Chapter 1 INTRODUCTION

1.1 Introduction

There are three elementary states of matter: solids, liquids and gaseous. The main difference between the three states is an atomic arrangement of atoms. In solid state, atoms are tightly bound to each other. The arrangement of the constituents (atoms/ molecules/ ions) of solid may be either in an ordered manner or in an irregular fashion, resulting in different properties. Depending upon the atomic arrangement, solids are classified into two categories: crystalline and amorphous. At an early stage in the study of chemistry we learn that there are four general types of crystalline solid and four associated material types: metals, ionic materials like sodium chloride (salts), molecular materials like methane, CH4, and network covalent materials like diamond. Crystalline solids have long range order which indicate the regular pattern of arrangement of atoms or molecules or ions which repeated over the entire crystal. Atoms or molecules or ions in this structure are situated at a particular position and form a building block. These building blocks of crystalline solids are arranged in orderly, three-dimensional, periodic arrays resulting in a definite external geometrical form. On the other hand, amorphous (in Greek, amorphous means no form) structure is random in nature. Atoms or molecules do not have a periodic arrangement and there is no long range order of the position of the atoms.

The properties of crystalline and amorphous materials differ significantly, due to the structural difference. Amorphous solids don’t possess geometrical shape, whereas, crystalline solids have characteristic geometrical shape. Crystalline solids have sharp melting point whereas amorphous solids melt over a wide range of temperature. Therefore, they can be moulded and blown into different shapes. The physical properties like refractive index, electrical resistance etc of amorphous solids are same in different direction. Therefore amorphous solids are isotropic and they remain same in all direction. Whereas physical properties of crystalline solids are different in different directions i.e. crystalline solids are anisotropic in nature. When amorphous solids are rotated about an axis, their appearance change so they are unsymmetrical but crystalline solids are symmetrical because when they are rotated about an axis, their appearance does not change.

The ordered or disordered structure of any solid are the conditions under which a solid is formed and the type of material. If the materials formation occurs in slow cooling, the atoms get sufficient time to attain a stable configuration and the solidification results in an ordered manner i.e. crystal. In this context, rapid cooling results in a randomly arranged solid. They have higher energy as compared to the crystalline solids. In the crystallization process, atoms are arranged in clusters in order to form a nuclei and the growth of these nuclei takes place subsequently. Further, stable nuclei grow in size which has attained a critical cluster size. Both nucleation and crystal growth in combination of each other form crystallization process. The result may be a single crystal structure or poly-crystal structure with many grains. There are many microscopic crystals (known as grains) of different sizes, separated by grain boundaries in Poly-crystals. Fig. 1.1 shows the arrangement of atoms/ molecules/ ions in crystalline, polycrystalline and amorphous solids.

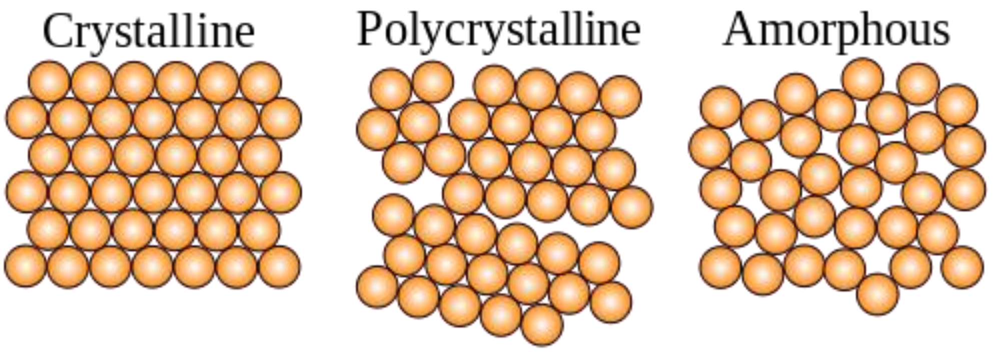

Fig. 1.1: Atomic/ molecular arrangement in Crystalline, Polycrystalline and Amorphous materials (Source: https://en.wikipedia.org/wiki/Crystal dated 09/10/18)

The term amorphous, glassy or vitreous, disordered are often used interchangeably in the literature and it causes conceptual confusion. So, we should distinguish between these terms using the following definitions [1.1]

Amorphous: Amorphous solids are not crystalline on any significant scale i.e. polycrystalline solids are excluded from this category.

