaining and analysing the RDF of amorphous alloys.

Various models have been put forward to explain the structure of the metallic glasses, and these are fully discussed. A dense random packing model or modifications thereof can best explain the structure and range of stability of amorphous alloys.

1. Introduction

Metallic glasses are formed from a metal or an alloy and most of which are stable at room temperature contain two or more constituents. These glasses are also called amorphous alloys. The usage of the word "amorphous" as applied to glasses has been questioned as it implies an absence of structure whereas glasses do have a short range order. Here the word "amorphous" will be used merely to imply that the glass does not have a crystalline structure, but can, and does, have a structure given by short range order.

Amorphous alloys have been produced by the following techniques: (1) vapour quenching on a cold substrate or vaposol quenching [1-5], (2) electro- and electroless deposition [6-11], and (3) rapid quenching from the molten state – liquisol quenching or splat-cooling [12-17].

Vaposol quenching gives rise to extremely drastic quenching rates and has been used to produce amorphous alloys in the Ag-Cu and Mg-Cu systems. Electro- and electroless deposition under suitable conditions have been used to produce glasses in the Ni-P system, but the majority of metallic glasses known today has been produced by liquisol quenching techniques [12, 17]. There has been widespread interest in the structure and properties of these amorphous alloys. Various studies have been conducted on the structure (see Table I), electrical [12, 18], magnetic [12, 19, 20], mechanical [12, 21] and thermodynamic [22] properties of amorphous alloys. These studies show that most of the amorphous alloys are made up of a transition metal such as Au, Pd, Pt, Fe and a metalloid such as Si, Ge, P or C in suitable combinations. The amorphous alloys give rise to broad diffuse peaks in their X-ray and electron diffraction patterns. Their electrical resistivity shows a sharp drop at the crystallization temperatures. Some of these amorphous alloys also show a glass transition temperature. Structural information on these glasses can be obtained by calorimetry, viscosity measurements, optical absorption, NMR and other techniques. Diffraction methods are also extensively used to study their structure. Diffraction methods essentially consist of obtaining the X-ray, electron or neutron diffraction pattern from the glass and analysing this to obtain structural information. The structural information thus obtained is, however, not as complete and accurate as in the case of crystalline materials. Only a statistically averaged picture of the structure of glass, i.e. a description of the distribution of atoms in the glass with respect to one another, can be obtained. Even this average is not accurate, as the analysis of diffraction patterns from a multicomponent glass involves the use of approximations that are not always justifiable. However, recent advances in experimental techniques [33-37] have made it possible to obtain more accurate diffraction data from glasses. The advances in theory [38-40] have made a more precise analysis of diffraction data from binary glasses possible.

TABLE I Structural investigations of amorphous alloys.

Amorphous alloy	Method of production	Diffraction procedure	Remarks	Reference
Ni-9.7 wt % P	Chemical deposition	X-ray	Diffractometer	[9]
Ni_xP_{100-x} ($x = 73$ to 81.4)	Electro deposition	X-ray	Diffractometer	[11]
$Ni_xPt_{75-x}P_{25}$ ($x = 15$ to 45)	Liquisol quenching	X-ray	Diffractometer	[16]
$Pd_{80}Si_{20}$	Liquisol quenching	X-ray	Camera	[23]
$Pd_{80}Si_{20}$	Liquisol quenching	X-ray	Diffractometer	[24]
$Fe_{80}P_{13}C_7$	Liquisol quenching	X-ray	Diffractometer	[25, 26]
Mn-P-C	Liquisol quenching	X-ray	Diffractometer	[27, 28]
$Ni_xPd_{80-x}P_{20}$ ($x = 10$ to 70)	Liquisol quenching	X-ray	Diffractometer	[29]
$Fe_xPd_{80-x}P_{20}$ ($x = 10$ to 70)	Liquisol quenching	X-ray	Diffractometer	[29]
$(Ni_{50}Pd_{50})_{100-x}P_x$ ($x = 15$ to 27.5)	Liquisol quenching	X-ray	Diffractometer	[30]
$Au_{70}Si_{30}$	Liquisol quenching	X-ray	Diffractometer	[31]
$Cu_{35}Mg_{65}$	Vaposol quenching	Electron diffraction	Scanning	[25, 32]
$Au_{55}Cu_{45}$	Vaposol quenching	Electron diffraction	Scanning	[25, 32]

The diffraction techniques by themselves can only give an average picture of the structure of glass. They cannot give an unequivocal answer to the question of whether glass is composed of a random arrangement of microcrystallites or is a continuous random network of the constituent atoms. Considerable effort and ingenuity have gone into the construction and analysis of models to check whether the observed structural information is compatible with a microcrystallite or a random network model of the structure of metallic glass. Resort has been made to small-angle X-ray scattering and electron microscopy. Field-ion microscopy [12] may throw light on this problem.

