CHAPTER I

INTRODUCTION

1.1 INTRODUCTION

There have been many scientific and technological breakthroughs in the field of Rapid Solidification of metallic alloys during the last two decades. As a result, the amorphous metallic alloys or the so-called metallic glasses have emerged as a new class of materials which has fascinated the materials scientists and the solid state physicists who channelised their research activities in understanding the various aspects of this hitherto unknown materials which appear to have potential technological applications.

A landmark in the history of rapid solidification was set by Prof. Duwez and his coworkers /1,2/ in 1960 when they, for the first time reported the formation of an amorphous metallic alloy by rapid quenching of a liquid Au-Si alloy to liquid nitrogen temperature. This discovery heralded the era of metallic glasses. Prior to this, amorphous metals had been prepared by other methods such as vapor deposition and electrodeposition /3,4/. Another remarkable scientific achievement of the Duwez group is related to the synthesis and production of ferromagnetic glassy alloys during 1966-1970. Tsuei and Duwez /5/ in 1966 and Duwez and Lin /6/ in 1967 found ferromagnetism in alloys of compositions Pd_{68}Co_{12}Si_{2}, Pd_{75}Fe_{5}Si_{20} and Fe_{83}P_{10}C_{7}. It was during this time that the potential for the possible industrial applications of metallic glasses was realized by the scientific community which led to a rapid advancement in the technique of rapid quenching. Once the interesting soft magnetic properties of the ferrous metallic glasses were discovered, a technological breakthrough in the production methods of the amorphous alloys on a commercial scale became inevitable. And this was realized at the beginning of seventies when the planar flow casting technique was invented to produce amorphous metals of sufficient width in a continuous operation /7,8/. The availability of the amorphous alloys drew the attention of many scientists who initiated research activities with a view to understanding the structure and physical, chemical, magnetic, mechanical and electrical properties of
these amorphous alloys by the application of a variety of experimental techniques. Besides an appreciable quantum of experimental work done so far, many attempts have been made to explain the structure of these amorphous alloys in terms of various models [9-14]. Moreover, many interesting properties of amorphous alloys were discovered in the seventies which also witnessed a growing interest in this new class of materials as became evident by a manifold increase in the number of research contributions. Another significant achievement has been the commercial availability of the amorphous alloys which were patented by such trade names as: METGLAS (Allied Corporation, USA), AMOMET (Japan), VITROVAC (Vakuumschmelze, FRG).

So far we have briefly traced the historical development of the amorphous metallic alloys. These amorphous alloys constitute a new class of materials and possess a variety of desirable properties some of which are even superior to their crystalline counterparts. These properties are determined by their atomic arrangements and are very sensitive to heat treatment leading to rearrangements of atoms in them. All processes which involve atomic rearrangement are controlled by the diffusion of atoms. Therefore, we shall briefly discuss in the following section some important aspects of metallic glasses which are also important from the point of view of understanding the atomic diffusion processes in them. In a later section some important points relating to the object of this study are discussed.

1.2 METALLIC GLASSES

Metallic glasses are non-crystalline or amorphous solids lacking the long-range periodicity of the atomic arrangement and are obtained by the rapid quenching of metallic melts. In contrast to the insulating oxide glasses, they are opaque, more densely packed and the interatomic bonding between them is essentially metallic in character. However, they do exhibit such properties as structural relaxation, a glass transition and crystallization which are commonly observed in nonmetallic glasses. In short, the metallic glasses may be considered to be solids with the liquid structure frozen in. A casual inspection would not differentiate between a metallic glass and a common metal,
however, the glassy nature of the former can be confirmed by observing a few diffuse halos in its X-ray, electron or neutron diffraction pattern.

1.2.1 Liquid-Glass Transition

A liquid of a single component system solidifies into a crystalline product when cooled below its melting temperature $T_m$. However, if by non-equilibrium cooling this step is suppressed, the liquid is supercooled into a glass. Fig.1.1 shows the typical plots of viscosity $\eta$, volume $V$ and internal energy $H$ for such a transformation /15/. As shown in Fig.1.1 these properties change discontinuously upon crystallization, but change rapidly and continuously with temperature as the liquid undergoes a transition into the glassy phase. At sufficient undercooling, $\eta$ becomes very large and consequently at such a high viscosity, atomic motions are retarded and relaxation times for atomic rearrangement become comparable to or greater than the time taken for experimental measurements. Therefore, spatial atomic configuration remains virtually unaltered during liquid-glass transition. The temperature $T_g$ that marks the transition from equilibrium to frozen-in non-equilibrium or iso-configurational structure is known as the glass transition temperature. This glass transition temperature $T_g$ of an alloy is not a unique parameter, but depends on the cooling rate. The higher the cooling rate ($q_1 > q_2$), the higher is the value of $T_g$ ($T_g1 > T_g2$). Upon subsequent heating at a rate slower than either $q_1$ or $q_2$, the glass tends to relax structurally to a more stable glassy state at temperatures far below $T_g$ as indicated by a dashed line in Fig.1.1(b). Annealing at elevated temperatures can also lead to the crystallization of a glass. This can be observed by performing a continuous heating experiment with a constant heating rate using a differential scanning calorimeter (DSC). The technique of DSC is used to determine $T_g$ and $T_x$, the temperature at which glass begins to crystallize as shown in a typical DSC thermogram in Fig.1.2. There can be a single or multiple exothermic peaks ($T_{x1}, T_{x2}$ as shown in Fig.1.2) demonstrating that the crystallization of the supercooled liquid into the equilibrium crystalline structures can involve number of transformation events. $T_g$ is determined by observing an endothermic effect over a small temperature interval. In cases where $T_g > T_x$, the glass crystallizes directly.
Fig. 1.1. Schematic drawings of the temperature dependence of (a) viscosity $\eta$ and (b) specific volume $V$ and heat content $H$ in a glassy alloy.

Fig. 1.2 A typical DSC thermogram showing glass transition temperature $T_g$ and crystallization temperature $T_x$. 
Besides formation of glass, such structural modifications in alloys as the extension of solid solubility, the formation of grains and the refinement of grain size of the solidified alloys and formation of metastable crystalline phases are also observed as a result of rapid solidification. This is determined by the degree of undercooling which is a function of several factors like the initial viscosity, the rate of increase of viscosity with undercooling, the volume density and efficiency of heterogeneously nucleating particles, the imposed cooling rate etc. /15/.

1.2.2 Glass Forming Ability (GFA)

The glass forming ability of metallic alloys (GFA) is a measure of the tendency of glass formation from their melts. The criteria for glass formation have been categorised as structural and kinetic. The structural criterion deals with geometric atomic arrangements, bonding and atomic size effects /16/ while the kinetic criterion considers the rate of cooling relative to the kinetics of crystallization /17/. In fact, these two criteria are complimentary.

Among the kinetic criteria, a simple parameter that has been found especially useful for expressing GFA is the reduced glass transition temperature, $T_{\text{gr}} = T_g/T_L$, the ratio of the glass transition temperature to the liquidus temperature. High values of $T_{\text{gr}}$ favour glass formation and $T_{\text{gr}} > 0.45$ for known glass-forming alloys. Chen and Jackson /18/ by drawing the time-temperature-transformation diagram (TTT curve) as given in Fig.1.3 showed that the critical cooling rate $\dot{T_c}$ for glass formation is the cooling rate necessary to bypass the 'nose' of the TTT curve and is given by

$$\dot{T_c} = (T_1 - T_N)/t_N. \quad (1.1)$$

where $T_N$ and $t_N$ are the coordinates of the nose in the TTT diagram. Typically, $\dot{T_c}$ varies from $10^{10}$ K/s for pure metals such as W to $10^2$ K/s for easy glass forming alloys such as Pd-Cu-Si and has intermediate values $\approx 10^6$ K/s for average glass formers such as Au-Si, the corresponding reduced glass temperatures being 0.25, 0.66 and 0.5 respectively. It was further pointed out by Donald and Daviss /19/ that a high cooling rate
Fig. 1.3. Schematic TTT diagram for crystal growth in an undercooled melt, showing (a) fast cooling to form a glass (b) isothermal heat treatment of the glass at a temperature $T > T_x$ giving crystallization at time $t_x$ and (c) slow heating of the glass producing crystallization at $T_x$.