Glassy/Vitreous: Those amorphous solids which can be prepared by cooling from the liquid state are commonly called glassy or vitreous.

Disordered: Amorphous solids are a subset of disordered solids. Crystalline solids in which there is substitution or compositional randomness are termed disordered, but not amorphous.

What is the speciality of the amorphous material? How are they important in the technological applications? The answers to these questions may give an idea about the motivation and interests lying behind the present investigations.

1.1.1 Amorphous Alloys

Alloys are solid solution, mixtures of metals or of a metal and one or more non-metals. Metals and their alloys are normally crystalline and therefore have an atomic structure that is ordered with translational periodicity. In Substitutional alloys, a second element takes the place of a metal atom while in interstitial alloys, a second element fills a space in the lattice of metal atoms. The alloy in liquid stage has high entropy. Therefore, long range order does not exist in liquids. Certain liquids may have short-range order in one direction and long-range order in another direction; these special substances are called liquid crystals.

The ordered structure of metallic alloys can be transformed. If the melt of alloy is cooled rapidly, the ordered structure transform into disordered one. Rapid cooling does not give sufficient time to the atoms/ molecules to arrange themselves in an ordered structure and the atoms get solidified in an amorphous form. Glass is a material that can be cooled rapidly from a liquid to a solid without crystallizing. These materials that are structurally amorphous having metals as constituent are termed as "metallic glasses" or "amorphous alloys". The structure of metallic alloy and amorphous alloy is shown in fig. 1.2.

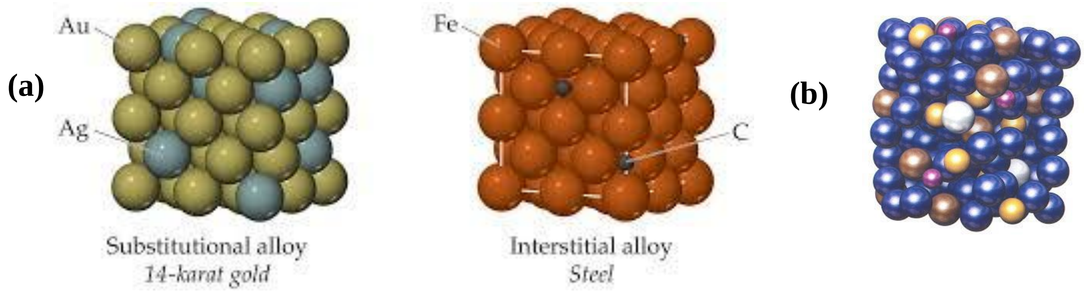

Fig. 1.2 (a) Structure of Substitutional alloys and interstitial alloy (b) Structure of amorphous alloy

Source: (*http://www.unf.edu/~michael.lufaso/chem2046H/2046chapter12.pdf* *http://smartmaterials2009.blogspot.in/2009/09/glass.html*)

Material scientists are working to find out new and advanced materials, with enhanced properties and characteristics. Ultimately, new materials have also been synthesized, which include metallic glasses, nano crystalline materials, high-temperature superconductors and quasi crystals etc. [1.2]. Metallic glasses /amorphous alloys, in contrast with metallic alloys, are homogeneous throughout the structure. Due to homogeneity they enable to achieve excellent properties that crystals lack. The cooling rate must be high enough to suppress the crystallization (~105 to106 K/sec) for the formation of amorphous alloys. Rapid cooling increases the viscosity of a metallic melt, thereby decreasing their diffusivity and the melt gets solidified before acquiring a thermodynamically stable configuration. Therefore, they are structurally meta-stable materials. There are so many methods to synthesis the metallic glasses. One of the most common methods used for the synthesis of metallic glasses is melt-spinning because it enables the formation of metallic glass ribbons at a very high cooling rate (~105 to 106 K/sec).