2. The structure of metallic glasses

The structure of glasses cannot be characterized in as precise a manner as the structure of crystalline materials. In this review attention will be confined only to diffraction methods for obtaining the structural information on glasses. The diffraction methods lead to two different approaches, namely the direct and the indirect analysis. In the direct method of analysis the coherent diffraction data are treated by Fourier transform methods to give the radial distribution function (RDF) of the glass. The RDF is then analysed to give the average interatomic distances and the near neighbour co-ordinations in the glass. The direct method, however, suffers from the following limitations.

1. Experimental difficulties prevent accurate coherent intensity data to high values of $k(= 4\pi \sin \theta/\lambda)$ being obtained. The higher the value of k to which accurate intensity data are available, the better the resolution achieved in the RDF. Emphasis is placed on the accuracy of data because errors, if any, at high k values tend to be magnified in the RDF analysis.
2. The information available from RDF is, in itself, incomplete as it is not possible to determine the contribution to the RDF due to the various constituent atoms of a multicomponent glass. Assumptions, which may not always be justifiable, must be made in the interpretation of the RDFs, especially of multicomponent glasses.

The indirect method consists of postulating various structural models for the glass and calculating the intensity function or the RDF corresponding to each of the models. The calculated intensity/RDFs are compared with the experimental intensity/RDFs until a suitable match is obtained.

The indirect analysis is especially attractive as it can account for the errors inherent in the RDF analysis. However, the accuracy of the analysis is still dependent on the accuracy of the intensity data and, hence, on the experimental procedures used to determine the diffraction data.

3. Experimental procedures

Electron, X-ray and neutron diffraction procedures have been used in the study of the structure of glass. Amorphous alloys in the form of thin (10 to 1000 Å) films may be investigated by high energy (25 to 100 keV) electron diffraction. The diffraction patterns may be recorded on film or, for more accurate analysis, by using scanning devices [34]. It is possible to use energy filters [34-37, 42, 43] in conjunction with the scanning devices to eliminate inelastic scattering experimentally.

Various X-ray diffraction procedures have been used to record the diffraction patterns of amorphous alloys. Early investigations used photographic techniques [23]. A crystal monochromatized X-ray beam was used to record the diffraction pattern in a Debye-Scherrer camera. A microdensitometer trace of the diffraction pattern could be obtained and analysed to give the coherently scattered intensity, after correcting for the background, air scattering, absorption, polarization and Compton scattering.

Diffractometer techniques using counters to monitor the diffraction pattern are more attractive as they can provide more accurate quantitative data than the photographic methods. It is also possible to eliminate Compton scattering in the experiment itself. The experimental elimination of Compton scattering is particularly attractive as this minimizes the inaccuracies in the experimental data due to the use of tabulated values of the Compton scattering. The tabulated values are approximate and in some cases may not be applicable to the atoms when forming part of a glass. This is important because the contribution of Compton scattering to the total scattering is pronounced in the sensitive high k region. Diffraction data from amorphous alloys have been recorded using a diffractometer with a diffracted beam monochromator together with a proportional/scintillation counter and pulse height analyser. The diffracted beam monochromator helps to eliminate the Compton scattering progressively as k increases. The efficiency of removal of Compton scattering can be estimated as a function of k and the coherent scattering determined [44, 45].

The fluorescence excitation technique of Warren and Mavel [46, 47] is a very powerful technique for the experimental elimination of Compton scattering. This method can be fruitfully used with Rh$K\alpha$ and Ag$K\alpha$ only [33]. So far, only Rh$K\alpha$ has been used in this manner [33]. An attempt to use AgKα [48] has failed. The fluorescence excitation technique has not yet been used in the study of the structure of amorphous alloys but has potential applications.