Fig. 1.4. Phase diagrams of (a) Fe-B, and (b) Zr-Ni systems. Glass Forming range is indicated at the bottom of the diagrams by the hatched regions.
as well as a small cooling increment \((T_1 - T_g)\) are required for glass formation. This emphasizes the necessity of a low liquidus temperature of the glass forming alloys.

All the glass forming alloys show strong interaction between constituent atoms as indicated by a negative heat of mixing \((\Delta H_m)\), and relatively low melting temperatures \(T_m\). This is commonly manifested by the formation of intermetallic phases of the \(A_2B\), \(A_3B\) or \(AB\) type in an alloy \(A-B\), which participate in relatively low melting eutectic reactions. \(T_E/T_m \approx 0.6\) for these glass forming alloys compared to \(T_E/T_m \approx 0.8\) for normal eutectic systems, \(T_E\) and \(T_m\) are the eutectic temperature and the melting temperature of the major element \(A\). Marcus and Turnbull /20/ defined a reduced liquidus temperature

\[
\Delta T_{lr} = \frac{(T_1^o - T_1)}{T_1} \tag{1.2}
\]

where \(\Delta T_{lr}\) measures the departure of the liquidus temperature \(T_1\) from the ideal solution (enthalpy of formation \(\Delta H = 0\)) liquidus temperature \(T_1^o\) which is estimated from the heat of fusion and melting temperature of the solvent and the concentration of the solute. Increasing positive values of \(\Delta T_{lr}\) indicate increasing ease of glass formation. This criterion fails for glass formers such as Nb-Ni or Cu-Zr, so Donald and Davies /19/ suggested the use of the departure of alloy liquidus temperature \(T_1\) from the rule of mixtures liquidus temperature,

\[
\Delta T_{lr}^o = \frac{(\bar{T}_m - T_1)}{T_m} \tag{1.3}
\]

where \(\bar{T}_m\) is the weighted average of the melting point of the components

\[
\bar{T}_m = T_m^A c_A + T_m^B c_B \tag{1.4}
\]

It was found that a value of \(T_{lr}^o = 0.2\) separates glass forming and non-glass forming systems.

From a large number of data compiled by Mader et al. /21/, it appears that a minimum atomic size difference of at least 10% is necessary to stabilize a metallic glass. More specifically, an appreciable size difference \((r_A/r_B < 0.88\ or > 1.12)\) between the components in the glassy alloy is a necessary requirement for ready glass formation. However, even in systems with an unfavourable size ratio (e.g. Pd-Si)
very stable glasses have been produced. So, the effect of size factor still remains inconclusive.

Based on a nearly free-electron solid model of a glass, Nagel and Tauc /22/ predicted that the glass phase should be relatively more stable at the compositions where the Fermi level is at a minimum in the density of states, and the Fermi vector $2K_F$ is equal to the wave vector of the first peak in the static structure factor, i.e.,

$$|\mathbf{Q}_p| = 2|\mathbf{K}_F|$$

(1.5)

This criterion also does not make any universal predictions. It was further suggested by Chen /18,23/ that the destabilization of the crystalline mixture near the eutectic composition determined the stability of the amorphous phase. The eutectic composition and the glass-forming region appear to be determined by the relative magnitude of $\Delta G$, the free energy difference, of the competing crystalline and liquid phases.

So far we have discussed various factors which can decide on the GFA of alloys. However, there does not exist a theory of glass-formation in metallic alloys which can make universal predictions. A classification, of the alloy systems that form metallic glasses, based on the chemical classification of constituents is given in Table 1.1. The phase diagrams of Fe-B (metal-metalloid) and Zr-Ni (metal-metal) systems are shown in Fig.1.4. It is clear that the glass forming composition range (as given in TABLE 1.1) in these systems lie near the eutectic composition.

Besides binary metallic glasses, ternary and multicomponent glasses such as Pd-Cu-Si, Fe-Ni-P-B have also been prepared. The admixture of glass forming binary alloys or the addition of third elements, which have different atomic radii and different crystalline intermetallic compound symmetry, enhance drastically both the stability and the glass-forming ability (GFA), mainly due to the lowering of the eutectic temperature.
TABLE 1.1 Classification of glass-forming alloys

<table>
<thead>
<tr>
<th>Class</th>
<th>Systems</th>
<th>Typical composition range (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T₂(or noble)-M (metal-metalloid)</td>
<td>Pd-Si, Fe-B Co-P, Au-Si, etc.</td>
<td>15-25M</td>
</tr>
<tr>
<td>T₁-T₂ (or Cu) (metal-metal)</td>
<td>Zr-Ni, Ti-Ni Zr-Cu Nb-Ni</td>
<td>30-40T₂ 30-65Cu 40-65Ni</td>
</tr>
<tr>
<td>A-B</td>
<td>Mg-Zn</td>
<td>25-35Zn</td>
</tr>
<tr>
<td>T₁- A</td>
<td>(Ti-Zr)-Be</td>
<td>20-60Be</td>
</tr>
<tr>
<td>Actinide- T₁</td>
<td>U-V, U-Cr</td>
<td>20-40T₁</td>
</tr>
<tr>
<td>T₂- R</td>
<td>Co-Gd</td>
<td>≈20Gd</td>
</tr>
</tbody>
</table>

A= Li, Mg metal groups; T₁= early transition metal (Sc, Ti, V groups);
T₂= late transition metal (Mn, Fe, Co, Ni groups); B=Cu, Zn, Al groups,
M= Metalloids B, C, Si, P, Ge; R= rare-earth metal.

1.2.3 Techniques of Glass Formation

Most metallic glasses are produced at a relatively high cooling rate of 10⁵ K/s or higher which is achieved by spreading a thin layer of liquid in good contact with a highly conductive substrate. We shall briefly describe below the various methods of glass formation.

Past Liquid Quenching Techniques

These include the so-called 'gun' technique, 'piston and anvil technique' and melt-spinning. In the 'gun' technique a small liquid alloy globule is propelled into small droplets by means of a shock tube and the droplets are sprayed into thin foil on a copper substrate (Fig. 1.5a). The disadvantages of the 'gun' technique, i.e., the non-uniformity in thickness and irregular shapes of quenched specimens could be overcome by the development of 'piston and anvil' technique. In the 'piston and anvil' technique a freely-falling droplet is caught and squeezed between a stationary anvil and a moving piston resulting in the production of a
Fig. 1.5. Schematic drawing of various glass formation techniques (a) gun technique, (b) piston and anvil technique and (c) melt spinning technique.
uniform disc of solid material (Fig. 1.5b).

