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We verily sent Our messengers with clear proofs, and revealed with them the Scripture and the Balance, that mankind may observe right measure; and He revealed iron, wherein is mighty power and (many) benefits for mankind, and that Allah may know him who helpeth Him and His messengers, though unseen. Lo! Allah is Strong, Almighty.

(57:25, Surrah Al-Hadeed, Al-Quran)
Dedicated to those who deserve the most, my family
Thesis Abstract

For decades, Metallic Glass, with its isotropic featureless structure while exhibiting outstanding mechanical properties was possible only at a high rate of quenching and with at least one dimension in the submicron regime. This limitation was overcome with the discovery of Bulk Metallic glasses, BMGs, containing three or more elements following the additional two empirical rules of optimum geometric size differences and negative energy of mixing among the constituent elements. Since then thousands of Fe-, Ni-, Al-, Mg-, Ti-based BMGs have been discovered and comprehensively investigated mainly by groups in Japan and USA. Yet the discovery of new combinations of elements for BMGs is alchemy. We do not know with certainty which element when added will make possible a transition from being a ribbon to a bulk rod.

In this thesis we report a discovery of castable BMG rods on substitution of Fe by nickel in an alloy of FeBNb which could otherwise have been only melt-spun into ribbons. For example, we find that substitution of just 6 at.% of Fe raises the glass forming range, GFA, to as much as ∆T_x=40K while the other parameters for GFA like T_{rg}, γ, and δ reach enhanced values 0.57, 0.38, and 1.40 respectively. Furthermore, the electrical conductivity is found to increase by almost a factor of two. Magnetically it becomes softer with coercivity 260mOe which further reduces to much lower values on stress relaxation. Ni does not seem to carry a magnetic moment while it enhances the magnetic transition temperature linearly with Ni concentration.

We have investigated the role of Ni in another more stable BMGs based FeBNbY system in which case ∆T_x becomes as large as 94K with comparable enhancement in the other GFA parameters. Due to the exceptional soft magnetic properties, Fe-based bulk metallic glasses are considered potential candidate for their use in energy transferring devices. Thus the effect of Ni substitution on bulk forming ability, magnetic and electrical transport properties have been studied for FeBNb and FeBNbY alloy systems. The role of Ni in these systems is densification of the atomic structure and its consequence.

We have exploited the superior mechanical properties of BMGs by fabricating structures that are thin and sustainable. We have therefore investigated studies on the thin films of these materials retaining their excellent mechanical properties. Magnetic properties of FeBNb alloy were investigated in thin films form (~200-400nm) in the temperature range of 5-300K. These Pulsed Laser deposited amorphous films exhibit soft magnetism at room temperature, a characteristic of amorphous metals, while they reveal a shift in hysteresis loop (exchange anisotropy, H_{ex}=18-25Oe), at liquid helium temperature. When thickness of films is reduced to few nanometers (~8-11nm), they exhibit high transparency (>60%) in optical spectrum and show appreciably high saturation Faraday rotation (12°/μm, λ= 611nm). Thin films (~200-400nm) of Ni substituted alloy (FeNiBNb) reveal spontaneous perpendicular magnetization at room temperature. Spin-reorientation transition was observed as a function of film thickness (25-400nm) and temperature (200-300K), and correlated to the order/disorder of ferromagnetic amorphous matrix as a function of temperature. These two phase films exhibits increased value of coercivity, magnetic hardening, below 25K and attributed to the spin glass state of the system.

Using the bulk and thin films we have developed prototypes of sensors, current meters and such simple devices although not discussed in this Thesis. 

Abstract contd…
Ti-based bulk metallic glasses have been attracting significant attention due to their lower density and high specific strength from structural application point of view. High mechanical strength, lower values of young’s modulus, high yield strength along with excellent chemical behaviors of toxic free (Ni, Al, Be) Ti-based glassy metals make them attractive for biomedical applications. In the present work, toxic free Ti-Zr-Cu-Pd-Sn alloys were studied to optimize their bulk forming ability and we successfully developed glassy rods of at least 14mm diameter by Cu-mold casting. Along with high glass forming ability, as-casted BMGs exhibit excellent plasticity. One of the studied alloy \((\text{Ti}_{41.5}\text{Zr}_{10}\text{Cu}_{35}\text{Pd}_{11}\text{Sn}_{2.5})\) exhibits distinct plasticity under uniaxial compression tests (12.63%) with strain hardening before failure which is not commonly seen in monolithic bulk metallic glasses.