The diffraction data are corrected for background, air scattering, and polarization and are normalized to yield the intensity in absolute units (electron units per unit of composition). The normalization can be achieved by subjective or objective [49] methods. The Compton scattering can be experimentally eliminated by the fluorescence excitation technique or by the use of a diffracted beam monochromator. As the Compton shift increases with the angle of scattering the amount of Compton scattering eliminated by either technique increases with the angle of scattering and, at a high enough angle, all the Compton contribution will be cut off. The fraction of Compton scattering eliminated can be evaluated as a function of 2θ and used to correct the normalized intensity. If there is complete elimination of Compton scattering, no correction will be necessary to the normalized intensity at these angles. Correction procedures [50] are available to eliminate any errors in the experimental data.

Neutron diffraction has not been used to study the structure of amorphous alloys, though it is a potentially useful technique especially for binary glasses.

4. Analysis of diffraction data

When a beam of monochromatic radiation of wavelength, λ, falls on an array of atoms, two scattering processes can occur; the modified or Compton scattering and the unmodified or coherent scattering. The Compton scattering does not contain any directly obtainable structural information. The unmodified scattering, however, can be directly related to the structure of glass by the Debye equation [51]

$$I_N(k) = \sum_m^N \sum_n^N f_m(k) f_n(k) \frac{\sin k\, r_{nm}}{k\, r_{nm}} \qquad (1)$$

$I_N(k)$ is the average unmodified intensity of scattering due to N diffracting atoms, $f_m(k)$ and $f_n(k)$ are the atomic scattering factors (for X-rays, electrons or neutrons as the case may be) of atoms m and n respectively, r_{nm} is the distance between two atoms m and n; m and n can refer to atoms belonging to the same or different atomic species.

The unmodified scattering from an assembly of atoms thus contains information regarding the interatomic distances r_{nm} and the number and types of atoms at distances r_{nm}. If Equation 1 can be rigorously solved, a complete description of structure can be obtained. The solution of Equation 1 is not straightforward for amorphous alloys. A solution is, however, possible and has developed along the following lines.

1. Zernicke and Prins [52] first suggested that a Fourier transform of the coherently scattered intensity can give rise to RDF of liquids. Warren and co-workers applied this to the case of simple oxide glasses [53].
2. Warren *et al* [54] applied an approximate analysis to the study of the structure of vitreous silica.
3. Waser and Schomaker [38] and Pings and Waser [39] showed that a rigorous analysis of diffraction data from a multicomponent glass is possible. Vineyard [55] suggested that a rigorous analysis of the structure of binary glasses is possible.
4. Mozzi and Warren [33] made a rigorous study of the structure of vitreous silica. This method has been applied [56-58] to a study of a few oxide glasses.

For glasses containing one type of atom only, it can be shown that the RDF is given by an equation of the type

$$4\pi r^2 [\rho(r) - \rho_0] = \frac{2r}{\pi}\int_0^{k_{\max}} ki(k) \sin rk \, \mathrm{d}k \qquad (2)$$

where

$$i(k) = \frac{I_N(k)}{Nf^2(k)} - 1 \, .$$

$I_N(k)$ is the total coherent scattering intensity due to N atoms, $\rho(r)$ is the density of atom centres at a distance r from a reference atom and ρ_0 is the average atomic density in the glass.

For a multicomponent glass the analysis is more complicated. An approximate solution was first developed by Warren *et al* [54] and gives

$$\frac{2r}{\pi}\int_0^{k_{\max}} ki(k) \sin rk \, \mathrm{d}k = 4\pi r^2\, \Sigma\, K_m\, g_m(r) - 4\pi r^2 g_0\, \Sigma\, K_m \qquad (3)$$

where

$$i(k) = \frac{(I_N(k)/N) - \Sigma f_m^2}{f_e^2} \, .$$

$I_N(k)$ is the coherent scattering intensity due to a volume of glass containing N units of composition, u.c. (e.g. SiO_2 can be taken as one unit of composition in the case of vitreous silica)

$$f_e = \frac{\sum_{\text{u.c.}} f_m}{\sum_{\text{u.c.}} z_m}$$

where z_m is the atomic number for atom m and $f_m = K_m f_e$; $\sum_m = \sum_{\text{u.c.}}$, and $k_{\max}$ is the maximum value of k to which intensity data are available. $g_m(r)$ is the average density of atom centres at a distance r from a central atom, m, multiplied by the appropriate K_m and g_0 is the average electron density. Pings and Waser [39] have shown that the experimental RDF can be analysed without the use of any approximations. When a suitable function of the experimental intensity is transformed, the result is a combination of the convolution products of the true pairwise atomic distributions with a function which is the Fourier transform of the normalized product of the atomic scattering functions for the corresponding pair of atoms in the glass. Considering a metallic glass containing n different atomic species