The most commonly employed technique for continuous production of metallic glasses is melt-spinning /8,24/. This involves the ejection of a stream of liquid on to a rotating substrate on which a molten puddle is formed (Fig. 1.5c). The lowermost layer of the puddle first gets solidified. When this layer moves forward its thickness progressively increases, till it leaves the puddle and then gets thrown off from the wheel by the centrifugal force. The thickness of the ribbon formed depends on the length of the puddle, linear velocity of the wheel rim and the rate of increase of the viscosity of the liquid with undercooling. The ribbon gets cooled at a faster rate on the wheel side (the side touching the wheel) compared to the air side (side exposed to air). Depending on the formation parameters the ribbon formed may be either partially or fully amorphous. In the case of a partially amorphous ribbon, the volume density of crystalline phase increases from wheel side to air side. Ribbons, \( \sim 50 \mu m \) thick and \( \sim 10 mm \) wide, have been successfully produced in the author's laboratory. Zr-based metallic glasses studied in this work were produced by this technique.

Electrolytic and Vapour Deposition

Electrolytic and vapour deposition techniques have been used much earlier to produce amorphous metals /3,4/. A number of nominally pure metallic elements, particularly high melting transition metals, have been produced in amorphous solid films by evaporation or sputtering on to a substrate at very low temperatures. However, the stability of the amorphous films is seen to be very sensitive to deposition conditions. These techniques have been used to produce a number of amorphous alloys Cu-Ag, Co-Au /21/ by co-evaporation and Ni-B by electrodeposition /25/.

Irradiation

Amorphization can also be achieved by irradiation of the crystalline material by neutrons, protons, deuterons, \( \alpha \)-particle, fission fragments etc. Amorphous alloy layers have also been produced by ion-implantation method /26/. A metallic glass can be formed on surfaces by
a laser beam (laser glazing). A detailed survey on various fabrication methods is given in references /27,88/.

1.2.4 Structure and Defects

X-ray, electron and neutron diffraction methods have mostly been used to characterize the structure of the metallic glasses. The Fourier transform of the scattered intensity is related to the radial distribution function (DRF) \( 4\pi r^2 \hat{\rho}(r) \), which represents the average number of atoms in a spherical shell of radius \( r \) and thickness unity and \( \rho(r) \) is the radial density function. Another important function commonly used in structure studies is the interference function \( I(k) \) which is the ratio of the measured scattered radiation from \( N \) atoms \( I_N(k) \) over the mean square of the scattering factors, namely

\[
I(k) = I_N(k) / \left[ N \left| f(k) \right|^2 \right] \quad (1.6)
\]

with \( k = 4\pi \sin \Theta / \lambda \) being the magnitude of the scattering vector. Other commonly used functions on structure determination are the reduced radial distribution function \( G(r) \) and the reduced interference function \( P(k) \), and the pair distribution function \( g(r) \) which are related by

\[
G(r) = 4\pi r \left[ \rho(r) - \rho_o \right] \\
P(k) = k \left[ I(k) - 1 \right] \\
g(r) = \frac{2}{\pi} \int F(k) \sin k r \, dk \\
g(r) = \frac{\rho(r)}{\rho_o} \\
\rho_o \quad \text{is the average atomic density of the glass.}
\]

The average atomic distributions in the gas, liquid, amorphous and crystal states as reflected in their respective pair distribution functions \( g(r) \) are shown schematically in Fig.1.6, where \( a_o \) represents the atomic hard core diameter. The atomic distributions in the amorphous state resemble more closely to that in the liquid state. In both the liquid and the amorphous states the atoms are randomly distributed in a nearly close-packed structure, with a short mean free path, comparable with the atomic size; the coordination number of nearest neighbour atoms
Fig. 1.6. Schematic diagrams of pair probability functions $g(r)$ in the gas, liquid, amorphous and crystal states.

Fig. 1.7. Radial distribution function (RDF), reduced radial distribution function $G(r)$, and pair distribution function of an amorphous $\text{Fe}_{80}\text{B}_{20}$ alloy.
is about 11 in both cases. However, the average atomic configurations in
the liquid state are more homogeneous than those in the amorphous state
when averaged over time and space because of the relatively high atomic
mobility in liquids. This means that the atomic configurations in the
amorphous state are more rigid compared with those in the liquid state.

The RDF, G(r) and g(r) of an amorphous Fe_{80}B_{20} alloy are illus-
trated in Fig.1.7. The general features of the structure of the
amorphous metals as observed from these plots are similar to those of
the liquid except a splitting in the second peak in case of the former.
The ratio (r_2/r_1) of the position of the first peak (r_1) to that of the
second peak (r_2) in the amorphous state is nearly equal to the constant
value of about 1.67. This is close to the mean value between the c/a
ratio in close-packed hexagonal structure (i.e. c/a = 1.63) and the
ratio of the third atomic shell radius to the nearest neighbour distance
in fcc structure (i.e. r/T = 1.73). This implies that the short range order
of the near neighbors in the amorphous state is affected more or less by
the atomic arrangement of crystalline state. However, from the similarity
of the gross features of G(r) and g(r), the basic configuration of atoms
seems to be liquid-like. Such investigations have led to the following
conclusions on the structure of metallic glasses:

(i) It is a homogeneous, but disordered structure. i.e., there exists
short-range topological order in a metallic glass, but no long range
order as observed in the corresponding crystal.

(ii) It is a densely packed structure having packing density comparable
to that in a crystalline structure. The first metallic coordination
number varies from 10 to 13 depending on the system.

(iii) Nonmetallic atoms (in metal-metalloid glasses) have about 9
metallic neighbours.

(iv) The smaller metalloid atoms in metal-metalloid (M-Me) glasses do not
come into direct hard sphere contact while in metal-metal (M-M) alloys
metal atoms are distributed more or less randomly. This may be partly
explained due to the relatively hard core of d shell of transition
metals and partly due to the weaker interatomic interactions in the
metal-metal system which favour random mixing. Moreover, the much
softer s-p type bonding of metalloid atoms facilitates preferred bonding among metal and metalloids /30/.

(v) Interatomic distances are not those found in fcc or hcp structures, except the first one. Significantly, \( \sqrt{2} \) atomic distance characteristic of octahedral sites in close-packed crystalline fcc and hcp structures is missing.

**Structural Models**

Based on such observations from diffraction studies, various structural models have been proposed: (i) continuous-random, (ii) microcrystalline, and (iii) amorphous cluster models. The application of any of these models to describe the structure of an amorphous system depends on how 'best' it can reproduce the experimentally observed diffraction data.

The first approach is similar to that of Bernal who first gave a model of randomly packed hard spheres to explain the structure of liquids /31/. The dense random packing has been established either by physical construction of a large number of equal steel balls /12,32-33/, computer algorithms, or theoretical calculations /34-35/. Different polyhedra which constitute a dense random packing of hard spheres (DRHS) are shown in Fig.1.8. The DRHS model leads to a structure that maximizes the local density. The packing fraction of the steel-ball model /12/ is 0.637 which is less than the value of 0.741 for fcc or ideal hcp close packing. The metallic glass structure resembles a close packing of tetrahedra. All these models yield the splitting of the second peak of \( G(r) \) as shown in Fig.1.7. However, the relative intensities of the two components of the split second peak are reversed and their relative positions \( r_2/r_1 \) and \( r'_2/r_1 \) are larger. This discrepancy between the model and experimental data may be eliminated either by relaxing the computer-built or physically constructed models /36-37/.

It has been further shown by diffraction experiments /38/ and extended X-ray absorption fine structure (EXAFS) measurements /39/ that a chemical short range order exists in metallic glasses. Gaskell /40/ has proposed that structural models for metal-metalloid glasses should be based on the random stacking of larger structural units such as trigonal
Fig. I.8.(a) Idealized polyhedral holes present in Bernal's DRPHS topology.