The first amorphous metallic glass (Au80Si20) introduced In 1960, by Duwez and co-workers [1.3]. They adopted rapid quenching techniques at 106 K/s to synthesize Au-Si ribbon. They reveal that the nucleation and growth of crystalline phase could be kinetically bypassed in some alloy melts which results a frozen liquid configuration, that is, *metallic glass*. Meanwhile, Chen and Turnbull synthesized amorphous spheres of ternary Pd-M-Si (with M = Ag, Cu or Au). They quenched the melts at room temperature at critical cooling rates of 102 Ks-1 to 103 Ks-1, specifically Pd77.5Cu6Si16.5 with a diameter of 0.5 mm [1.4]. Since the first discovery, a number of alloy systems such as Fe-C-P, Fe-B, Co-

Fe-B, Nd-Fe-Al etc have been found to form amorphous alloys till the date.

Bulk Metallic Glasses (BMG)

‘*Bulk Metallic Glasses*’ are the certain alloys whose dimensions are in the order of millimetres (mm) instead of microns (μ). The far lower cooling rates (~ 102 *K/s*) are required for these systems [1.5]. BMGs are The most famous synthesize techniques of BMGs are water quenching, copper mould casting, arc melting method, suction casting method, etc. Chen and collaborators prepared the first bulk metallic glass and formed millimetre diameter rods of ternary Pd-Cu-Si alloys. [1.6].They used simple suction casting method with sufficiently low cooling rates in the range of 103 K/s. Turnbull’s group produced Pd40Ni40P20 with a diameter of 5 mm, they increased critical casting thickness to 1 cm at cooling rates in the 10 Ks-1 regions. The studies of bulk metallic glasses on Pd-Cu-Si, Au-Pd-Sb and Pd-Ni-P alloys were reported earlier. Later in 1980s, several amorphization techniques based mechanisms like mechanical alloying, ion beam mixing, hydrogen absorption, inverse melting had been developed [1.7]. In 1988, new multi component alloy systems like La-Al-Ni and La-Al-Cu were founded by Inoue and co-workers with lower critical cooling rates [1.8].Since then, this group has developed several quaternary amorphous alloys at cooling rates under 100K/s with the critical casting thickness up to several centimetres [1.9]. The Zr-Ti-Cu-Ni-Be glasses with significantly lower critical cooling rates (~ 1K/s) and super cooled liquid regions up to 135K were developed by Peker and Johnson [1.10]. Among these alloys the Zr41.2Ti13.8Cu12.5Ni10Be22.5 known as Vitalloy 1 (vit1) has the lowest critical cooling rate and is the most extensively used BMG. These alloys were cast in the form of fully glassy rod with diameters ranging up to 5–10 cm. Most of the recently discovered BMGs can be described as pseudo ternary alloys of the composition ETM100-x-yLTMxSMy, where ETM is the combination of early transition metals (Zr, Ti, Nb), LTM a combination of late transition metals (Cu, Ni, CO, Fe) and SM a simple metal element (Be, Mg, Al)[1.11]. Recently, Q. Jiang et al [1.12] have reported the formation of a series of Zr-(Cu, Ag)-Al bulk metallic glasses with diameters at least 20 mm. However, taking attention back to Pd based alloys, large glass formation by water quenching using B2O3 flux has been reported in Pd40Cu30Ni10P20 alloy with diameter up to 72 mm [1.13], which is one of the largest size of bulk metallic glasses reported [1.14]. Further advanced research in the field of metallic glass is found. The light elements such as Ti, Al and Mg in environmentally safe Mg-Y-Cu, Mg-Y-Ni etc were developed [1.15] along with family of Be free multi component Zr-based BMGs (eg. Zr-Cu-Ni, Zr-Cu-Ni-Al BMGs)[1.16].