$$\bar{\rho} r\, H(r) = \frac{1}{2\pi^2}\int_0^{k_{\max}} ki(k) \sin rk \, \mathrm{d}k \qquad (4)$$

where $i(k)$ is the experimental interference function given by

$$i(k) = \frac{(I_N(k)/N) - \sum_{i=1}^{n} x_i f_i^2(k)}{[\sum_{i=1}^{n} x_i f_i(k)]^2} \, .$$

$I_N(k)$ and N have the same significance as in Equation 3. $x_1, x_2, \ldots, x_i$ are the atom fractions of atoms of types 1, 2, . . . , i, respectively.

$f_1(k), f_2(k), \ldots, f_i(k)$ are their scattering factors

$$rH(r) = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i\, x_j \int_{-k_{\max}}^{k_{\max}} y\, h_{ij}(r)\, j_{ij}(r - y)\, \mathrm{d}y \qquad (4a)$$

i.e. $rH(r)$ is the weighted convolution product of $j_{ij}(r)$ and $h_{ij}(r)$ where

$$j_{ij}(r) = \frac{1}{\pi} \int_0^{k_{\max}} \frac{f_i(k) f_j(k)}{[\Sigma x_i f_i(k)]^2} \cos rk\, \mathrm{d}k \qquad (4b)$$

and $h_{ij}(r) = \dfrac{\rho_{ij}(r)}{\bar{\rho}_j} - 1$.

$\rho_{ij}(r)$ is the density of j-type atoms at a distance r from an i-type atom and $\bar{\rho}_j$ is the average density of j type atoms. $j_{ij}(r)$ can be calculated for all the i-j type interactions possible in the glass. $h_{ij}(r)$ values can be calculated assuming various structural models till a good fit is obtained between the experimentally determined right hand side and the calculated value of $\bar{\rho} rH(r)$. This procedure has so far been applied only to simple glasses, e.g. vitreous silica which consists of two components and where the oxygen atoms are known to be tetrahedrally arranged about the silicon. In the case of amorphous alloys, however, it is not possible to determine or make an *a priori* assumption about the number and types of atoms involved in the nearest neighbour interactions. Hence, the structural information is not completely obtainable by direct methods.

A rigorous solution is possible in the case of binary glasses. One can define an $i_{ij}(k)$ as

$$k i_{ij}(k) = 4\pi \bar{\rho} \int_0^{\infty} r\, h_{ij}(r) \sin kr\, \mathrm{d}r \qquad (5)$$

where $i_{ij}(k)$ is the partial interference function due to the interactions of atoms of type i and j only and $i(k)$ is then given by

$$i(k) = \sum_{i=1}^{n} \sum_{i=1}^{n} x_i\, x_j\, F_{ij}(k)\, i_{ij}(k)\,. \qquad (5a)$$

For a binary glass containing atomic species 1 and 2, the experimental interference function, $i(k)$, can be written as

$$\begin{aligned} i(k) &= x_1^2 F_{11}(k)\, i_{11}(k) \\ &\quad + 2x_1 x_2 F_{12}(k)\, i_{12}(k) \\ &\quad + x_2^2 F_{22}(k)\, i_{22}(k)\,. \end{aligned} \qquad (6)$$

$F_{ij}(k)$ are functions of the atomic scattering factors f_i and f_j and can be varied by isotopic substitution, anomalous scattering [59] or by a suitable combination of electron, X-ray and neutron diffraction. In practice, this approach is not very successful as the differences in $F_{ij}(k)$ are small and the values of f_i and f_j are not very accurately known in many cases. There is no known case where anomalous scattering of X-rays has been used in the study of the structure of an amorphous alloy.

Urnes [60] studied the structure of a series of Li_2O-Al_2O_3-SiO_2-GeO_2 glasses by RDF methods. If Ge replaced Si isostructurally in the glass the Si-Si and Si-O peaks of the RDF should increase with increasing substitution of Si atoms by Ge. This was found to be the case and it appears that a similar approach may be applicable to glasses of the system Au-Si-Ge.