Fig. I.8(b) Regular trigonal prismatic coordination polyhedron (as used by Gaskell)
prismatic units instead of single atoms. This was done in case of \( \text{Pd}_{80}\text{Si}_{20} \) and a continuous random structural model was constructed by choosing a ten atom unit consisting of central Si atom and its nine Pd neighbours in the form of a capped trigonal prism.

It has been suggested that some amorphous alloys have a microcrystalline structure /41,42/. Microcrystalline models propose a heterogeneous structure in which misoriented crystallites containing several atoms are separated by regions of noncrystalline material /43,44/. However, an unambiguous differentiation between a fully amorphous and a microcrystalline metal is not possible from diffraction experiments because of the line broadening effect which occurs as the crystals become progressively smaller, i.e., a metal with a grain size of 8 to 16\( \mu \) would have a first peak width typical of that observed for amorphous metals /45/.

Amorphous cluster models constitute another type of heterogeneous structural models, based on noncrystallographic but highly ordered low energy atomic clusters as the structural units. Hoare /46/ and Briant /47/ have proposed that low energy, non-crystallographic clusters may be important as structural units in some amorphous metals or alloys. However, microcrystalline and amorphous cluster models suffer from a drawback that the interconnecting configurations at the boundaries and the crystallite orientations are not described. On the contrary, the continuous random models are homogeneous. All these structural models are determined by sophisticated computation methods using computer simulation techniques, molecular dynamics or Monte Carlo methods /48-50/.

Qualitatively, the DRPHS structural models yield a \( g(r) \) in good agreement with the experimental data for amorphous metals and many typical metal-metalloid glasses such as Pd-Si, Ni-P and Fe-P /12,51,52/. However, the agreement between the model and experimental distribution functions for Fe-B alloys is relatively poor /52/ (see Fig.1.9). The structural models based on DRPHS give only a poor description of the experimental diffraction patterns in case of metal-metal glasses showing several features that are indicative of a relatively high degree of short range
Fig. 1.9. A comparison of the structures of (a) Ni$_{76}$P$_{24}$/51/, and (b) Fe$_{84}$B$_{16}$/ amorphous alloys.
order as observed in case of Nb-Ni, Ta-Ni, Cu-Ti /41,53/. A structural model for amorphous intertransition metal alloys based on a random stacking of the typical co-ordination polyhedra (icosahedra and Frank-Kasper polyhedra) was proposed by Wang /54/.

Defects

So far we have briefly discussed the various structural models of amorphous alloys. Now the question arises: What kind of defects exist in an amorphous metallic alloy? A definite answer to this question is still elusive. However, the positron annihilation experiments have shown that (i) amorphous alloys do not contain many 'open spaces' larger than the atomic volume /55/, and (ii) plastic deformation, e.g., cold-rolling induces neither vacancy-like defects nor highly localized atomic defects /56/.

A theoretical approach to the study of defects in amorphous systems is to introduce defects similar to crystalline point or line defects in highly ordered structural models and to observe their evolution and stability. Such studies have indicated that vacancies are not stable in an amorphous system /57,58/. Dislocation like defects have been postulated to explain the sharp bands that occur during plastic deformation at high stresses and low temperatures /59,60/. However, there is no direct evidence available for their occurrence.

With the present knowledge of defects in amorphous alloys, it can only be stated that defects in amorphous systems differ in many ways from those in crystals. Both point and line defects seem to be more delocalized or diffuse in amorphous systems. Another classification has been made for the defects in amorphous systems based on local fluctuations in the short-range order (SRO). Depending on the property that is used to characterize the SRO, the fluctuations can be characterized in different ways /61/. This approach is used to characterize the transport properties of liquids and polymers. The basic feature in a diffusive atomic rearrangement is a change of nearest neighbours. This is accomplished by vacancies in crystals, but in amorphous systems it can be assumed to occur by a 'diffusion defect' based on free-volume fluctuation model.
This model, developed by Turnbull and Cohen /62/ is based on a specific 
atomic mechanism for defect rearrangement. The average atomic free 
volume \( V_f \) of a system is defined as the difference between its average 
atomic volume \( V \) and the average atomic volume of dense random packing (DRP). 
It is assumed that the free volume can be redistributed among all the atoms 
without changing the energy of the system. If the local free volume of an 
atom becomes larger than some critical value \( V^* \), the atom can escape from 
its nearest neighbour 'cage' and perform a diffusive or shear flow jump, 
thus giving rise to 'diffusion' or 'flow' defects. The critical free 
volume \( V^* \), is roughly equal to the volume of the metal ion \( x_0 \). Although 
the original formulation of the free volume model involved only a single 
atom jump, it can be generalized to involve the motion of several atoms, 
contained in a local defect volume say \( V_0 \). When the enough free volume is 
collected in \( V_0 \), the atom can undergo a shear transformation under the 
action of a stress. Another important feature of these defects is their 
annihilation. The annihilation of these defects or the 'extra free volume' 
is important during structural relaxation in the glassy state, where the 
system contains a nonequilibrium amount of free volume which is continually 
being annihilated until metastable equilibrium is reached. Hence, a 
'relaxation defect' can be visualized in an amorphous system and it can be 
any site in the amorphous system which, upon rearrangement of atoms after 
a free volume fluctuation, moves at least part of this volume elastically 
out to the specimen boundary. This distinction made above between 
'diffusion', 'flow' and 'relaxation' defects is helpful in providing a 
qualitative explanation for possible difference in the respective atomic 
transport properties.

We have very briefly brought out some salient features concerning 
the structure of amorphous alloys and possible defects in these 
materials. A more detailed account on this subject can be found in many 
excellent reviews available in literature /61,63-69/.

1.2.5 Properties

A general comparison of the characteristic properties of metals, 
metallic glasses and oxide glasses /79/ is presented in TABLE 1.2.
Metallic glasses display unusual combination of physical, mechanical, magnetic and chemical properties which often make them superior to their crystalline counterparts. A few important properties will be briefly mentioned in the following paragraphs.

<table>
<thead>
<tr>
<th>Property</th>
<th>Traditional Metal</th>
<th>Traditional Glass</th>
<th>Metallic Glass</th>
</tr>
</thead>
<tbody>
<tr>
<td>structure</td>
<td>crystalline</td>
<td>amorphous</td>
<td>amorphous</td>
</tr>
<tr>
<td>bonding</td>
<td>metallic</td>
<td>covalent</td>
<td>metallic</td>
</tr>
<tr>
<td>yield stress</td>
<td>non-ideal</td>
<td>almost ideal</td>
<td>almost ideal</td>
</tr>
<tr>
<td>workability</td>
<td>good, ductile</td>
<td>poor, brittle</td>
<td>good, ductile</td>
</tr>
<tr>
<td>hardness</td>
<td>low to high</td>
<td>very high</td>
<td>very high</td>
</tr>
<tr>
<td>UTS</td>
<td>low to high</td>
<td>low</td>
<td>high to very-high</td>
</tr>
<tr>
<td>Optical transmission</td>
<td>opaque</td>
<td>transparent</td>
<td>opaque</td>
</tr>
<tr>
<td>thermal conductivity</td>
<td>very good</td>
<td>poor</td>
<td>very good</td>
</tr>
<tr>
<td>resistance</td>
<td>very low</td>
<td>high</td>
<td>very low</td>
</tr>
<tr>
<td>corrosion resistance</td>
<td>poor to good</td>
<td>very good</td>
<td>very good</td>
</tr>
<tr>
<td>magnetic properties</td>
<td>various</td>
<td>non-existent</td>
<td>various</td>
</tr>
</tbody>
</table>