**Key Words:** Bulk Metallic glasses, glass forming ability, soft magnetism, thin films, magnetic properties, magnetic hardening, plasticity, biocompatibility.
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(* all the experimental work, data analyses and the writing of preliminary manuscripts were carried out by Mr. Ansar Masood)

1. The observation of surface-softening in Fe-based metallic glass
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2. The effect of Ni-substitution on physical Properties of Fe_{72-x}B_{24}Nb_{4}Ni_{x} Bulk Metallic Glassy alloys
   Ansar Masood, A. Biswas, V. Ström, L. Belova, J. Ågren and K. V. Rao
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6. Exchange bias in amorphous Fe-B-Nb thin films
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9. Low temperature magnetic hardening in nanocrystalline Fe-Ni-B-Nb thin films
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   To be submitted

10. Distinct Plasticity of Biocompatible Ti-Zr-Cu-Pd-Sn Bulk Metallic Glass

11. Excellent bulk forming ability and high plasticity of biocompatible Titanium based bulk metallic glasses
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- **Design of biocompatible Ti-Zr-Cu-Pd-Sn bulk metallic glass — A CALPHAD approach**
  H. Mao, Ansar Masood, J. J. Oak, K. V. Rao, and J. Ågren
  (Manuscript)

- **Magnetic and electronic properties of glassy (Fe_{72}B_{24}Nb_{4})_{96.5}Y_{4.5} ferromagnetic thin films fabricated by pulse laser deposition technique**
  S. Nagar, Ansar Masood, L. Belova, V. Ström, and K. V. Rao
  (PhD thesis: S. Nagar)

- **A new material for magneto-optical applications: (Fe_{72}B_{24}Nb_{4})_{96.5}Y_{4.5} glassy thin films**
  S. Nagar, Ansar Masood, L. Belova, V. Ström, and K. V. Rao
  (PhD thesis: S. Nagar)

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- Oral presentation on ‘Magnetic, optical and transport properties of Fe_{77}B_{17}Nb_{6} thin films’, 11\textsuperscript{th} joint MMM Intermag Conference, Jan. 18-22, 2010, Washington DC, USA.

- Presentations, Oral & Posters, at various meetings and workshops related to Hero-M program.


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CHAPTER 1

1-INTRODUCTION

Inquisitive nature of mankind is the major driving force that has led man to unlock the mysteries of life and to discover new era of evolution. This journey has prevailed upon a due course of centuries. Man has always been reliant on natural resources in this quest. He has made use of precious metals around him like steel and many other alloys. Almost everything in our use is either made from steel or its products in some way or the other. Steel, an alloy consisting mostly of Iron (Fe) and Carbon (C), has got significant strength, and due to its springy nature, it could be pressed and shaped into desired forms for structural applications such as infrastructure, vehicles and machines etc. Also, Silicon steel (Fe with Si) has been used for long time as a core material for energy transformation in commercial transformers. Despite these widespread applications, these metal alloys exhibit limited process ability which results in restricted versatility of shapes and precision, convincing to think of some new class of material even more flexible in nature. Plastics, the second generation of materials, have also revolutionized the field of material science. Their plasticity during manufacturing allows them to be casted, processed or extruded into variety of shapes but their low strength hinders their application as a structural material [1]. An “ideal material” possessing combined structural properties of steels and versatile process ability like plastics was a dream which came into reality by the discovery of material called GLASSY METAL considered as third generation of materials, and these alloys when casted in dimension of at least millimeter thickness are known as BULK METALLIC GLASSES (BMGs).

“METALLIC GLASS” is a frozen liquid metal possessing no long range atomic order; formed by rapid solidification bypassing through crystallization process during the cooling of constituents from the gas or liquid phases. This new class of material combines the structural properties of steels and versatile process ability of plastics and has revolutionized the field of material science, and hence justifying its use as a sustainable engineering material.

Unique nature of disordered structure in glassy metals provides them combination of exceptional physical properties like at one end they are among the hardest materials ever made
while on the other end pretty easier to work and form despite their hardness [1, 2]. Due to the lack of long range periodicity and related grain boundaries with defects, BMGs are reaching the limits of the theoretical strength [3]. Their net shape processability by Cu-mold casting, suction casting and super plastic forming (a similar method of processing like thermoplastics) in Newtonian viscous flow regime (supercooled region) have led these materials to replicate in small features and in thin sections with high aspect ratios [4-7]. Also, BMGs do not require post-cast processing or heat treatment, as all properties are already achieved in as-cast state. Also they could be fabricated and processed at lower temperatures comparative to their crystalline counterparts [1, 2]. Almost zero shrinkage (~ 0.5%) during fabrication for these alloys makes them perfect for precision casting [1]. For example, the world smallest gear motor with dimension 1.5mm (even less) has been fabricated with Cu-mold casting method which was not possible with mechanical machining method [8, 9].

Glassy metals are extremely soft magnets used as a core material in power distribution transformers while they also exhibit hard magnetism [10-19]. The outstanding magnetic softness with high resistivity as compared to crystalline counter parts and other favorable characteristics such as frequency response of nearly zero magnetostriction alloys makes the amorphous materials ideal for magnetic cores and electronic devices. Highly magnetostrictive alloys can be used as excellent sensing elements for detecting stresses. Amorphous alloys are used as magnetic field detectors, in encoding devices, and in antitheft systems [20-26].

Contrary to crystalline materials, glassy metals are known to be homogeneous, isotropic and free from lattice defects with grain boundaries which are limiting factors in reduction of patterning especially when working in nanometer regime [7, 27]. Processing advantages of bulk metallic glasses with structure less surface morphology and exceptional functional properties like high corrosion resistance, good soft magnetic properties with high saturated magnetic flux density, make BMGs as a potential material for micro-and/or nano-electromechanical systems (MEMS/NEMS), for nanotechnology application point of view [7, 27-29].