5. Structural models of metallic glasses

One of the important questions in the study of the structure of metallic glasses is the question whether the atoms in the glass are arranged in a random fashion or form randomly oriented microcrystalline regions. Diffraction techniques can be applied to solve this question to a limited extent only. Originally, this question also arose in the case of oxide glasses. Zachariasen [61] suggested that an oxide glass consisted of a three dimensional random network of a unit of structure (for example an SiO_4 tetrahedron in the case of vitreous silica). Warren and co-workers [53, 54] obtained X-ray diffraction results for vitreous silica and other oxide glasses which could be satisfactorily explained on the basis of this random network model. Valenkov and Porai-Koshits [62] were among the first proponents of a microcrystalline model of the structure of glass. Warren [63] argued that microcrystallinity should give rise to small angle X-ray scattering. He was not able to observe any small angle scattering in the case of vitreous silica and, hence, concluded that vitreous silica is not microcrystalline. Bienenstock and Bagley [64] have shown that even if a glass consisted of randomly oriented microcrystallites it will be difficult to detect the small angle scattering from such a glass. The large angle scattering from a glass can also give an idea regarding the size of microcrystalline regions if any. It can be shown [27, 43] that if

$$\gamma(r) = \frac{2}{\pi} \int_0^{k_{\max}} k[I(k) - 1] \sin rk\, \mathrm{d}k \qquad (7)$$

where $I(k)$ is the scattering intensity per average atom in absolute units. The radial distribution function is given by

$$4\pi r^2 \rho_0 g(r) = 4\pi r^2 \rho_0 V(r) + r\gamma(r) \qquad (7a)$$

where ρ_0 is the average atomic density and $g(r)$ is a properly weighted density distribution function. In regular RDF work one calculates a function

$$4\pi r^2 \rho_0 + r\gamma(r) = 4\pi r^2 \rho^*(r) \qquad (7b)$$

which is related to the true RDF taking into account $V(r)$, the size factor, which is 1 inside a diffracting domain and zero outside it, by the equation

$$\begin{aligned} 4\pi r^2 \rho^*(r) &= 4\pi r^2 \rho_0 + r\gamma(r) \\ &= 4\pi r^2 \rho_0 [1 - V(r)] + 4\pi r^2 \rho_0 g(r) V(r) \qquad (7c) \end{aligned}$$

A function $g^*(r)$ can be defined equal to $\rho^*(r)/\rho_0$. Then

$$g^*(r) = 1 - V(r) + g(r) V(r) \qquad (7d)$$

$\rho^*(r) \rightarrow \rho_0$ when $g(r) \rightarrow 1$ or when $V(r) \rightarrow 0$. For an amorphous material $g(r) \rightarrow 1$ before $V(r) \rightarrow 0$. For a microcrystalline material $V(r) \rightarrow 0$ before $g(r) \rightarrow 1$. Hence if an idea of the value of r at which $g^*(r) \rightarrow 1$ is obtained, the size of the microcrystallites, if any, can be deduced. A value of r_S beyond which microcrystalline order ceases to exist can be calculated. Values of size r_S for a few glasses assuming $g^*(r) = 1 \pm 0.02$ are given in Table II [32]. The X-ray intensity functions of the amorphous alloys such as Pd-Si, Fe-C-P, Mn-P-C, Ni-Pd-P, Ni-P, Ag-Cu all show a strong first peak and a shoulder on the large k side of the second peak. This is shown very well in the case of three typical metallic glasses (Fig. 1). Dixmier *et al* [9] were the first to observe this in the case of a chemically prepared Ni-P alloy. They concluded that such a pattern would indicate a structure made up of a random packing of close-packed layers of finite dimensions similar to the structure of carbon black [63]. If this model is correct we can calculate the dimensions of the diffracting domains, L_a in the plane of close packed layers from the second peak in $I(k)$ and L_c normal to the layers from the first peak in $I(k)$ using the following equations [63]:

$$\begin{aligned} L_a &= 2\pi\,(1.84/\Delta k) \\ L_c &= 2\pi\,(0.89/\Delta k) \qquad (8) \end{aligned}$$

where Δk is the peak width at half-maximum height. A few values of L_a and L_c are also shown in Table II.