The density of metallic glasses is only 1 to 2% less than that of the corresponding crystalline alloys which is in strong contrast to the large change of 10% in non-metallic materials. The Young's modulus and shear stiffness of quenched metallic glasses are generally lower by 20 to 40%, but the bulk modulus by ~7% than in the crystalline state. Amorphous metals are capable of undergoing extensive plastic flow without hardening and, in addition, this deformation is often accompanied by the formation and propagation of shear bands. The fracture strength $\sigma_f$ in metallic glasses approaches the theoretical strength apparently because of the absence of translational periodicity and line defects, e.g., some Fe-based glasses have $\sigma_f \sim 350 \text{Kg/mm}^2$ exceeding that of high strength steels.
Because of the absence of crystalline symmetry, metallic glasses are mechanically strong and hard but are magnetically soft (glasses containing ferromagnetic elements) implying that they can be easily magnetized and demagnetized /70,71/. The ease of magnetization indicates the presence of a relatively homogeneous structure. The small coercivity of amorphous metals combined with their high resistivity causes low magnetic power losses when applied in alternating devices, such as transformers. A good account of magnetic behaviour of metallic glasses is given in reference /72/. The high degree of atomic disorder causes a high electrical resistivity ($>10^4 \ \Omega \cdot cm.$) which has a very small temperature coefficient and can be positive, negative or even zero, depending upon the composition chosen. The high corrosion resistance and electrochemical behaviour of some amorphous alloys is remarkable /73/. In particular, amorphous alloys containing chromium possess very high corrosion resistance in both neutral and acid solutions.

We have briefly outlined above the properties of metallic glasses. However, there are many review articles /74-80/ which provide a good description of their nature and properties.

1.2.6 Effects of Heat Treatments on Metallic Glasses

Metallic glasses can be called as super cooled liquids and possess one-half to two-third of the heat of fusion of the liquid phase /77/. This stored energy is given out during structural transformations of a glass by thermally activated atomic movements. Hence, this stored energy in the glassy state is one of the factors affecting the thermal stability of metallic glasses, which in turn is dependent on the glass forming ability (GFA) of the alloy. The two important structural changes which can occur during the heat treatment of the metallic glass are structural relaxation and crystallization.

1.2.6.1 Structural Relaxation

A metallic glass, as ordinarily prepared is not in an internal equilibrium state and relaxes structurally to the latter whenever atoms attain an appreciable mobility as indicated by line L-d in Fig.1.1(t)
depicting the plot of specific volume or enthalpy of the glass versus the temperature. As prepared glasses have an excess enthalpy and volume as compared with those of the corresponding equilibrium glassy states that can be obtained by annealing near $T_g$ or by slow cooling /75/.

In general, the properties of glasses may be considered to be a function of the excess enthalpy during isothermal annealing over the temperature range below $T_g$. It has been observed that many physical properties (atomic diffusivity, mechanical ductility and magnetic anisotropy in particular) alter drastically with structural relaxation /81-83,113/.

A detectable structural change occurs when the time constant $\tau$ for atomic rearrangement is comparable to the corresponding experimental time constant as given by:

$$t_{\text{mea}} = \frac{(kT_g^2 \dot{\phi} \rho_a)}{Q_a} \sim \tau_{\text{mea}}$$

(1.11)

where $Q_a$ is the apparent activation energy for structural relaxation of the supercooled liquid and $\dot{\phi}$ denotes the cooling or heating rate. If a glass is held at a temperature in the region of glass transition, its structure will relax towards that of the 'perfect' or equilibrium glass. The total change in properties during relaxation in reasonable times is largest at some intermediate temperature. At high temperatures near $T_g$, the kinetics of stabilization of the glass are rapid, but the initial departure from equilibrium is small, and hence the total change in properties is also small. At low temperatures, the initial departure from equilibrium is large, but the kinetics of relaxation are slow, and in reasonable times, only little relaxation is observed.

It was shown by Egami /84/ that two types of changes occur during relaxation: (i) topological short range order (TSRO) and (ii) chemical short range order (CSRO). TSRO refers to geometrical packing, and increases when packing becomes denser and so it seems to be a highly collective phenomenon. CSRO refers to the probability of finding chemically unlike nearest atomic species. This approach has been used to
explain the relaxation behaviour of metallic glasses.

The structural relaxation may be studied by all methods allowing measurements of the structure-sensitive properties of solids. A few of these methods are based on measurements of internal friction /85/, stress relaxation and creep /86,87/, specific heat /88/, magnetic annealing /89/, electrical resistivity /90/, sound velocity changes /91/, microhardness /92/ and diffusivity /93/.

1.2.6.2 Crystallization

Amorphous to crystalline transformation generally occurs on thermal annealing of the glass. The crystallization of metallic glass is accompanied by a densification of about one percent, a decrease in enthalpy equivalent to about one half the latent heat of melting (\(<\sim \text{ a few } \text{kJ/mol}\)) and significant changes in most physical properties. The process of crystallization involves nucleation and growth of crystalline phase. A number of reviews have appeared in literature on crystallization of metallic glasses /94-96/.

There are various methods to study amorphous to crystalline phase transformation. Due to the large heat effect of crystallization, the process can be conveniently followed by DSC while complimentary structural investigations are needed using microscopic studies (TEM, SEM) and diffraction technique. In addition, methods involving physical property measurements like electrical resistivity, Mossbauer spectroscopy can also be used for following the changes occurring during crystallization.

The study of crystallization processes is important because of two reasons (i) crystallization results in a change or loss of many desirable properties and this limits the operating times at elevated temperatures, and (ii) secondly, it is becoming increasingly clear that the partial or full crystallization of metallic glasses can be used to produce novel and useful microstructures unobtainable by other means.

A useful parameter which indicates crystallization of the glass is its crystallization temperature $T_x$, usually measured at a practical heating rate (5-50 K/min) in a differential scanning calorimeter. However, this is not an indicator of the upper limit of operating temperatures of a
metallic glass because during long-term operation at temperatures much lower than this, the glass may crystallize. Fig. 10(a) and (b) depict the phase diagrams and variation of $T_x$ of Fe-B (metal-metalloid) and Zr-Ni (metal-metal) glasses. It can be seen that in many binary metal-metalloid glasses $T_x$ is a maximum near the equilibrium eutectic composition while it monotonically decreases with increasing zirconium content in metal-metal glass (Ni-Zr) despite the existence of two eutectics and an intermetallic compound. This behaviour has been explained by correlating the relative thermal stabilities of different glasses to thermodynamic, crystallographic and electronic factors /97-100/.

The driving force for crystallization is the free-energy difference between the glass and the appropriate crystalline phase(s). We shall explain different crystallization processes by considering the hypothetical free-energy diagram for Fe-B as shown in Fig. 1.11. The curve $G$ represents the free-energy curve for the glassy phase and will be concave downwards and since the glass is metastable, it will always be higher than that of at least one crystalline phase. Here there are two stable phases: a terminal solid solution $\alpha$-Fe and an intermediate phase Fe$_2$B. Also shown is a phase Fe$_3$B which, although it has a lower energy than the glass, is metastable with respect to equilibrium mixture of $\alpha$-Fe and Fe$_2$B.

