1.1 Introduction

Matter can exist in three states: Solid, liquid and gaseous. The major difference between the three states lies in atomic arrangement of their constituent atoms. Solids can be classified as crystalline or amorphous. Crystalline solids are those materials which have periodic arrangement of their constituent atoms or molecules or ions and have a definite external geometrical form. On the other hand, amorphous solids are those materials which does not have a periodic arrangement of atoms and there is no long range order of the position of the atoms.

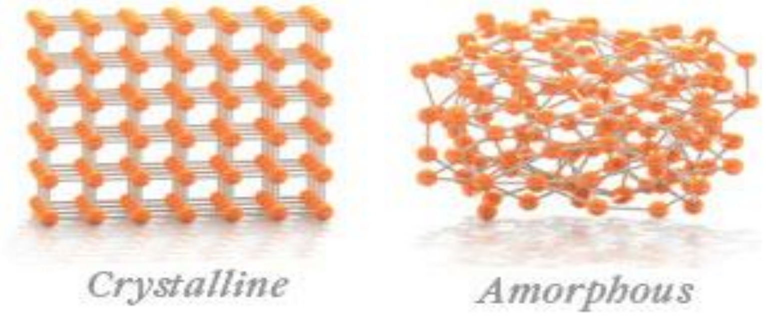


Fig.1.1 Structure of crystalline and amorphous materials
(Source: https://www.researchgate.net/file.)

The properties of crystalline material are different from the amorphous material because of the atomic structure. Crystalline materials have a sharp melting point while amorphous material melts in wide range of temperature i.e. it does not have a particular temperature of melting. Physical properties of amorphous solids are same in different direction, i.e. amorphous solids are isotropic whereas physical properties of crystalline solids are different in different directions i.e crystalline solids are anisotropic in nature. Amorphous solids are unsymmetrical but crystalline solids are symmetrical because when they are rotated about an axis, their appearance does not change.

1.2 Metallic Glasses & Bulk Metallic Glasses

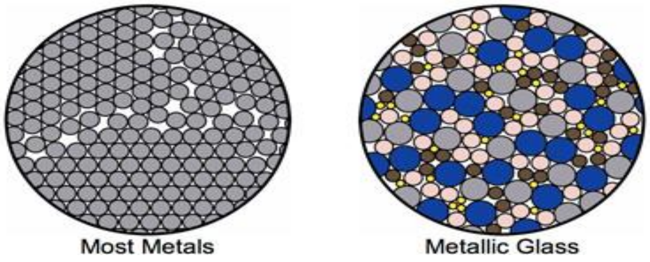


Fig.1.2 Structure of metals and metallic glass.
(Source: http://education.mrsec.wisc.edu).

Metals and their alloys are generally crystalline in nature and possess a long range order of the atom, with translational periodicity. Glass is any material that can be cooled from a liquid to a solid without crystallizing. Most of the metals crystallize when they are cooled, arranging their atoms into a highly regular spatial pattern called a lattice. But if crystallization is avoided then atoms settle into a nearly random arrangement and the resulting form is a metallic glass. Amorphous alloys also known as "**Metallic glasses**" are non-crystalline and random in nature. Metallic alloys are formed by combining two or more different metals and then heating to high temperature resulting into a metallic melt. This metallic melt can be converted into metallic glasses by cooling their melt at a high rate i.e. 10^5 to 10^6 K/s, such that their molecules does not get sufficient time to occupy stable configuration. These super-cooled metallic alloys with a disordered atomic scale arrangement and connected by metallic bonds are known as "metallic glasses

(MGs)”. It shares the property of both metals and alloys. Consequently, the forming of metallic glasses can be realized by solidification of liquid alloys at cooling rates sufficiently high to suppress the nucleation and growth of competing crystalline phases. If the cooling rate is faster, atomic mobility of the atom reduces, as cooling rate is too fast the formation of the crystals does not take place and the material gets “locked in” a glassy state. It is also known as “frozen liquid” as the structure is freezed between solid and liquid. They are kinetically meta-stable materials.