These ideal properties have made possible their use in a number of fields ranging from very sophisticated tools like micro-geared motors to major commercial applications in the present world [8, 30]. The micro-geared motors are expected to use in advanced medical equipment like endoscope, micro pumps, precision optics, and micro-machines [8, 9, 30]. The major applications of these precious metals are in sports items, hard casings, aircrafts, surgical instruments, industrial coatings and energy savings as amorphous core transformers and in various kind of sensors i.e. pressure sensor in auto mobile industry for injection control, oil
pressure control, air conditioning, clogging monitor, brake control, and magnetic and magneto-optical sensors i.e. current sensation and optical communication [30-42].

1.1 Aim of thesis

The aim of the thesis is to explore the functional properties of glassy metals from bulk dimensions to nanometer scale for their applications as a future material. Two classes of magnetic materials, FeNbB, and FeNbBY with partial substitution of Fe by Ni have been produced in the form of ribbons, bulk rods and thin films. Most of their physical properties including mechanical, magnetic and magneto-optical properties have been investigated.

Thus, the present work focuses on different aspects of glassy metals. To enable Fe-based glassy metals as a functional material, bulk forming ability, thermal stability, magnetic and electrical transport properties and mechanical properties were investigated and found to be significantly enhanced especially on Ni substitution. When these alloys were deposited in thin film form by pulsed laser technique, they exhibit very interesting technologically important phenomena. For example, thin films of FeBNb alloy exhibits soft ferromagnetism at room temperature while they revealed exchange bias anisotropy at low temperatures. When the thickness of the films is reduced to few nanometers, they are highly transparent even in the UV regime of the optical spectrum and possess appreciably high saturation Faraday rotation. When these alloys with Ni were prepared in thin film form, spontaneous perpendicular magnetization was revealed for thicker films which disappeared when thickness of the films was decreased to few nanometers and temperature lowered to 200K. At liquid helium temperatures these films revealed magnetic hardening. The above properties have been exploited to produce prototypes of sensors although not discussed in the Thesis.

We have also carried out studies of biocompatible Ti-based glassy metals and focused to fabricate them in bulk dimensions for their use as biomedical materials. Our findings reveal that Ti-Zr-Cu-Pd-Sn can now be fabricated in the form of cylindrical rods of at least 14mm directly by Cu-mold casting. Along with excellent bulk forming ability these glassy metals also revealed excellent mechanical properties. It noteworthy to mention that one of the biocompatible alloy, (Ti_{41.5}Zr_{10}Cu_{35}Pd_{11}Sn_{2.5}) revealed distinct plasticity (12.63%) under compression tests along with strain hardening before failure which is not common for monolithic bulk metallic glasses.
CHAPTER -2

2- BULK METALLIC GLASSES–THE FLAWLESS MATERIALS

In this chapter, we will describe a brief historical background. Also, some of the fundamental concepts related to BMGs and the basic mechanism behind their exceptional properties will also be described.

2.1 A brief historical development

The first reported metallic glass was an alloy Au$_{75}$Si$_{25}$ (at. %) produced at CALTECH by Duwez et al. [46] in 1960. These early glass forming alloys had to be cooled extremely rapidly (on the order of million Kelvin per second) to avoid crystallization [46]. An important consequence of this was that metallic glasses could only be produced in a limited number of forms (typically ribbons, foils, or wires) in which one dimension was small so that heat could be extracted quickly enough to achieve the necessary cooling rate. As a result, metallic glass specimens (with a few exceptions) were limited to thicknesses of less than one hundred micrometers [47]. The first iron based amorphous alloy was produced accidentally in 1966, an iron-phosphorous-carbon alloy. This was found to have exceptional magnetic properties and high induction saturation making possible its use in transformer cores, a milestone of that time. In 1969, an alloy of 77.5% palladium, 6% copper, and 16.5% silicon was found to have critical cooling rate between 100 to 1000 K/s. In 1976, H. Liebermann and C. Graham developed a new method of manufacturing thin ribbons of amorphous metal on a super-cooled fast-spinning wheel. This was an alloy of iron, nickel, phosphorus and boron. The material, known as METGLAS, was commercialized in early 1980s and used for low-loss power distribution transformers (Amorphous metal transformer). METGLAS-2605 is composed of 80% iron and 20% boron, has Curie temperature ($T_c$) of 373°C and a room temperature saturation magnetization of 1.56 Tesla. In the early 1980s, glassy ingots with 5 mm diameter were produced from the alloy of 55% palladium, 22.5% lead, and 22.5% antimony, by surface etching followed with heating-cooling cycles. Using boron oxide flux, the achievable thickness was increased to a centimeter.
The research in Tohoku University and CALTECH yielded multi-component alloys based on lanthanum, magnesium, zirconium, palladium, iron, copper, and titanium, with critical cooling rate between 1 K/s to 100 K/s, comparable to oxide glasses.