Depending on various phase transformations, the following crystallization processes can be identified:

(a) Primary Crystallization

During this process the solute is rejected from the growing crystals into the glass, i.e., the formation and the growth of $\alpha$-Fe crystals occur by rejection of boron atoms into the remaining glassy phase. The boron enrichment of the glassy phase continues until further crystallization is stopped by reaching a metastable equilibrium between $\alpha$-Fe and the metastable amorphous Fe-B phase with 25% boron content. This amorphous phase will transform to stable crystalline Fe$_2$B phase by a subsequent transformation. Many iron-metalloid glasses /101/, Cu-Zr/102/ and Ni-Zr/103/ transform in this manner.
Fig. 1.10. Liquidus temperature and $T_x$ as a function of composition for (a) Fe-B alloys and (b) Zr-Ni alloys.
Fig.1.II. (a) Hypothetical free energy diagram for the various phase in Fe-B alloys as a function of composition. Arrows indicate: 1. polymorphous crystallization of α-Fe, 2: primary crystallization of α-Fe, 3: eutectic crystallization of αC-Fe + Fe3B, 4: polymorphous crystallization of Fe3B, 5: eutectic crystallization of αC-Fe + Fe2B; (b) Schematic diagram of typical crystallization reactions in Fe-B alloys.
(b) Polymorphous Crystallization

In this case the glass transforms to a crystalline phase of the same composition. A good example of this is the formation of tetragonal phase Fe$_2$B in Fe-B glasses containing between 24 and 26 atom % of boron /104/ and of Zr$_2$Ni in Zr-Ni glass of the same composition /103/.

(c) Eutectic Crystallization

In this case, the glass can reduce its free energy to a point on the common tangent between either α-Fe and Fe$_2$B or α-Fe and Fe$_3$B, i.e., the two crystalline phases grow in a coupled fashion analogously to the eutectic crystallization of liquids. The proportions of the phases are such that the overall composition of the crystallized product is the same as that of the amorphous matrix (e.g. α-Fe + Fe$_2$B formation or α-Fe + Fe$_3$B formation). Crystallization of Fe$_{50}$B$_{20}$/96/ and Fe$_{40}$Ni$_{40}$P$_{14}$B$_6$/105, 106/ follows eutectic crystallization.

In the case of eutectic and polymorphic reaction the growth of crystals has been found to be linear with time. On the other hand, growth of primary α-Fe crystals has been found to be parabolic /95/. Such a parabolic growth is indicative of the growth controlled by long range diffusion. Therefore, the study of amorphous to crystalline transformation is important as it provides a method of evaluating self-diffusion data. Diffusion coefficients can be estimated from measurements of crystal growth during primary crystallization /107, 108/. Using the Zener equation for diffusional growth:

$$ R = \alpha (Dt)^{1/2} \quad (1.13) $$

where crystal size $R$ is parabolic in time $t$ and dimensionless rate constant $\alpha$ depends on crystal morphology and composition, and amorphous matrix composition near and far from the crystal matrix interface. The disadvantages of this procedure are that the rate controlling diffusion species is not known, $\alpha$ can only be evaluated for a simple crystal morphology, and crystal and amorphous matrix interface compositions are not usually known. Therefore, the diffusion data obtained by this method should be treated with caution.
Activation energy for crystallization can be estimated either by isothermal experiments or by isochronal heating in a Differential Scanning Calorimeter (DSC) at selected heating rates and measuring the shift in the peak crystallization temperature (Kissinger method)/109/. Isothermal heating experiments are also useful /95/ for estimation of the Avrami-exponent and the activation energy. These experiments give the overall kinetics of crystallization. In some cases attempts have been made to separate the activation energy for nucleation and growth /110/.

Another type of reaction is called phase separation which involves the decomposition into two amorphous phases. This can happen by nucleation and growth process or by spinodal decomposition /94/.

1.3 OBJECT OF THE PRESENT STUDY

1.3.1 Diffusion in Metallic Glasses

We have earlier mentioned that when metallic glasses possess sufficient atomic mobility (i.e. on annealing at a suitable temperature), they can lower their free energy by altering their amorphous structure due to the structural relaxation of the glass and this is manifested by significant changes in many properties. Other processes which involve significant rearrangements of atoms leading to a change in their structure are phase separation and crystallisation. Many properties of amorphous alloys are structure sensitive and undergo significant changes on heat-treatment. To mention a few, mechanical ductility and magnetic anisotropy alter drastically upon structural relaxation and crystallisation. All these processes are controlled by the diffusion of atoms through the structure of the amorphous alloy. Therefore, a knowledge of the atomic transport in metallic glasses becomes important in understanding the crystallisation behaviour and pre-crystallisation changes in structure-sensitive physical and mechanical properties. Moreover, an understanding of atomic diffusion in amorphous alloys is also important from technological point of view because it can help in developing heat-treatments suitable for optimizing amorphous alloy properties during its fabrication and also in knowing safe working temperatures which prevent degradation of its properties during service life.
A major hindrance to study the atomic transport behaviour of metallic glasses is their tendency to crystallize. So, the problem in the measurement of diffusion rates in amorphous alloys arises mainly because of the experimental difficulties associated with measuring very small diffusion rates (typically lying in the range \(10^{-18} - 10^{-23} \text{m}^2/\text{sec.}\)) at temperatures sufficiently low to avoid crystallisation. Probably this may be one of the reasons for the limited data on diffusion studies in metallic glasses which are available in literature (see the literature survey in CHAPTER II). Therefore, a systematic study of diffusion of a single solute in different glasses and of different solutes in the same glass becomes desirable for making a meaningful comparison of diffusion rates and hence in understanding the diffusion process in metallic glasses. In view of this objective, the present study on diffusion in amorphous alloys was undertaken.

The fundamental understanding of atomic transport in amorphous solids is not as well developed as that of transport in crystalline materials. In crystalline materials, atomic transport is governed by the presence and motion of well-characterized defects. The periodic lattice in crystalline materials provides an obvious reference structure for the definition of point, line and planar defects. Contrary to this, in amorphous materials it seems plausible that atomic motion can also occur more easily at certain special sites in the system, but the identification of these sites as 'defects' is difficult due to the lack of a well defined reference state. Positron annihilation studies on amorphous alloys /55/ have shown that they contain few open spaces larger than single vacancies. The concept of free-volume fluctuations has also been applied to understand the structure of amorphous alloys /62/. Many other theoretical studies have been done by introducing point defects in dense random packed (DRP) and tetrahedrally coordinated amorphous systems, and line defects in DRP systems using both static relaxation and molecular dynamics simulation /51,66/. Kijek et al. /111/ have summarized the possible diffusion processes in amorphous metals. It has been argued that larger atoms diffuse by a cooperative process while the smaller atoms diffuse possibly by an interstitial mechanism. The latter mechanism has also been
theoretically discussed by Ahemdzadeh and Cantor /112/.

The study of atomic transport in amorphous alloys is intrinsically more complicated since they are in a thermodynamically unstable state and hence undergo a continuous structural change through successively lower free-energy states on annealing. As normally understood the effect of structural relaxation should be to lower the diffusivity in amorphous alloys /113/, but there are now experimental evidences which indicate that structural relaxation may not significantly affect the diffusivity /114,115/. Therefore, it can be said that the present knowledge about the atomic transport in amorphous alloys is not sufficient to give a clear picture and still requires a lot more investigations.

1.3.1.1 Experimental Techniques

Atomic transport can be studied experimentally by applying either a mechanical driving force, as in viscous flow, or a chemical one, such as a concentration gradient in a diffusion experiment or a free-energy difference in a phase transformation. We shall be more concerned here with the second type of methods.