TABLE II Values of r_S of ordered regions beyond which $g^*(r) = 1 \pm 0.02$ and values of L_c and L_a for some amorphous alloys (after Wagner [32]).

Alloy	r_S (Å)	L_c (Å)	L_a (Å)
$Pd_{80}Si_{20}$	16	16	15
$Ag_{55}Cu_{45}$	14	11	11
$Fe_{80}P_{13}C_7$	16	15	14
$Ni_{77}P_{23}$	14	12	12
$Cu_{35}Mg_{65}$	15	14	13

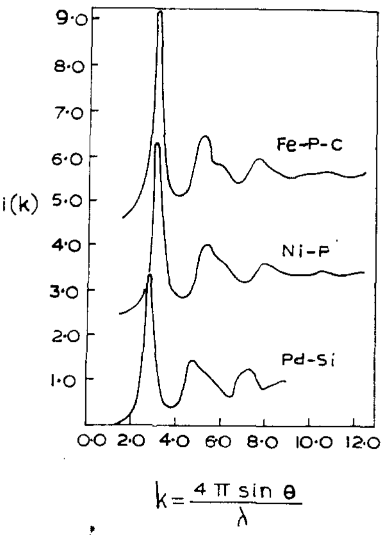

Figure 1 Interference function $i(k)$ versus k for amorphous $Fe_{80}P_{13}C_7$, $Ni_{81.4}P_{18.6}$ and $Pd_{80}Si_{20}$ showing shoulder on high k side of the second peak. Zero positions vertically displaced. (After Wagner [25], Cargill [11], Crewdson [23].)

Both r_S and L_a (or L_c) are of the order of 10 Å and it is possible to imagine small regions where the order is slightly greater than the order in an amorphous substance. It should be noted that the intensity functions for liquid metals and alloys do not show a shoulder on the high k side of the second peak.

The RDFs for these glasses show a splitting of the second peak. RDFs of $Fe_{80}P_{13}C_7$, $Ni_{81.4}P_{18.6}$ and $Pd_{80}Si_{20}$ are given in Fig. 2 and clearly show this feature. This feature is absent in the case of the RDFs of liquid metals.

The co-ordination number n can be derived from the RDF as

$$n = \int_{r_0}^{r_0'} 4\pi r^2 \rho(r)\, \mathrm{d}r \qquad (9)$$

where r_0 is the value of r below which $4\pi r^2 \rho(r)$

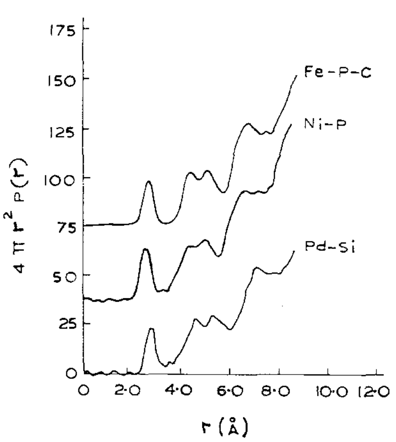

Figure 2 RDFs of amorphous $Fe_{80}P_{13}C_7$, $Ni_{81\cdot4}P_{18\cdot6}$ and $Pd_{80}Si_{20}$ showing split second peak. Zero positions vertically displaced. (After Wagner [25], Cargill [11], Crewdson [23].)

is zero and r'_0 is the position of the first minimum in the RDF. Wagner [32] has determined the co-ordination number for a few amorphous alloys. His results for the co-ordination numbers as well as the ratio r_2/r_1 where r_1 and r_2 are the first and second peak positions in the RDF are given in Table III.

TABLE III Values of r_1 and r_2 and the co-ordination number, *n*, (after Wagner [32]).

Alloy	r_1	r_2	r_2/r_1	n
$Pd_{80}Si_{20}$	2.75	4.7	1.71	11.6
$Ag_{55}Cu_{45}$	2.83	4.9	1.73	13.0
$Fe_{80}P_{13}C_7$	2.56	4.3	1.68	12.0
$Ni_{77}P_{23}$	2.55	4.27	1.68	12.5

The co-ordination number is around 12 and the ratio r_2/r_1 is very near the ideal c/a ratio (1.63) which is observed for the hexagonal close packed metallic structures. In liquid metals the ratio varies between 1.80 and 2.0.