In 1988, alloys of lanthanum, aluminum, and copper were found to be highly glass forming. In the 1990s, however, new alloys were developed that form glasses at cooling rates as low as one Kelvin per second. These cooling rates can be achieved by simple casting into metallic molds. These "bulk" amorphous alloys can be cast into parts of up to several centimeters in thickness (the maximum thickness depending on the alloy) while retaining an amorphous structure. The best glass-forming alloys are based on zirconium and palladium, but alloys based on Iron, Titanium, Copper, Magnesium, and other metals are also known. Many amorphous alloys are formed by exploiting a phenomenon called the "confusion" effect. Such alloys contain so many different elements (often a dozen or more) that upon cooling at sufficiently fast rates, the constituent atoms simply cannot coordinate themselves into the equilibrium crystalline state before their mobility is stopped. In this way, the random disordered state of the atoms is "locked in". In 1992, the first commercial amorphous alloy, Vitreloy 1 (Zr\textsubscript{41.2}Ti\textsubscript{13.8}Cu\textsubscript{12.5}Ni\textsubscript{10}Be\textsubscript{22.5} at. %), was developed at CALTECH. In 2004, two groups succeeded in producing bulk amorphous steel, one at Oak Ridge National Laboratory, and the other at University of Virginia. The Oak Ridge group refers to their product as "glassy steel". The product is non-magnetic at room temperature and significantly stronger than conventional steel, though a long research and development process remains before the introduction of the material into public use.

2.2 Physics of metallic glass

For historical reasons, only amorphous materials produced by rapid quenching from the liquid state are called glass [48]. During the cooling of melt, competing process between liquid phase and crystalline phases starts. Thermodynamically materials must exist at the lowest energy state. During natural cooling of alloys, mobility of atoms is high enough to arrange them in periodic forms and this result in crystalline materials, the lowest energy state of mater. During the cooling of melts, the viscosity of the melts increases resulting into low mobility of atoms. Rapid quenching (fast cooling rate) of melts reduces the mobility of atoms by lowering the driving force (Gibbs Energy) and hence, glass is formed. The ease of formation of glassy phase by suppressing crystallinity during solidification is known as glass forming ability (GFA) of material. The lowest cooling rate required to produce glassy material from the melt is called critical cooling rate ($R_c$) and it is the measure of the glass forming ability of an alloy. Higher the $R_c$, lower is the GFA of the material and vice versa. Another measure of the GFA is critical casting
thickness \( (D_{\text{max}}) \) of an alloy and defined as maximum thickness at which a material can be developed in glassy phase. Figure 2.1 shows the BMGs of Ti-Zr-Cu-Pd-Sn alloy in bulk form produced by Cu-mold casting with the \( D_{\text{max}} \sim 12 \text{mm} \).

![Image of 12mm Ti-based bulk metallic glass](image_url)

**Fig. 2.1.** Optical image of 12mm Ti-based bulk metallic glass fabricated by Cu-mold casting.

On heating the glassy metals, one could observe the glass transition temperature \( (T_g) \) from where the mobility of atoms increases as a function of temperature. The increased mobility allows the glass to form into various shapes. However, on further heating amorphous state of glass transforms to crystallinity at crystalline temperature \( (T_x) \). The temperature range between \( T_g \) and \( T_x \) is known as supercooled region \( (\Delta T_x = T_x - T_g) \). This information can be achieved by differential scanning calorimetry (DSC) which accounts the extent of heat energy absorbed or released by the system during heating, cooling or held at constant temperature. A typical DSC trace of the Ti-Zr-Cu-Pd-Tn glassy metal studied for present thesis work is shown in figure 2.2 which illustrate the \( T_g \) and \( T_x \) with arrows.

![DSC trace of Ti41.5Zr10Cu35Pd11Sn2.5 glassy ribbon](image_url)

**Fig. 2.2.** Differential scanning calorimetry (DSC) trace of Ti41.5Zr10Cu35Pd11Sn2.5 glassy ribbon performed at heating rate of 0.67K/s which exhibits glass transition temperature \( (T_g) \) followed by supercooled region \( (\Delta T_x) \) and crystallization temperature \( (T_x) \).
The physics of glass transition is still confusing and different views are reported. The most accepted argument of glass transition is that it's the temperature above which glassy alloy starts to flow. Above the $T_x$, alloy transforms to crystalline configuration by releasing the heat energy and could be observed as an exothermic peak in DSC curve. The ability of the metallic glass to resist crystallization above $T_g$ is called thermal stability and depends upon temperature and time. $T_g$ and $T_x$ are the function of heating rate. The $T_g$ usually occurs at higher temperatures for faster cooling rates and also influenced by strain. Supercooled region is a one measure of thermal stability. Various glass forming parameters derived by using thermal data are discussed in more detail in section 2.3.