So, metallic glass is liquid alloy which is cooled below its thermodynamic melting point and then fails to crystallize, but solidifies nevertheless. As the cooling rate required for the formation of the metallic glass is very high, the alloy has a limited achievable size. Efforts have been made to produce metallic glasses in larger sizes which can be used for practical applications. Technology has been improved in both for higher achievable cooling rates and searching for good glass forming alloy systems with lower critical cooling rates. During the past several years, advances have been made in this field as a result of the discovery and development of several families of alloys with substantially improved glass forming ability. Previously, metallic glasses were generally formed by cooling the melt at rates of 10^5–10^6 K/s, but now more recently developed alloys require much lower cooling rates. So, a new class of metallic glass has been designed referred as ‘bulk glass formers’ or ‘bulk metallic glasses’. Metallic alloys which fail to crystallize during solidification even at low critical cooling rate i.e less than 100 K/s form “bulk metallic glasses (BMGs)” with thickness ranging from 1 mm to several centimeters due to smaller cooling rates. Good glass forming alloy systems feature low eutectic points and large supercooled liquid regimes, which result in lower cooling rates to form metallic glasses with bulk sizes. This new materials can be cast from the molten state into glassy objects with dimensions up to several centimeters as compared with maximum thickness or diameter of 10–100 µm for rapidly quenched ribbons.

The most crucial step to get low critical cooling rate for bulk metallic glasses is suppressing the crystallization which has enabled with the discovery of new compositions. MGs and BMGs are prepared by different synthesis routes. Melt spinning technique is used to prepare amorphous ribbons of metallic alloys which involves rapid cooling. On the other hand, BMGs are formed by different methods such as copper mould casting, arc melting, which require comparatively low cooling rate. These metastable materials possess excellent properties such as high strength, high hardness, exhibit good corrosion resistance and attractive soft magnetic behavior [1.1].

1.2.1 History of Metallic glasses

The first metallic glass was discovered by rapid quenching of Au-Si binary metallic melt at a very high cooling rate (approximately 10^6 K/s) in the early 1960's at the California Institute of Technology by Duwez and his coworkers [1.2-1.3]. This work is carried out by the technique known as "splat cooling" which attains cooling rates in the range 10^6-10^8 K/s as liquid alloy is solidified.

In the 1970's, Chen and collaborators [1.4] developed ternary Pd-M-Si (with M = Ag, Cu or Au) specifically synthesized Pd-Cu-Si alloys in the form of rods having diameter in mm (0.5mm) at critical cooling rates of 10^2 K/s to 10^3 K/s by means of a "suction casting" method. This was the first achievement of increasing the size of cast metallic glass from the micron to millimeter range and during this period Allied Chemical Corporation developed continuous casting processes for commercial manufacturing of metallic glass ribbon and sheets [1.5].

The synthesis of metallic glasses in a bulk form was led in 1976 with thickness greater than 1 mm which was successfully achieved in $Pd_{40}Ni_{40}P_{20}$ alloys [1.6]. Akihisa Inoue [1.7] and his coworkers in Sendai, Japan, in the late 1980s, have discovered better glass forming multicomponent La-, Mg-, Zr-, Pd-, Fe-, Cu-, and Ti-based alloys with large undercooling and low critical cooling rates of 1K/s to 100 K/s with the critical casting thickness ranging upward toward 1 cm [1.8]. In 1991 using Copper (Cu) mold casting method metallic glass $La_{55}Al_{25}Ni_{20}$ was cast up to 5 mm thick and metallic glass $La_{55}Al_{25}Ni_{10}Cu_{10}$ up to 9 mm thick [1.9]. Also during this period Mg-TM-Y (TM=Transition Metals) was also shown to have high glass-forming ability (GFA) in the form of $Mg_{65}Cu_{25}Y_{10}$ [1.10]. An extended supercooled liquid region (to 127 K) [1.11] was achieved for Zr-Al-Ni-Cu, with a critical casting thickness of 15 mm [1.12] for $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$.