Greer [1.17] proposed ‘confusion principle’, which means that more number of components involved, the greater the chance of glass formation [1.18]. Inoue summarized the results of glass formation in multi component alloys and proposed three empirical rules [1.19]. The super-cooled liquid region, ($\Delta Tx = Tx\text{-}Tg$) is larger than metallic glass ribbons, where Tx and Tg are crystallization temperature and glass transition temperature respectively. For example, the value of ΔTx Pd based amorphous alloy is equal to 131K [1.20]. Due to this, BMGs possess more stability towards thermal fluctuations. The value of Tx, Tg, and enthalpy of crystallization (ΔHx) are same for same composition of metallic glass ribbons as well as for BMGs but the value of structural relaxation enthalpy (i.e., glass transition) of ribbons and BMGs at Tg ($\Delta Hrelax$) is differe from each other [1.21]. BMGs have more relaxed structures than metallic glass ribbons because they are made at lower cooling rates as compared to ribbons. Hence, the $\Delta Hrelax$ values for ribbon samples are almost double than the $\Delta Hrelax$ values for BMGs.

The discovery of new BMGs is going on worldwide. This promising research work will improve the prospects for practical manufacturing because these amorphous alloys possess impressive properties.

1.1.2 Properties of Amorphous Alloys

i. Chemical Properties

- The homogeneous microstructure and chemical arrangement contributes to a high corrosion resistant material [1.22]. In general, the corrosion resistance of metallic glasses is higher than a crystalline alloy. For example, the corrosion resistance of Fe-based metallic glass is higher than Fe-Cr metallic alloy [1.23-1.25]. Further, addition of some corrosion resistant elements (like Mo, Nb, Ta, etc) to a metallic glass enhances its corrosion resistance.

ii. Thermal Properties

- Thermal conductivity and thermal diffusivity of metallic glasses are almost independent of temperature, i.e., they show a weak dependence on temperature.
- Thermal conductivity of metallic glasses are lower than crystalline materials and higher than glassy materials.

iii. Mechanical Properties

- Metallic glasses have high hardness. Regarding the hardness, BMGs lie between metals and ceramics. They are less hard than conventional metals
- Due to these properties metallic glasses have high wear and abrasion resistance and they undergo low mechanical damping.

The strength and elastic limits of glassy alloys are higher than that of titanium alloys and steel

- They have good wear resistance as compared to metals.
- Due to the homogeneous microstructure and absence of grain boundaries, metallic glasses have high strength [1.26-1.28], but less stiffness as compared to crystals. For example, the tensile strength of Vitreloy is almost twice than the strength of titanium [1.29]. Further Zr- [1.30], Cu- [1.31], Ti- [1.32], and Pd- based metallic glasses [1.33] have very high fracture toughness. High strength and flexibility makes them very elastic i.e., they can rebound high elastic strain energy.
- Few Fe-based glasses loose ductility upon annealing without crystallization [1.34]. But this is not true for all metallic glasses.

iv. Electrical Properties

- Electrical conductivity of metallic glasses is lower than crystalline material and higher than conventional glassy materials.
- Metallic glasses have high electrical resistivity, which is insensitive towards temperature variations.
- They have small (or negative) temperature coefficient of resistivity (TCR) [1.35-1.36].This make them suitable for applications in electronic circuits.

v. Magnetic Properties

- Fe, Cu and Ni based metallic glasses get magnetized and demagnetized very easily, and thus their hysteresis energy loss is very minimum.
- They possess soft-magnetic properties [1.37-1.41], i.e., they have narrow hysteresis loop. They have low magnetic coercivity and a high susceptibility towards magnetization.