It is noteworthy to mention that metallic glass is entirely different from that of conventional amorphous alloys. A schematic diagram presented in figure 2.3 clarifies the difference between conventional amorphous alloys and bulk metallic glasses. Both possess amorphous structure that cannot be differentiated by diffraction techniques. When bulk metallic glass is heated from room temperature with constant heating rate, it enters into a supercooled region by crossing $T_g$. Further heating can lead to the crystallization. Finally system enters into liquid state. In the supercooled region metallic glasses can be treated like plastics. They could be molded and brought into different shapes. Contrary to that, conventional amorphous alloys do not show any supercooled region. They simply crystallize when heated from room temperature. Existence of supercooled region in bulk metallic glasses makes them attractive due to processing capabilities into different shapes even at lower temperatures.

**Phase transformations of metallic glass**

![Phase transformations of metallic glass](image)

Fig. 2.3. A schematic diagram which illustrates the difference between conventional amorphous alloys and bulk metallic glasses.
Atoms in crystalline materials are arranged periodically on three dimensional lattices with a particular space group. Unit cell is the basic building block of the crystalline materials. X-ray diffraction patterns of these metals exhibit sharp diffraction peaks by confirming the presence of long range periodicity (order) of the atoms. Contrary to that, a metallic glass does not possess any long range order in structure and said to be amorphous in nature. To be very precise, atoms are not truly randomly distributed in glasses. The particular distribution of atoms in glassy metals could be seen by the diffuse intensity peak in diffraction patterns and attributed to the short range order of the atoms. Figure 2.4 represents the x-ray diffraction (XRD) pattern and transmission electron micrograph (TEM) of Ti-Zr-Cu-Pd-Sn glassy samples. However, few amorphous metals are considered to possess order over a length scale larger than short range, known as medium range order (MRO), but it does not exhibit periodicity [49-51]. Contrary to crystalline materials, glassy metals do not possess any microstructural features (i.e. grain boundaries, dislocations, etc.). Very specialized instrumentation is required to investigate the complicated short range order of glassy metals. With advanced state of the art instrumentation, it is still hardly possible to differentiate between amorphous, short- and medium range order, and crystalline phases when their size is close to few unit cell dimensions.

![Figure 2.4](image)

Fig. 2.4. X-ray diffraction pattern of Ti-Zr-Cu-Pd-Sn bulk metallic glass. The presence of broad halo and absence of Brag peaks confirms the amorphous nature of the BMGs. Inset of the figure represents the transmission electron micrograph (TEM) of the same sample. SAD patterns of the shows the diffuse ring confirming the amorphous structure of sample. High resolution bright field image does not show any phase separation in the sample.

### 2.3 Assessment of glass forming ability

The glass forming ability (GFA) of a material is the potential of an alloy melt to form the glassy phase by passing through or suppressing crystalline phase during the solidification process. It is a competing process between liquid phase and the crystalline phases [52, 53]. One of the fundamental and long-standing problems of glassy metals is the low GFA. For the development
of sustainable products, the understanding of glass formation along with GFA is the key to developing new BMGs with superior properties.

Glass forming ability could be measured by examining the critical thickness ($D_{\text{max}}$) of the fabricated glass or by measuring the critical cooling rates ($R_c$) required to produce the in bulk form. An alloy possessing higher value of GFA could be achieved in larger dimensions of BMGs and vice versa [54]. Measuring cooling rates of alloy melts during solidification is difficult, while $D_{\text{max}}$ of BMGs depends on method used for the fabrication. However, tremendous efforts have been devoted to develop different parameters to assess the GFA of the alloys. To understand why some compositions last in glassy phase and other are hardly possible, there have been many criteria’s proposed to predict the GFA by indicating about the formation of glass but kinetics of glass formation was not considered [55-60]. However, recently, by considering the kinetics processes (the crystal growth rate, the nucleation rate, or transformation kinetics) some simple glass forming parameters were derived which significantly improve the progress in this area of research [52, 61-63]. Here we define some of the very basic and important parameters which could help to predict the GFA of alloys. All of these parameters use transition temperatures in one or other way by considering kinetic processes, crystal growth rates, transformation kinetics.

2.3.1 Reduced glass transition temperature ($T_{rg} = T_g/T_l$)

An important and earliest parameter proposed by Turnbull for the prediction of GFA of alloys is the reduced glass transition temperature ($T_{rg}$) defined as $T_g/T_l$ where $T_g$ and $T_l$ are the glass transition temperature and liquidus temperature of the alloy respectively [64]. When the liquid alloy is cooled from the molten state down to $T_g$, the viscosity of the melt increases to a high value ($10^{12}$ Pa-s) and as a consequence glass is formed. Therefore, higher values of $T_g$ and lower values of $T_l$ (or higher values of $T_{rg}$) for alloy composition are always favorable for the formation of glassy phase. It was concluded that if the value of $T_{rg}$ is $\geq 2/3$ then homogeneous crystal nucleation will be essentially suppressed and formation of crystalline phases are hardly possible [64]. Typically, the $T_{rg}$ value of the known metallic glasses varies in the range of 0.4-0.7. This criteria only considers the condition under which glass is formed without the accounting the thermal stability of BMGs [54].