The experimental procedure for direct measurements of diffusion coefficients normally consists of ion-implanting or of depositing a thin or thick film of diffusing atoms on to the amorphous alloy surface. The concentration profile after diffusion annealing as a function of time or distance at a given temperature is obtained by a suitable experimental technique and results are compared with the thin or thick film solution of the diffusion equation.

In amorphous alloys, as heat-treatments are limited to low temperatures and short durations in order to avoid crystallisation of the glass, the diffusion coefficients and diffusion distances are correspondingly small, the latter being of the order of a few hundreds of angstroms only. Therefore, the experimental technique chosen for obtaining the concentration profile of the diffusing species must have a good depth resolution typically in the range 10-2000 Å. The techniques which have been widely used for diffusion studies include ion erosion, sputter profiling by Auger electron spectrometry (AES), secondary ion mass spectrometry (SIMS)
and Rutherford back-scattering spectrometry (RBS). Ion-erosion /116-118/
requires ion-implantation of a suitable radioactive isotope below the
amorphous alloy surface and then the surface after diffusion annealing
is gradually bombarded with argon ions and the concentration profile is
obtained by measuring the radioactivity of the material removed as a
function of time. The concentration profiles can also be obtained by
simultaneously recording the Auger electron signals /119/ of the
diffusing element during the bombardment with argon ions. In secondary
ion mass spectrometry /120/, the surface of a specimen is again ion-eroded,
and a mass spectrometer is used to analyze the composition of the material
removed. Another important technique which provides a good depth resolu­
tion without destroying the specimen by ion-erosion is Rutherford
backscattering spectrometry (RBS)/113, 121-123/. In RBS, a specimen is
irradiated with a monoenergetic beam of alpha-particles and the energy
spectrum of the alpha-particles scattered by heavy nuclei in the specimen
can be used to determine the concentration of scattering nuclei as a
function of depth below the specimen surface. The method of nuclear
reaction /124/ in which the specimen alloy surface is irradiated with
high energy protons and alpha-particles emitted as a result of a nuclear
reaction are detected. This method is suitable for investigating the
diffusion of light elements whose nuclei can be made to undergo a nuclear
reaction.

So far we have listed the direct methods for determining the
diffusion coefficients. Several indirect methods have been used to measure
the diffusion coefficients. Self-diffusion coefficients have been estimated
from measurements of crystal growth rates during crystallisation,
/95, 125, 126/, by assuming a specific model for the mechanism and kinetics
of crystal growth. This has already been mentioned in section 1.2.6.2.
Self-diffusion coefficients have also been estimated by measuring the
segregation of the alloy component to a free surface /114/, again by assuming
a specific kinetic law for the segregation process. Inter diffusion studies
in metallic glasses have also been done using compositionally modulated
thin films /127/. In this technique specimens are prepared by depositing
alternate thin layers of two amorphous alloys and interdiffusion of the
two alloys is measured from the decay in the intensity of the
small angle X-ray peak corresponding to the interlayer separation.

The measurement of viscosity of amorphous alloys can also be used to study diffusion. The scaling relation between viscosity and diffusivity is given by:

$$\gamma D = \frac{KT}{L}$$

(1.14)

where L is a characteristic length related to the dimensions of the defects governing diffusion and flow /128/. The Stokes-Einstein relationship with $L = 6 \pi \eta r$ in Eqn. (1.14) where r is the average ionic radius holds well for several liquid metals /129/. Chen et al. /113/ measured the diffusivity of Au in Rh57.5Cu5.5Si16.5 just above $T_g$ and compared it with the viscosity of the glass in the same temperature range. They found good agreement between diffusion and viscosity data for $T > T_g$. However, at $T < T_g$, D was greater than $D_\eta$ by several orders of magnitude and the values depended strongly on the previous heat-treatment. In general, for $T \geq T_g$, D and $D_\eta$ scale according to the Stokes-Einstein relation which implies that the same defects govern both processes in this regime and for $T < T_g$, the isoconfigurational activation energy for $\eta$ and D is same in similar systems. Moreover, recent diffusivity measurements in Rh-Si/Fe-B compositionally modulated films /130/ seems to support the validity of Stokes-Einstein relation below $T_g$. The continuity of the scaling relation between $\eta$ and $1/D$ indicates that viscous flow and diffusion were governed by the same kind of defects. A full understanding of diffusion and viscous flow is, therefore, very important in understanding the defects in amorphous alloys.

The diffusion data obtained by these indirect methods should be treated with caution, because additional assumptions have to be made about the kinetics of the process being studied /131/. Various methods used for studying diffusion in metallic glasses are presented in TABLE 1.3.

It would be interesting to know that the measurements of diffusion of hydrogen, the smallest atom, are rather different and have been studied by many researchers using both the indirect and direct approaches /132-135/. The interest in the studies of hydrogen absorption and diffusion behaviour in amorphous alloys has been largely due to the possible technological importance of hydrogen, for instance for hydrogen storage or
hydrogen embrittlement. The topic of hydrogen diffusion will not be a part of this work, however, it will be very briefly mentioned later in this work for the sake of completeness of diffusion data. An extensive literature survey on diffusion studies in amorphous alloys is presented in Chapter II of this thesis.

Diffusion of Au, Sb, Pb, Cu, Al, Ni and Fe in some iron-based (Fe$_{82}$B$_{18}$, Fe$_{80}$B$_{20}$) metal-metalloid and zirconium based (Zr-31 at % to 39 at % Ni) metal-metal metallic glasses have been studied using the techniques of Rutherford backscattering spectrometry (RBS) and by Auger electron spectrometry (AES) in conjunction with argon ion sputtering and the results are reported and discussed in this work. The diffusion studies were carried out on different structural states of the amorphous alloys, namely, the as-quenched and relaxed by subjecting the alloy to a short-time anneal near $T_g$ - the glass transition temperature of the alloy, and also on pre-crystallized specimens. This was done to know the effect of structural relaxation and crystallization on the diffusivity.

1.3.2 Oxidation of amorphous alloys

As mentioned earlier, amorphous alloys are free from inhomogeneities associated with the crystalline state such as grain boundaries, dislocations and second phase particles. Therefore, the amorphous alloys must possess interesting corrosion and oxidation properties. It is known that metallic glasses have superior corrosion resistance compared to their crystalline counterparts /136,137/. However studies on oxidation of amorphous alloys are not that extensive in literature /138/. The techniques of X-ray photoelectron spectroscopy and Auger electron spectroscopy are being increasingly used in corrosion and oxidation studies on amorphous as well as crystalline alloys as it provides a true characterization of the top surface and the layer underneath. We have conducted a few experiments relating to the oxidation and corrosion of some iron-based commercial amorphous alloys (METGLAS 2605 Series of Allied Corporation, USA, See Section 1.3.3) using the surface sensitive techniques X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). The native oxide layer on these glasses and their oxidation behaviour in
air as well as in an aqueous medium containing 0.5 M $K_2SO_4$ adjusted to a pH 4.0 by the addition of $H_2SO_4$ were studied using these surface sensitive techniques. A comparison of the oxidation behaviour of amorphous alloys with the corresponding crystallized alloys was also made. It was found that the former possessed superior oxidation resistance than the latter. The role of the various alloying additions in improving these properties was also investigated.