Peker and Johnson [1.13] in 1993, developed Zr-Ti-Cu-Ni-Be glasses with significantly lower critical cooling rates (~ 1K/s) and supercooled liquid regions upto 135K. Among these alloys the $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ known as Vitreloy1 (vit1) has the lowest critical cooling rate and is the most extensively used BMG. The alloys were cast in the form of fully glassy rod with diameters ranging up to 5–10 cm. Pd based alloys are found to have large glass formation developed by water quenching using B_2O_3 flux. It has been reported that $Pd_{40}Cu_{30}Ni_{10}P_{20}$ metallic alloy with diameter up to 72 mm [1.14] was synthesized, which is the largest size of bulk metallic glasses reported so far [1.15]. Further increasing research in the field of metallic glass the light elements such as Ti, Al and Mg in environmentally safe Mg-Y-Cu, Mg-Y-Ni etc were developed [1.16] along with family of Be free multicomponent Zr-based BMGs (eg.Zr-Cu-Ni, Zr-Cu-Ni-Al BMGs) [1.12].

1.2.2 Properties of Amorphous Alloys

A random atomic structure is the attracting characteristic of the metallic glass which differentiates it from ordinary metals. The structure of the metallic glass is tightly packed so displacement of the atoms is blocked. Due to its irregular atomic structure the mechanical and magnetic properties are outstanding. Also the traditional metals are relatively easy to deform or bend permanently out of shape because their atomic structure is periodic whereas metallic glass absorbs less energy upon stress and come back to its original shape much more readily. MGs possess high strength, high hardness, high toughness, high elasticity and ductility compared to metallic materials as they are non-crystalline in nature and do not contain any dislocations or no crystal defects. Metallic glasses have a higher elastic modulus and elastic limit than the crystalline variant of the same material. This means that such a material can reversibly store energy. The yield stress and hardness of BMGs is found to be twice as those of steels, in addition, they exhibit more elastic strain and fracture toughness than ceramics and less brittle than conventional oxide glasses [1.17]. The metallic glass having their constituent element as Boron (B), Silicon (Si), Phosphorus (P) and ferrous magnetic transition metals Fe, Co, Ni are good glass former and possess excellent soft magnetic properties. Easy magnetization and demagnetization allow lower losses in applications, operation at high temperature with minimal flux density reduction and annealing.

The major advantages of metallic glasses are that they are generally homogeneous in composition, offer strong and superior corrosion resistance. MGs possess good corrosion resistance because it has homogenous microstructure and does not have grain boundaries. The corrosion resistance of Zr-based alloys was better than 316L stainless steel and Ti-6Al-4V alloy in different artifical body fluids and was significantly enhanced by the addition of Nb [1.18].