- These materials have low eddy current losses when subjected to alternating magnetic field due to high electric resistivity.
- Due to their good ferromagnetic properties they can be used in transformer cores.

vi. Other Properties

- Metallic glasses, in contrast with conventional glasses, are opaque, good electrical and thermal conductors, their brittleness is low.
- Some of the Ti-, Co-, Zr- and Fe-based metallic glasses are biocompatible in nature owing to their good corrosion resistance in biological fluids [1.42-1.45].
- Metallic glasses can be casted in various shapes and designs having good finishing. They have highly polished structure and durability.

1.1.3 Applications of Amorphous Alloys

The chemical, mechanical and magnetic properties of BMGs are outstanding, due to its irregular atomic structure. All these properties, in combination with each other, lead to various applications that are discussed below:

i Biomedical Applications: Metallic glass is ideal for corrosion and wear resistant medical applications. They are used in knee-replacement devices, pacemaker casings, dental implants & ophthalmic scalpel blades [1.46]. BMGs have much better corrosion properties in physiological solution compared to many common metallic biomaterials [1.47]. Magnesium-zinc based BMGs have been developed for application as biodegradable and biocompatible bone implants (Fig. 1.3) [1.48].

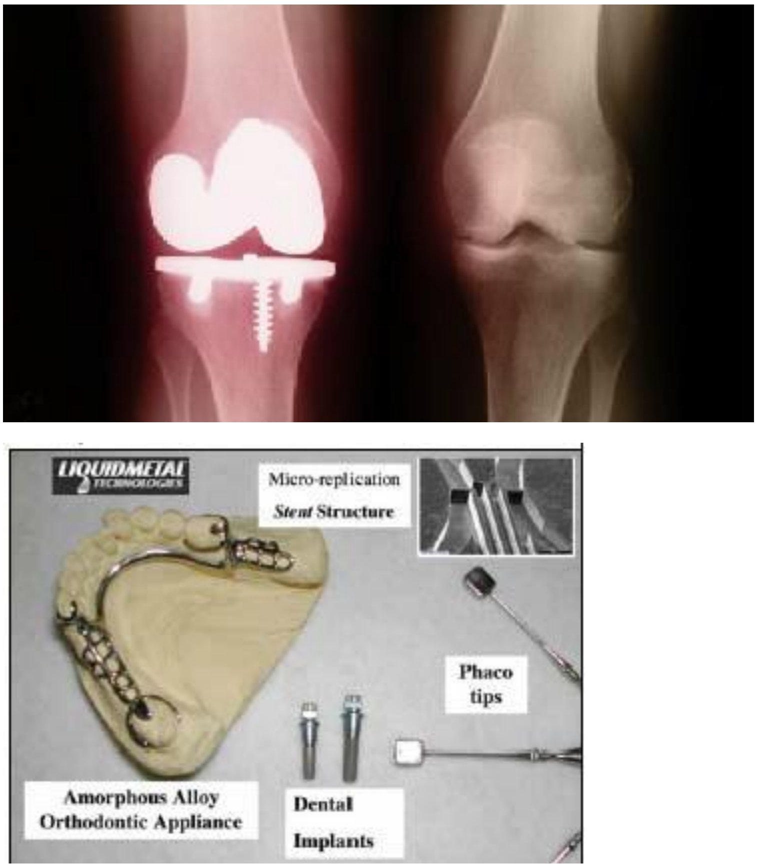

Fig. 1.3: (a) Biodegradable bone implants made of metallic glass, (b) Metallic glass hardware produced by Liquidmetal Technologies [Credit: (a) http://physicsworld.com (b) Liquidmetal Technologies].

ii Structural Applications:

The first application of these glassy metals is found to be as golf club heads in shapes and sizes. Other applications in sports equipment are: frames of tennis rackets, fishing equipment, hunting bows, guns, scuba gear, baseball bats etc. They are also useful for marine applications and bicycle frames [1.49], micro- and nano-sized metallic parts, micro- and nano-machines. [1.50]. Pressure sensors are constructed with a metallic diaphragm [1.51-1.53]. Using these BMG gear parts micro-motors were constructed (Fig. 1.4)