2.3.2 Supercooled region ($\Delta T_x = T_x - T_g$)

The supercooled region ($\Delta T_x$) is the difference in the onset of crystallization temperature ($T_x$) and glass transition temperature ($T_g$). It was suggested that BMGs with wider $\Delta T_x$ are more resistant to crystallization by exhibiting adequate thermally stability. On this basis, Inoue
proposed that GFA of the BMGs scales up with the ΔTx [65, 66]. By various studies it came to know that Tg and Tl are independent of thickness and the production method of glassy metals by revealing that it only considers the thermal stability without considering the ease of glass formation.

However, Inoue proposed three empirical rules to predict high GFA of metallic glasses which are quite helpful to select the alloys composition [65, 67] and illustrated in Fig. 2.5. These rules were defined by considering the thermodynamics, kinetics and topological aspects and are listed below.

1. The alloys composition should contain at least three constituent elements.
2. There must be atomic size difference of at least 12% for the main constituent elements.
3. The elements should have large negative heat of mixing.

Fig. 2.5. Inoue's empirical rules to improve the supercooled region (ΔTx) of glassy metals.

2.3.3 The γ parameter [γ = Tg/ (Tg + Tl)]

Thus ΔTx provides the information about the thermal stability and Tg deals only with the ease of formation of glassy phase. GFA is specified as the ease by which a glass forming liquid can be cooled to form an amorphous material without formation of crystalline phases [52, 63]. Lu et al. [63] suggested a new parameter (γ) which includes stability of liquid phase as well as competing process between liquid phase and crystallization phases (i.e., resistance to the crystallization). This parameter is quite use full for the prediction of GFA and is widely accepted among the scientists. The detailed derivation could be found in the literature [52, 53, 63].
2.4 Soft magnetic bulk metallic glasses

Amorphous alloys consist of a random array of atoms, and are normally considered to be isotropic on a long range scale. As a consequence, the ferromagnetic magnetization vector does not contain any type of special anisotropy. It provides a strong drive for the development of soft magnetic materials, and in fact excellent soft magnetic properties were achieved in various amorphous ferromagnetic materials based on iron, cobalt and nickel alloys [68].

2.4.1 Magnetism in amorphous metals

The shape of the magnetic materials can be determined by magnetic free energy associated with the field energy (Zeeman energy), self-field (demagnetization energy), wall energy, and magnetic anisotropy energy. Magnetic Helmholtz energy of the materials could be written as

$$F_M = \int \left[ A(r) \left( \frac{vM}{M_s} \right)^2 - K_1(r) \left( \frac{M \cdot n}{M_s} \right)^2 - \mu_0 (M \cdot H) \right] dr$$ (1)

where $A(r)$ is the local exchange stiffness, $K_1(r)$ is the local magnetic anisotropy energy density, $M$ is the magnetization vector, $n$ is the unit vector parallel to the easy direction of the magnetization and $H$ is the sum of the applied field and demagnetization field vectors. The magnetic anisotropy energy describes the angular dependence of the magnetic energy [69-71]. Anisotropy energy could be further divided into magnetocrystalline, shape and stress energies. Magnetic anisotropy of the materials is the deciding factor for their soft or hard magnetism. For soft magnetic materials, magnetic anisotropy must be extremely small. For the case of crystalline alloys, for example FeNi (Perm alloy) or FeCo, soft magnetism could be achieved by minimizing the magnetocrystalline anisotropy by tuning the chemistry of alloys while shape and stress anisotropy could be minimized by having magnetic grains with large aspect ratios and nearly zero magnetostriction respectively [71].

Due to the random structure amorphous metals are considered the special class of soft magnetic materials [71]. For the case of amorphous metals there is no structural magnetic anisotropy however; internal stresses give rise to the appearance of magnetic anisotropy through magnetoelastic coupling, which is proportional to the saturation magnetostriction constant [72]. One of the important aspects of the rapid solidification related to the magnetic applications is high atomic mobility in the metastable structures. This allows achieving stress relaxation at relatively low temperatures, thus increasing the magnetic softness of the material [72].
2.4.2 Random anisotropy model (RAM) of amorphous alloys

Magnetocrystalline anisotropy of amorphous materials could be understood by the concept of random local anisotropy presented by Alben [73, 74] in his random anisotropy model (RAM) originally developed by Harris [75] by considering the problem of averaging over randomly oriented local anisotropy axes. According to this model, the magnetocrystalline anisotropy could be averaged out by giving rise to the effective magnetic anisotropy \( K_{\text{eff}} \). Contrary to crystalline materials, the idea of crystal field which determines magnetic anisotropy for crystalline materials is replaced by the concept of short-range local field on the scale of several Å where its symmetry, which depends upon the local coordination and chemical short range order, determines local magnetic anisotropy \( K_1(r) \) of amorphous metals [71]. The local anisotropy could be sufficiently large but it averages out due to the fluctuations in the orientation of easy axis. The statistical averaging of the local anisotropy is considered to take place over a length scale that is comparable to ferromagnetic exchange correlation length, \( L_{\text{ex}} \) [71].