1.3.3 Metallic Glasses used in present studies

Our object was to study the diffusion of various elements (Au, Pb, Sb, Bi, Cu, Al, Fe and Ni) into metallic glasses and for this the following simpler binary alloys were chosen:

Metal-Metalloid : Fe$_{80}$B$_{20}$, Fe$_{82}$B$_{18}$

Metal-Metal : Zr$_{61}$Ni$_{39}$, Zr$_{65}$Ni$_{35}$, Zr$_{67}$Ni$_{33}$

The metal-metalloid alloys were procured from Allied Corporation, USA while the metal-metal alloys were fabricated in our laboratory on a melt-spinning device. The oxidation studies were carried out on the following metal-metalloid glasses, which too were obtained from Allied Corporation USA:

Metal-Metalloid : Fe$_{80}$B$_{20}$ (METGLAS 2605)

Fe$_{67}$Co$_{18}$B$_{14}$Si$_{1}$ (METGLAS 2605 CC)

Fe$_{81}$B$_{13.5}$Si$_{3.5}$C$_{2}$ (METGLAS 2605 SC)

In the following TABLES, a collection of various properties of these metallic glasses is presented. However, a good account of comparative properties of ferrous metallic glasses vis-a-vis crystalline materials has been given by Gilman in reference 140.
TABLE 1.3  Methods for diffusion studies in Metallic Glasses

Direct Methods

Based on measurement of concentration profile
of the diffusing species by the following technique:

(i) Radio tracers + microsectioning by ion
erosion /116-118/

(ii) Rutherford Backscattering Spectrometry
(RBS) /121-123/

(iii) Auger Electron Spectrometry (AES) + Sputtering /119/

(iv) Secondary Ion Mass Spectrometry (SIMS) /120/

(•) Nuclear Reaction Analysis /124/

The D is obtained by using thin or thick film
solution of the diffusion equation /139/:

\[ C(x,t) = \frac{M}{(\pi Dt)} e^{-\frac{(x-x_0)^2}{4Dt}} \]

\[ C(x,t) = \frac{M_0}{2} \left[ 1 + \text{erf} \left( \frac{x-x_0}{2\sqrt{Dt}} \right) \right] \]

Indirect Methods

(i) Crystal growth /95,125/
\[ R = \kappa_0 (Dt)^{\frac{3}{2}} \]

(ii) Viscosity measurements /113/
(creep experiments)
\[ \eta D = \frac{kT}{6\pi r} \]

(iii) Segregation Kinetics /114/
\[ C_S = C_D \left[ 1 + \frac{2}{a} \left( \frac{Dt}{\pi} \right)^{\frac{1}{2}} \right] \]

(iv) Interdiffusion studies /127/
using compositionally modulated
thin films and observing decay
of X-ray satellite peak.

(v) Hydrogen diffusion has mostly
been studied using methods such as
internal friction /132/,
Electrochemical permeation
/135/, NMR /133/.
TABLE 1.4 Data Relating to Metallic Glasses Used

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Density (gm/cm³)</th>
<th>T_g (°C)</th>
<th>T_x (°C)</th>
<th>Amorphous to crystalline Transformation</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe_{80}P_{20}</td>
<td>7.4</td>
<td></td>
<td>726</td>
<td>Eutectic</td>
<td>/96,144,</td>
</tr>
<tr>
<td>Fe_{82}P_{18}</td>
<td>7.48</td>
<td></td>
<td>725</td>
<td>Primary followed by polymorphic</td>
<td>/141/</td>
</tr>
<tr>
<td>Zr_{67}Ni_{33}</td>
<td>7.04</td>
<td></td>
<td>701</td>
<td>Polymorphic</td>
<td>/142/</td>
</tr>
<tr>
<td>Zr_{65}Ni_{35}</td>
<td>7.08</td>
<td></td>
<td>710</td>
<td>Primary followed by polymorphic</td>
<td>/145,146/</td>
</tr>
<tr>
<td>Zr_{61}Ni_{39}</td>
<td>7.20</td>
<td></td>
<td>741</td>
<td>Polymorphic</td>
<td>/143/</td>
</tr>
<tr>
<td>Fe_{67}Co_{18}P_{14}Si_{1}</td>
<td>7.56</td>
<td></td>
<td>715</td>
<td></td>
<td>/143/</td>
</tr>
<tr>
<td>Fe_{81}B_{13.5}Si_{3.5}C_{2}</td>
<td>7.32</td>
<td></td>
<td></td>
<td></td>
<td>/143/</td>
</tr>
</tbody>
</table>

* Determined at a heating rate of 20°C/min in a DSC.

TABLE 1.5 Mechanical Properties

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Hardness VH (Kg/mm²)</th>
<th>Yield Strength (Kg/mm²)</th>
<th>Young's Modulus (Kg/mm²)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe_{80}P_{20}</td>
<td>1100</td>
<td>370</td>
<td>17.2 x 10³</td>
<td>/79/</td>
</tr>
<tr>
<td>Steel</td>
<td>450</td>
<td>170</td>
<td></td>
<td>/79/</td>
</tr>
<tr>
<td>(AISI 4340)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1.3.4 Importance of the Present Work

The major part of the work reported in this thesis was aimed at doing diffusion studies in amorphous alloys. For an easy interpretation of the data, simpler binary alloys (Fe-B, Zr-Ni) having varying physical parameters were chosen for the purpose of diffusion work. A meaningful comparison of the diffusion measurements was made on the basis of some physical parameters such as the melting point, electronegativity and
TABLE 1.6 Magnetic Properties

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$B_s$ (KG)</th>
<th>$T_c$ (Curie)</th>
<th>$\mu_{max}(x10^3)$ permeability</th>
<th>$H_c$(Oe)</th>
<th>$\rho$((\mu\Omega\cdot cm)) Resistivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Satur-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>magnet-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>ization (K)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe$<em>{80}$B$</em>{20}$</td>
<td>16.0</td>
<td>647</td>
<td>320</td>
<td>0.04</td>
<td>140 /79/</td>
</tr>
<tr>
<td>Fe$<em>{4}^\text{Ni}</em>{40}^\text{P}<em>{14}^\text{B}</em>{6}$</td>
<td>8.3</td>
<td>523</td>
<td>1100</td>
<td>0.007</td>
<td>180 /79/</td>
</tr>
<tr>
<td>Fe$<em>{81}^\text{B}</em>{13}^\text{Si}<em>{3}^\text{C}</em>{2}$ (2605Sc)</td>
<td>15.7</td>
<td>643</td>
<td></td>
<td>0.08</td>
<td>125 /140/</td>
</tr>
<tr>
<td>Fe$<em>{67}^\text{Co}</em>{18}^\text{B}<em>{14}^\text{Si}</em>{1}$ (2605Sc)</td>
<td>17.5</td>
<td>698</td>
<td></td>
<td>0.08</td>
<td>130 /140/</td>
</tr>
<tr>
<td>Permalloy</td>
<td>18.2</td>
<td>733</td>
<td>400</td>
<td>0.028</td>
<td>55 /179/</td>
</tr>
</tbody>
</table>

atomic size of the diffusing species. In the light of these investigations suggested possible diffusion mechanisms have also been discussed. In addition to this, the effect of structural relaxation and crystallization on diffusivity in the alloys undertaken in this work was also studied. Besides giving an insight into the atomic transport in metallic glasses, the data reported here do certainly contribute to the scarcely explored field of diffusion in amorphous metallic alloys.

The oxidation studies carried out in this work are not that extensive. However, the results are important from the point of view of understanding the role of various alloying additions in improving the oxidation and corrosion properties of some important commercial metallic amorphous alloys which do have some practical applications.
REFERENCES

34. C.H. Bennett, J. Appl. Phys. 43(1972) 2727.


138. Chapter II of this Thesis.


143. 'METGLAS-Electromagnetic Alloys', an information booklet from Allied Corporation, USA.

144. C. Kim, T. Kim and M. Takehashi, in ref. 115, p.723.