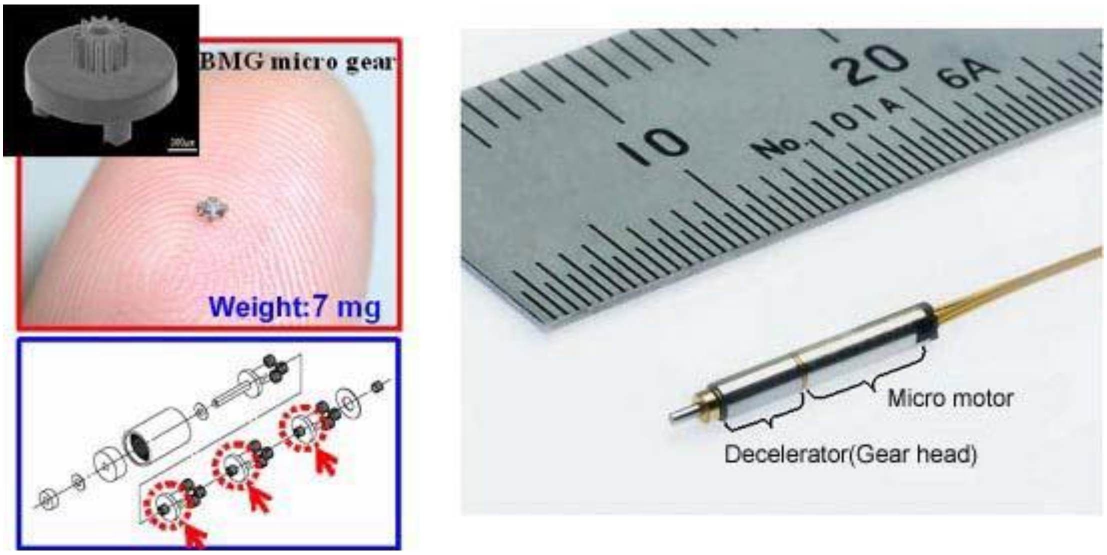

Fig. 1.4: Micro- geared motor constructed by Ni- based glassy alloy
(*Source: http://www.arcmg.imr.tohoku.ac.jp/en/topics/inoue.html*)

iii Electronic Applications:

Metallic glasses are used to make cell phone and watch cases (Omega watches use metallic glass to create designer pieces), outer shield of SanDisk USB memory stick (Fig. 1.5). Liquid metal Technologies, US, is working with design firm Ideo to create a vitreloy encased laptop that rolls up like a piece of paper [1.54].

1.5: USB drive case (Source: (a) http://allthatmatters.heber.org

iv Magnetic Applications:

Magnetic metallic glasses are useful in fabrication of soft magnetic chock coils, transformer cores, magnetic sensors, soft magnetic high frequency power coils and magnetic iron core for high rotation speed motor [1.55].

v Chemical Applications:

Metallic glasses are suitable to be used in fuel cell separators because of their excellent corrosion resistance.

vi Miscellaneous Applications:

Miscellaneous applications of BMGs include jewellery, mobile phone circuitry, watch cases and military applications such as aircraft and missile components, composite armour, electronic components, optical components etc. BMGs are captured for jewellery making by Fine Jewellery Industry due to their unique properties. [1.56]. Many military components, like composite armour, missile components and aircraft fasteners are being developed using BMGs by US Department of Defence (DOD) [1.57]. Zr-based BMGs are used to coat circular passive collector arrays in Genesis space craft for catching Solar wind. (Fig.1.8-(b)) The diffraction gratings of 1 um interval are also fabricated on Pt-based BMG [1.58]. Fabrication of holograms with metallic glass is also possible.