1.2.3 Applications of MG’s and BMG’s

1. Structural Applications:

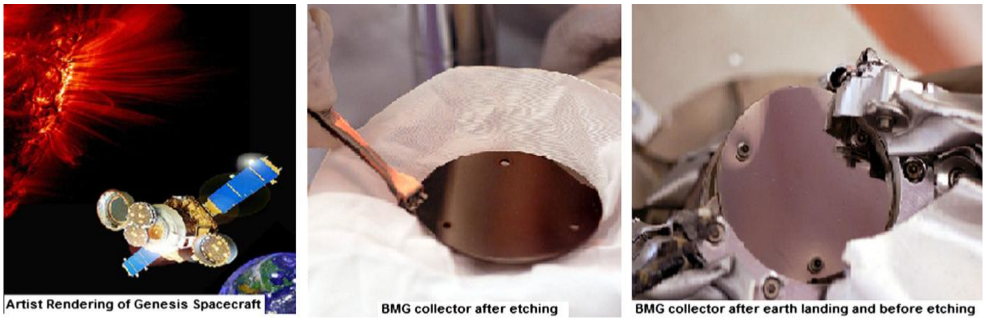
Due to superior properties such as high yield strength, low young’s modulus, large elastic strain limit and easy formability in the supercooled region makes BMGs attractive for structural applications. Due to the fact that new glass-forming compositions have been found that have a critical cooling rate of less than 100 K/s and can be made glassy with dimensions of 10 mm or more, which also makes them useful for many applications. The ability of this material to store a high amount of elastic energy has made it a potential spring material. The first application to be found is in sporting goods, especially golf club heads [1.19]. The golf club head made up of BMG is twice as hard and four times as elastic as Ti drivers. BMGs are also used in other high-end sporting goods such as tennis rackets, and may also find applications for baseball bats, bicycle frames and edged tools such as axes. BMGs with appropriate composition can be used in automobile valve springs. It is estimated by using BMGs in automobile valve springs, the weight of engine is reduced and also the fuel consumption. BMGs are also used in diaphragms for pressure sensor which are used for fuel-injection control to lower the fuel consumption of automobiles and thus reduce toxic and CO_2 exhaust emissions. The sensitivity of the Zr-based BMG diaphragm used in pressure sensor is 3.8 times greater than a conventional diaphragm [1.20]. BMGs are homogeneous and ideal isotropic materials free of grain boundaries so they are used in optical mirror devices. BMGs have metallic luster and are appropriate for the reflective parts of optical devices. The Zr-based BMG has a smooth surface and exhibits good reflection.

2. Chemical Applications:

BMGs are being examined as a replacement material for fuel-cell separators, because of their high strength, superior corrosion resistance, and viscous deformability. Due to the required high corrosion resistance, Ni-based BMGs have been selected among the metal–metal systems for this application. It is concluded that the Ni-based BMG is a promising material for next- generation separators in fuel cells.

a)Diaphragm for pressure and its final products
(Source: http://www.arcmg.imr.tohoku.ac.jp/en/topics/inoue.html)

b) Die casting produced pieces BMGs c)BMG in Kinetic Energy Penetrators ‘‘KEPs’ (d)Golf club head
(Source: http://www.liquidmetal.com/applications)



e) Images with spacecraft and BMG components for Genesis Mission
(Source: http://genesismission.jpl.nasa.gov image credit NASA/JPL – Caltech/USC)

Fig.1.3 Various applications of BMGs.

3. Magnetic Applications

Since metallic glasses have soft magnetic properties, they are used in tape recorder heads, cores of high-power transformers, metallic shields, soft magnetic chock coils, magnetic sensors, soft magnetic high frequency power coils and magnetic iron core for high rotation speed motor [1.21]. Ferrous (Fe) metallic glasses are among the most easily magnetized of all ferromagnetic material so they are commonly used metallic glass for magnetic application.

4. Biomedical Applications

BMGs have various applications in the field of medical. BMGs have strong properties like non toxic, high tensile strength, corrosion resistant, and biocompatible makes it suitable for medical applications. BMGs are used to develop products for reconstructive devices, fractured fixations, spinal implants, ophthalmic surgery and cataract surgery. BMGs are also used in surgical blades which are sharper and long lasting than steel. BMGs are used for the dental implants.

5. Electronics goods

Since metallic glasses have high electrical resistance, they are used to make accurate standard resistance, computer memories and magnetic resistance sensors. Mobile phones and digital still cameras with BMG casing are already developed [1.22]. BMGs are ideal materials for Micro Electro- Mechanical systems (MEMS) fabrication where high yield strain, low-loss coefficient and good fatigue resistance is required.

6. Jewelry industry

BMG’s are used in jewelry industry because of its exceptional properties like high hardness, high luster and scratch resistant. Also BMGs have the ability to be precision net shape cast which enables jewelry designers to create bold lines and sensual unique shapes not easily achieved in traditional metals.

7. Defense and Aerospace

BMGs are also used to develop military equipments that are stronger, lighter and more effective at high temperature and stress. The currently used depleted uranium penetrators, which are suspected of biological toxicity, are nowadays replaced by BMGs.