The local anisotropy correlation length could be determined by balancing exchange and anisotropy energy densities [71]. By considering these terms, Helmholtz free energy could be expressed as

\[
F_v = A [\nabla m]^2 - K_1 [m \cdot n]^2
\]  

(2)

where \( A = A(r) \) is the local exchange stiffness, \( m = M(r)/M_s \) is the reduced magnetization, \( n \) is the local direction of an easy axis, and \( K_1 = K_1(r) \) is the leading term in the expansion of the local magnetic anisotropy. The chemical and structural fluctuations \( (L_s) \) in the amorphous metals are considered in the order of 10Å [71]. For soft magnetic amorphous materials, \( L_{cs} > L_s \) and statistical averaging is warranted. All local anisotropies lead to a scaling of \( K_1(r) \) by \( (L_{cs}/L_s)^{3/2} \) to arrive an effective anisotropy \( (K_{\text{eff}}) \) by following the random walk through a volume \( L_{\text{ex}}^3 \). This scaling attributes to the significant reduction of magnetic anisotropy in amorphous alloys [71].

2.4.3 Magnetic properties of amorphous transition metals–metalloid (TM-M)

Transition metal metalloid (TM-M) is the most vital class of glassy metals where exceptional soft magnetic properties are very significant for technological application point of view. TM-M glassy alloys contain around 70-80 atomic % of iron, nickel and cobalt with different glass forming elements like boron, phosphorous, silicon, carbon. These alloys are typically produced with rapid quenching of the melt by various techniques i.e. melt spinning, mold casting, extrusion method. These glassy metals with directionless properties resulted in a unique
combination of extremely low coercivity ($H_C$), appreciable saturation magnetization ($M_s$), and low hysteresis losses with high permeability and high resistivity as compared to their counterparts making them attractive for their use in power distribution transformers, electronic transformers, magnetic recording heads, magnetic sensors, magnetic shielding etc. Figure 2.4 represents the coercivity as a function of resistivity and saturation magnetic induction of different materials. The advantages of combination of different properties of metallic glasses are obvious from these illustrations.

![Fig. 2.4](image.png)

Fig. 2.4. (a) Relationship between coercivity and electrical resistivity for BMGs. (b) Relation between saturation magnetization and coercivity. Conventional amorphous alloys and nanocrystalline materials are also presented for comparison. [76].

### 2.5 Mechanical properties of bulk metallic glasses

The study of mechanical properties of metallic glasses started in the early 1970s. Metallic glasses deform elastically with almost negligible plasticity (<0.5%) under uniaxial tension. Britteness of the BMGs is associated with the rapid propagation of shear band. Several theoretical models were proposed to explain the formation of shear bands and their propagation but it was rather difficult to confirm due to the limited dimensions of the samples. However, after the development of metallic glasses in bulk form in last few decades, tremendous efforts have been devoted to understand the deformation of these metals.

#### 2.5.1 Inhomogeneous deformation

Metallic glasses deform inhomogeneously at room temperature and attributed to the nucleation of shear bands which propagate inhomogeneously by giving rise to the catastrophic failure. A typical stress-strain curve of BMGs under uniaxial tension test exhibits only elasticity with a maximum fracture strain of 2% [77]. However, uniaxial compression tests of bulk metallic glass reveal elasticity followed by yielding and perfect plasticity without showing any strain hardening mechanism. Regardless of limited plasticity, local strain within the shear band can be sometime
remarkably high [78]. Width of a shear band is almost in the range of 10-20nm [79]. The catastrophic failure of the BMGs by the rapid propagation of shear band is well explained by free volume theory [80, 81]. Figure 2.5 summarizes data from literature in the yield strength ($\sigma_y$) and the Vickers hardness as a function of young’s modulus (E) for bulk metallic glasses and crystalline metallic alloys [67]. It is clear from figure that strength of the bulk metallic glasses as a function of young’s modulus is almost three times higher than what is reported for crystalline counterparts. It is also obvious that yield strength and hardness of BMGs has a linear relationship with young’s modulus while crystalline materials do not.

![Graph](image)

Fig. 2.5. (a) Tensile strength and (b) Vickers hardness vs. Young’s modulus for various amorphous and crystalline samples [67].

### 2.5.2 Strain hardening or softening

It is has been found that uniaxial compression tests of BMGs do not show any strain hardening before failure and attributed to the absence of dislocations contrary to that of crystalline counterparts. There are only few reports about the observation of strain hardening in literature. For example, glassy metal of Cu-Zr-Al alloy exhibited significant increase in flow stresses during compression with large plasticity (18%) by evidencing the observation of strain hardening in glassy metals [82]. These findings were attributed to the special microstructural features at the atomic scale which facilitated easy and homogeneous nucleation and branching of shear bands during deformation. In contrast to hardening, strain softening was also reported for Zr-based bulk metallic glass [83]. Compression experiments were performed to various strains and hardness of the deformed samples was measured. As a result, hardness of the compressed samples was found to decrease with increasing compression deformation strain and a simple composite model was utilized to explain the hardness variation as function of shear band density.
To summarize, there is no general criteria to examine either strain hardening or softening happens in BMGs.