1.2Experimental Techniques

Calorimeter is an instrument which measures the heat into or out of a sample. The heat of sample relative to a reference is measured by a differential calorimeter. Differential Scanning Calorimetry (DSC) is a technique in which difference in heat flow to a sample and to reference pan is monitored against time or temperature. The experiments in DSC can be done either isothermally or non-isothermally [1.59-1.63]. The analysis of the procured DSC data gives the values of kinetic parameters of any thermally activated event. The phase transitions and reactions in materials, and how they contribute to the properties and characteristics of the material can be understood by the DSC. DSC is an efficient and powerful tool by which we can determine of the specific heat quickly and enthalpy change during the primary or secondary phase transition. [1.64]. Chapter 2 involves the detailed instrumentation of DSC and the evaluation of different kinetic parameters using these instruments.

1.3 Thermodynamic Properties of metallic glasses and polymers

Thermodynamic properties are divided into two broad types: intensive properties (it can exist at a point in space) and extensive properties (depends on the size). Heat capacity, specific heat capacity, enthalpy, entropy, Gibbs free energy, Helmholtz free energy, internal energy, pressure, temperature, thermal conductivity, thermal diffusivity, thermal expansion, volume etc can be listed. Among all these properties, heat capacity difference ΔCp enthalpy difference, entropy difference and Gibbs free energy difference of two states are the most important for the study of phase transformation of material. Gibbs free energy differenceΔG can be calculated by integrating the heat capacity difference ΔCp from the equation:

$$\Delta G = \left[\Delta Hm + \int_{T}^{Tm} \Delta Cp dT\right] - T\left[\Delta Sm + \int_{T}^{Tm} \frac{\Delta Cp}{T} dT\right] \tag{1.1}$$

Where ΔHm = enthalpy difference and ΔSm =entropy difference at melting point Tm respectively. [Low value of ΔG is preferable for suppress the crystallization and glass formation.] The value of ΔG becomes lower by small ΔHm and large ΔSm. The entropy is proportional to number of microscopic states [1.65] and therefore, the increase in the number of alloy components leads to the increase in ΔSm and resulting in increment in the degree of dense random packing. Thus, it favours the decrease in ΔHm and the solid/liquid interfacial energy. The free energy at a constant temperature also decreases in the case of low chemical potential caused by the low enthalpy and high value of Trg as well as the large liquid/solid interfacial energy. Hence, multi component alloys are expected to be associated with large ΔSm. Thus, the Gibbs free energy difference (ΔG) between the supercooled liquid and the crystalline solid is the crucial parameter for the prediction of the GFA of multi component alloys.

1.4 Glass Forming Ability of Metallic Glasses, ZBLAN glass & Polymers

The ability of a liquid to form a Glass is known as Glass forming ability (GFA). The glass transition temperature, Tg, is the temperature where liquid bypass the crystallization to glass transition temperature when cooling the melt. Molecules have little relative mobility below Tg. The reduced glass transition temperature Trg = Tg/Tm, with Tg and *Tm* being the glass transition and melting temperature of the alloy, is a criterion for determining the GFA according to Turnbull [1.66]. A liquid with Tg/Tm = 2/3 can only crystallize within a very narrow temperature range because it becomes very sluggish within small time scale [1.67]. Glassy state can be easily obtained at a low cooling rate by such undercooled liquid. This is a fundamental criterion which has played a key role in the development of various metallic glasses including BMGs.

Inoue proposed three empirical rules for glass formation in multi component alloys [1.68]:

- Multi component systems consisting of more than three elements
- The significant difference in atomic sizes with the size ratios above 12% among the three main constituent elements
- Negative heats of mixing among the three main constituent elements.

The alloys satisfying these three empirical rules have special atomic configurations in the liquid state which significantly differed from those of the crystalline phase. The GFA in BMGs tends to increase as more components are added to the alloy. This is called the "*confusion principle*" [1.69]. It implies that competing crystalline phases are destabilized which may form during cooling by larger number of components in an alloy system. This effect makes the melt more stable relative to the crystalline phases and frustrates the tendency of the alloy to crystallize.