1.3 Glass forming ability of metallic glasses

Glass forming ability (GFA) is the measure of easiness with which a metallic melt can be converted into metallic glass. It is important to study the GFA of metallic glass because if GFA is known then metallic glass with higher GFA can be designed for many practical applications. It is also known that the materials are more stable in the crystalline counterparts than amorphous state so thermodynamic and kinetic aspects are the key parameter to understand the glass formation. Inoue et al [1.23] summarized the results of glass formation in multicomponent alloys by combining all the theoretical contributions such as thermodynamic, kinetic and structural to optimize GFA of the alloys and proposed three empirical rules: 1) Multi-component alloys of three or more elements: increased complexity and size of the crystal unit cell reduces the energetic advantage of forming an ordered structure of longer-range periodicity than the atomic interactions. 2) Atomic size mismatch between elements, greater than 12% leads to a higher packing density and smaller free volume in the liquid state compared with metallic melts, and requires a greater volume increase for crystallization. 3) Negative heat of mixing between the main elements increases the energy barrier at the liquid-solid interface and decreases atomic diffusivity which retards local atomic rearrangements and the crystal nucleation rate. The first rule is known as the ‘confusion principle’ (multicomponent rule) [1.24-1.25] which states that if there are more elements involved lower will the chance for the alloy to occupy crystal structures, and the greater the chance of glass formation. Turnbull [1.26] predicted that a ratio, referred to as the reduced glass transition temperature $T_{rg} = T_g/T_m$, with T_g and T_m being the glass transition and melting temperature of the alloy can be used for as a criterion for determining the GFA of the alloys. Like this, there are many defined GFA parameters which are calculated based on the characteristic temperatures such as glass transition, melting, crystallization, fusion enthalpy, etc. But none of the GFA parameter can be considered as ideal for the prediction of GFA of metallic glass. There always lie some exceptional cases. Further, the GFA of metallic glass can also be studied by a thermodynamic parameter, Gibbs free energy (ΔG) difference between the glassy phase and the corresponding crystalline phase. So, theoretically the GFA can be evaluated by GFA parameters and by thermodynamic parameter. Now to predict which parameter better reflects the GFA of alloys they are correlated with the critical size (d_c). Critical size is the experimental parameter and defined as the maximum size upto which a metallic alloy remains in the fully amorphous state and does not any crystalline phase. A linear regression analysis is carried out to correlate GFA parameters and thermodynamic parameter with d_c.

The driving force of crystallization (ΔG) provides very important information about the GFA of metallic glasses. To calculate ΔG, knowledge of specific heat difference ΔC_p, between the glassy state and corresponding crystalline phase is required. But the measurement of ΔC_p is difficult experimentally so various theoretical estimation of ΔC_p, results in variety of expression of ΔG. Chapter-2 gives some idea about the prediction of GFA of different multicomponent metallic glasses. The thermodynamic parameter, ΔG is calculated by different expressions based on different ΔC_p approximation. The merits and demerits of different expressions of ΔG, and also which expression provides better result in accordance with the experimental results, are discussed in detail.

Further, the GFA of different Mg-Ni-Pr based metallic alloys is studied through Gibbs free energy difference, ΔG as a function of temperature and entropy difference using Lad et al. [1.27-1.28] expressions. Other GFA parameters are also calculated for different Mg-Ni-Pr based multicomponent metallic alloys. On the basis of these parameters excellent glass forming composition is identified. Different GFA parameters of Mg-Ni-Pr based alloys are studied in air and argon atmosphere to predict whether this Mg-Ni-Pr based can be successfully fabricated in air or not, with high glass forming ability.

The thermodynamic parameter, ΔG and various GFA parameters of metallic glass forming alloy has been obtained for Cu-Pr based amorphous alloy. Further the enhancement of GFA is verified after the minor addition of Ti and B to Cu-Pr based alloys by evaluating ΔG in the entire undercooled region. The Gibb's free energy difference is calculated using different theoretical expression. So thermodynamically the GFA of the metallic alloys can also be predicted and alloy with higher GFA can be designed.