These considerations tend to show that the arrangements in these amorphous alloys are slightly more ordered than in the liquid state. It should be noted that some amorphous alloys such as Au-Si [31] and Ni-Pt-P [16] do not show either the shoulder on the high *k* side of the second peak or the split in the second peak of the RDF.

Cargill [11] made a detailed analysis of the diffraction data from a series of amorphous alloys in the system Ni-P. He tried to explain the observed interference functions by assuming various structural models starting with hexagonal close packed layers and proceeding to models containing microcrystallites of various sizes with superimposed line-broadening effects due to strains in the microcrystals as well as due to the presence of stacking faults. He found that these models were not compatible with the experimentally observed intensity functions for these glasses. The density difference between the amorphous alloy and the same alloy after crystallization is a sensitive index of the density deficit due to the (amorphous) boundary regions between possible microcrystallites in glass. Based on density deficit considerations Cargill calculated a minimum crystallite size of $D \sim 57$ Å – which is inconsistent with the experimental intensity data.

Dixmier and Duwez [30] also discount a quasicrystalline model given by Maitrepierre [29] as a model for the structure of some Ni-Pd-P alloys. They show that a Bernal dense random packing (DRP) of atoms can account for the observed features in a few amorphous alloys of the type $(Pd_{50}\text{-}Ni_{50})_{100-x}P_x$ where x varies from 15 to 27.5.

Turnbull and Cohen [65-67] were the first to suggest that a Bernal [68-70] dense random packed structure may properly model an amorphous monatomic Van der Waals solid. Finney [71] has determined a high resolution RDF for dense random packing of hard spheres. The characteristic feature of Finney's hard sphere RDF is a split second peak. This led Cargill [41] to suggest that the Ni-P amorphous alloys may be considered to be produced due to a dense random packing of hard spheres of Ni and P atoms. However, the density of the DRP of hard spheres is about 16% less than the density of a crystalline close packed arrangement [71]. The densities of the amorphous alloys are very nearly the same as those of the alloys after crystallization; amorphous Ni-P alloys are about 1% less dense than their crystalline counterparts; this is 2.4% for the alloy $Pd_{80}Si_{20}$. This difference can be accounted for by considering models with spheres [72] which are not so hard as in Finney's model. This would imply a random mixture of the different types of atoms involved and would not explain the observed composition dependence of the formation of amorphous alloys in some systems.

Polk [73, 74] has reviewed the structural studies of amorphous alloy systems consisting of a transition metal such as Au, Pd, etc. and a metalloid such as Si, P, etc. The region of stability in these glasses is around 80 ± 5 at. % of the metal. Polk [74] showed that a DRP of the metal atoms with the metalloid atoms occupying the larger holes in the DRP structure can account for the composition dependence and the amorphous density in a rather elegant manner. The lower limit, i.e. 15 at. % of metalloid would be accounted for by the minimum number of holes which have to be filled for the amorphous structure to be stable with respect to the crystalline structure. The upper limit is imposed by the filling up of all holes which are large enough to hold metalloid atoms at about this composition.

Bennett *et al* [75] also point out that liquid alloys of the type A_3B-A_5B have large negative heats of formation. These systems (e.g. Ni-P, Pd-Si) exhibit abnormally deep eutectics at compositions near A_4B. The formation of amorphous alloys around these compositions bear out the idea of Cohen and Turnbull [76, 77] who suggested that a deep eutectic near the metallic element in a noble metal–non-metal binary system is most conducive to the formation of non-crystalline phases on rapid cooling from the molten state.

The composition ranges in splat-cooled amorphous alloys in the systems Pt-Ge, Pt-Si, Pt-Sb, Au-Si, Al-Ge and Pb-Sb do not follow these rules. These results indicate that Polk's model may not be directly applicable to all amorphous alloys. For example in amorphous alloys of the Cu-Ag system the composition range is 35 to 65 at. % of either component. In the Cu-Zr [78] system the range varies from 40 to 75 at. % Zr.

In this connection, the recent work of Simpson and Hodginson [79] is of interest. Using a bubble raft model, Simpson and Hodginson showed that amorphous assemblages near 50-50 at. % could be produced by mixing together soap bubbles of diameters differing by 10 to 15%. The diameter of the bubbles were of the order of 1mm. (i.e. corresponding to metal atoms). The RDF for the two dimensional mixtures show characteristics similar to Finney's DRP model. When the mixing was not complete, small regions were found with rather ordered arrangement of atoms. The RDFs however showed an ordered structure to higher values than the DRP RDFs.