The fabrication of BMG requires very low critical cooling rates (~1-102K/s). For this, the correct choice of elemental constituents is important. The intrinsic factors of the alloys like the number, purities and the atomic size of the constituent elements, composition, cohesion among the metals etc. play the key role in glass formation.

The Gibbs free energy difference, ΔG between the under cooled liquid and the corresponding crystalline state is a good indicator for glass forming ability of metallic glasses. From the thermodynamic point of view, the ΔG is driving force for crystallization. So, theoretically the GFA can be evaluated by GFA parameters and by thermodynamic parameter. Different expressions are used to calculate ΔG, using linear and hyperbolic variations of ΔCp in the under cooled region for ZBLAN glasses. Different GFA criteria are also evaluated.

1.5 Crystallization Kinetics of Metallic Glasses and ZBLAN Glass

The transformation of an amorphous material into a crystalline material, upon heating, is known as crystallization. Crystallization is a thermally activated process in non-crystalline and amorphous solids. It is happened because the atoms or molecules of the constituting elements tend to move towards a low energy state thereby transforming a random structure into an ordered one. As a result, the material changes its phase in order to acquire a stable configuration. The crystallization of metallic glasses involves nucleation and growth of nuclei. Nucleation is a rapid process as compared to growth. Crystallization is a first order phase transformation, i.e., it requires latent heat for the phase transformation. Crystallization Kinetics refer to the change in any thermally activated process such as crystallization, glass transition, etc, with respect to changing heating rate. There are two methods: isothermal and non-isothermal [1.70-1.74]. In isothermal method, the sample is brought quickly to a glass transition temperature and the heat liberated during the crystallization process is recorded as a function of temperature. While in non-isothermal method the sample is heated at a constant heating rate and the heat evolved is measured as a function of time or temperature. Among both, the non-isothermal transformation kinetics becomes important. The information about kinetic process in terms of kinetic parameters is given by crystallization kinetics. kinetic parameters namely activation energy (E), pre-exponential factor ($k0$) and Avrami exponent (n) are studied in crystallization kinetics. Firstly, activation energy (E) is the energy required by the atoms/ molecules to overcome the barrier in order to form stable nuclei. A smaller value of E indicates that small amount of energy can convert the material into a crystal. In other words, if activation energy is small, an amorphous material can transform into a crystal easily. Secondly, Pre-exponential factor ($k0$) indicates the number of jumps required to overcome the activation energy barrier. A smaller $k0$ value indicates that the molecules can overcome the barrier with a little effort. Thirdly, the Avrami growth exponent (n) informs about the dimensionality of crystal growth, i.e., it tells whether the growth of nuclei is taking place in one, two, or three dimensions. If E, $k0$, and n are known, we can get total information of crystallization process undergoing in an amorphous material upon heating.

Various methods based on non-isothermal experiments have been worked out in order to determine the kinetic parameters (activation energy, avarami exponent). These methods can be analysed as: (i) isoconversional and, (ii) isokinetic. The isoconversional methods require the knowledge of temperatures $T\alpha(\beta)$ at which an equivalent stage of reaction occurs for various heating rates [1.75-1.76]. The isokinetic methods [1.77-1.78] depend on the reaction model. It also assumes the Arrhenius temperature dependence of the rate constant $K\ (T)$. Iso-conversional methods are known as *model free methods* because it does not depend on any model for the calculation of kinetic parameters. These methods provide E values depending on the degree of conversion (or the crystallized fraction (α)). Further *isokinetic methods* provide single E value for the entire crystallization process. Isokinetic methods depend upon some reaction models for the calculation of kinetic parameters. Hence they are also known as model fitting methods.

Generally, two or more number of elements make the metallic glasses. Different elements crystallize at different temperatures. Hence a metallic glass can crystallize in a single step or it may undergo several crystallization events in order to crystallize completely. So, entire crystallization process can’t explain with a single reaction model. Different models must be taken into account and their applicability must be checked in advance. With regard to this, model free methods can be considered to be superior over model fitting methods.

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