1.4 Time-Temperature-Transformation (TTT) diagram of metallic glass

When the melt is undercooled and if crystallization is avoided the formation of glass takes place. The formation of glass will be more favored if the rate of cooling is more rapid and less time will be available for crystallization. The glass forming ability (GFA) of metallic alloy can be expressed in terms of critical cooling rate (R_c) or critical size (Z_c). R_c is defined as the minimum cooling rate required for the formation of fully amorphous structure whereas Z_c is defined as the maximum size upto which the material exists in fully amorphous state. But the measurement of Z_c involves many errors. So, R_c is regarded as the ideal way to predict GFA of metallic glasses. Low value of R_c corresponds to high GFA. Measuring R_c experimentally for the amorphous alloys is undoubtedly an ideal route for the prediction of GFA. But this method is rarely used and it is much complicated. So, another route to determine R_c is theoretically explored.

The simplest and most widely employed method for the prediction of R_c is the Time-Temperature-Transformation (TTT) diagram. Critical cooling rates for the glass formation can be computed by cooling curve which just passes through the nose of a TTT curves. It is also known as “Nose method”[1.29]. In order to construct TTT curves various parameters are required in the nucleation and growth equations. It is very difficult to obtain all these parameters experimentally. As a result different approximations are taken. One such important parameter required in nucleation and growth equations to construct TTT for different glass forming systems is Gibbs free energy difference (ΔG).

Experimental determination of ΔG is very difficult. So, for the calculation of ΔG, knowledge of specific heat difference (ΔC_p) between the glassy phase and corresponding crystalline phase is necessary. Chapter-3 reports how the different approximations taken for deriving ΔG expressions affect the TTT curves for different metallic glasses. Different theoretical models of ΔG, based on different ΔC_p approximations, are incorporated in nucleation and growth equation to study the effect of ΔG for the prediction of R_c.

1.5 Crystallization kinetics of metallic glass

Metallic glasses undergo change in their structure i.e., from amorphous metastable state to a stable crystalline state followed by melting of alloy when the thermal energy is applied. The properties of amorphous alloys are entirely different from their corresponding crystalline phase. The crystallization of metallic glasses involves nucleation and growth of nuclei. Nucleation is a rapid process as compared to growth. The solid state processes which are thermally stimulated can be analyzed by two methods i.e. isothermal and non-isothermal. In isothermal method the heat liberated during the crystallization process is recorded as a function of temperature when the sample is brought quickly to a glass transition temperature and in non-isothermal method the sample is heated at a constant heating rate upto specified temperature and the heat evolved is measured as a function of time or temperature. A disadvantage of the isothermal method is the impossibility of reaching a test temperature instantaneously and during the time, which system needs to stabilize, no measurements are possible This drawback is eliminated in the non-isothermal method [1.30]. Since, many phase transformations take place simultaneously under isothermal conditions measurement with the experimental apparatus becomes difficult. So, the non-isothermal transformation kinetics becomes important for the study of kinetics of crystallization of different metallic glasses. One of the most widely used thermo-analytical techniques for studying the kinetics of crystallization of metallic glass is the differential scanning calorimetry (DSC). DSC enables us to study the crystallization process in metallic glass, by providing data of crystallized fraction with temperature or time. Both isothermal and non isothermal conditions can be used in DSC for studying crystallization kinetics.

Two routes are followed for the analysis of the crystallization event namely, iso-conversional and iso-kinetic models. Both the models, in combination with each other, are used for the determination of the kinetic triplet, i.e activation energy (E), frequency factor (k_0) and Avrami exponent (n). The values of E, obtained by both methods, provide information about the energy required by constituents to overcome the barrier for the occurrence of the event (crystallization). Smaller value of E indicates that a reaction is easily feasible. k_o is the number of jumps required by an atom to overcome the barrier and form stable nuclei. n gives information about crystal growth. Relative merits and limitations of various analytical approaches have been presented and results obtained have been discussed in light of them.

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