The random packing concept with suitable modifications seems to account for the observed structure of amorphous alloys. These considerations also suggest that structure plays an important part in the formation of amorphous alloys.

Davies and Hull [13] however, contend that kinetic considerations govern whether a glass will be formed or not. This would mean that any composition could be produced in the amorphous state provided a high enough cooling rate is supplied. Chen and Turnbull [24] found that a critical cooling rate (10^2 °C sec^{-1}) was necessary for the formation of glasses in the Pd-Si system.

The electron microscope has also been used in the study of amorphous alloys. Lack of contrast in the transmission micrograph has been considered as evidence for the amorphous nature of the film [2]. Electron diffraction patterns show diffuse rings [29] for many amorphous alloys. Ruhl and co-workers [80, 81] interpret the electron diffraction patterns of some splat-cooled alloys in the Nb-Ni (42 to 46 and 52 to 67 at. % Ni) system as being due to the formation of a microcrystalline phase with an average crystallite size of about 150 atoms. This is also the case in the system Ta-Ni (33 to 45 at. % Ni). It is difficult, however, to consider a "crystalline" region consisting of 5 to 7 atoms on edge (i.e. 2 to 3 unit cells) when the essence of crystallinity is long range order. It would therefore seem that the phases obtained by Ruhl *et al* can also be properly termed amorphous alloys [12]. Giessen and Wagner [27] contend that in the case of metallic glasses the criterion of a 10 Å resolution achievable in transmission electron microscopy will not be admissible due to the overlap of microcrystalline regions if any in the glass. It is interesting to note that Revcolevschi and Grant [82] studied a splat-cooled amorphous alloy of copper containing 40 at. % Zr using high resolution electron microscopy and were unable to detect any contrast in the as-splatted condition. However, heating of the sample gave rise to nucleation and crystallization which could be followed.

Hence, it seems that the metallic glasses can be properly called amorphous and can be described by a dense random packing type of structure. The formation and range of stability of glassy alloys such as Pd-Si, Pd-Ni-P, Fe-P-C etc. seem to depend on structural considerations [83] subject to a minimum cooling rate from the liquid state. The binary alloys Pd-Si, Pd-P, Fe-P, Fe-C, Ni-P etc. exhibit stable intermetallic phases near the glass forming compositions and exhibit deep eutectics in the same range. The crystalline phases exhibit a tetradecahedral arrangement. Owing to the strong bonding between the metal and metalloid atoms, the short range order may be expected to be preserved in the liquid and in the splat-cooled alloys. Glassy alloys such as Au-Si [31] and Pt-Ni-P [16] do not show either the split second peak in the RDF or a shoulder on the high k side of the intensity curve. Sinha and Duwez [16] interpreted this as being due to a greater degree of disorder in these glassy alloys. Chen and Park [84] point out that Au-Si is a purely eutectic system with no intermetallic compound. A metastable γ phase was formed on crystallization of the amorphous Au-Si alloy. The γ phase is similar in structure to γ-brass with Si atoms located substitutionally. The same short range order seems to persist into the liquid state. In the case of Pt-P system, a miscibility gap is exhibited in the liquid state in the composition range 26 to 52 at.% P. This is in strong contrast with the strong binding between the metal and metalloid atoms in the tetradecahedral structures.

The partial molar volumes of Cu and Si in glassy Pd-Cu-Si alloys are approximately equal and about 15% smaller than that of Pd [84]. However, the Si content alone determines the glass forming region. The addition of Cu as well as Ag, Au, Ni, Co and Fe stabilized the glass phase but had little effect on its initial formation. Similar considerations hold for the roles of P and the transition metals in the systems Pd-Ni-P, Pd-Fe-P and Pt-Ni-P, This shows that chemical bonding is also an important factor in the formation and stability of amorphous alloys.

6. Conclusion

The structure of metallic glasses can be best explained by a dense random packing model or modifications thereof. The formation and range of stability of the amorphous alloys seem to be mainly dependent on structural considerations such as relative atomic sizes and the bonding between the atoms in the amorphous alloys. It is not yet known how dominant the role of kinetic considerations is in the formation of amorphous alloys.

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