2.5.3 Nucleation of Shear bands and their propagation

Catastrophic failure of BMGs is attributed to the extremely rapid propagation ($10^{-5}$ s) of shear bands [84]. Thus, the rate controlling process for shear banding is the nucleation. Stress serration during the compression has been observed for several BMGs and is associated with the emission of shear bands [85, 86]. Nanoindentation experiments performed on different BMGs exhibited stepped load displacement curve (pop-in) by showing discrete burst of plasticity [87-89]. These “pop-in” events corresponded to the activation of individual shear bands and strongly dependent on loading rate. A detail observation of plastic and elastic contributions reveal that at sufficiently low indentation rates plastic deformation occurs entirely in discrete events of isolated shear bands.

2.5.4 BMG composites: A way to improve the ductility and toughness

BMGs typically display very high strength but nearly zero plasticity which limits their application as a structural material. This disadvantage led to significant efforts to improve the mechanical properties of BMGs materials, and to develop BMGs composites by in-situ or ex-situ precipitating nanocrystalline phases or dendrites [90-94]. This approach resulted in successful fabrication of some BMGs composites with improved ductility and toughness [90-95].
CHAPTER 3

3-FABRICATION AND EXPERIMENTAL TECHNIQUES

This chapter ‘Fabrication and Experimental techniques’ is divided into two sections. The first section describes the fabrication techniques of metallic glasses and thin films, and the second section explains the instruments used for characterization and investigation of the different properties.

3.1 Amorphous metal technology and fabrication techniques

The first amorphous metal was prepared by Duwez and his coworkers in 1960 with Au-Si alloy system by using splat quenching technique [46]. In this experiment, the samples were rapidly quenched by achieving extremely highly cooling rates ~ $10^6$K/s. Later on, researchers discovered new classes of amorphous metals with more complex systems and multi-constituent elements. These new alloys were possible to fabricate with lower cooling rates (≤100K/s) [67, 96-102]. After recognizing the potential of amorphous metals in various applications and specially the use of soft magnetic properties in amorphous metal power distribution transformers, a tremendous research was carried out to improve fabrication techniques [103]. In this regard, “melt spinning” was developed which resulted to produce high quality, thin and continuous ribbons of uniform thickness with isotropic properties. Various methods of rapid quenching were developed to produce ribbons as well as bulk samples in which single roller melt spinning, copper mold casting, suction casting and tilt casting are very famous for the production of metallic glasses. Here we describe few fabrication techniques which we utilized in the present thesis work.

3.1.1 Arc Melting and Induction Furnace

Preparations of master ingots for the production of BMGs need special care during the melting of constituent elements as the casting of glassy metals is very sensitive to contamination of impurities and oxidation. Inert gas plasma heating method (arc-melting) and induction heating are the two basic techniques used for the preparation of master ingots in the field of BMGs.
Inert gas plasma heating method or arc-melting method uses a continuous arc discharge to provide current flow between tungsten electrode and a refrigerated copper mold as an electrical ground. A flow of cooling water is always maintained to lower the temperature of copper hearth. Current intensities ranges from 100-150A to raise the temperature of alloy to 1500-2500K. A high inert atmosphere and getter process in the presence of Zr/Ti pellets avoids the oxidation of the master ingots.

Induction heating method requires a radio frequency generator to power an inductance coil made of copper pipe. Cooling water always flow inside the copper pipe to lower its temperature. Boron nitride crucible is usually used as a vessel to keep alloying elements inside the induction coil. For the efficient heating, proper matching of the generator’s LC circuit impedance and coil inductance is tuned which induces rf-currents around the crucible. The magnetic permeability of material to the rf-currents responses to eddy current heating.

Fig. 3.1. An optical image of the ingots during the fabrication process inside the twin arc-melter (left). Optical image of the Twin arc-melter used for the preparation of master ingots (right).

In this thesis work we utilized induction furnace and arc-melting furnace for the preparation of master ingots. The whole process was carried out in highly pure (99.9999%) inert gas atmosphere. Intensive care was devoted to keep the designed compositions of the samples. Master ingots were melted several times (at least 5 time each side) to get the homogenous composition inside. Figure 3.1 illustrate the ingot on Cu-hearth during the fabrication process. Twin arc-melter used for this process in Tohoku University, Sendai, Japan is also shown in figure 3.1.

3.1.2 Melt spinning

Melt spinning is more versatile and commonly used technique to produce thin amorphous ribbons. A melt spinner consists of a copper wheel fixed with an induction motor which could rotate it with extremely high speeds (~ 10,000rpm). The surface of the copper wheel is just a
shiny flat plane. This massive copper wheel works as a heat sink for melt. The smoothness and cleanliness of wheel surface is important otherwise in contact surface of ribbon reflects the imperfections of the wheel. There is an induction heating coil made of copper pipe, with flowing cooling water to maintain the lower temperatures, situated just above the copper wheel. This induction coil with radio frequency generator could be used to melt the alloy samples. A quartz tube, as a crucible, could be fixed with a holder which translates along x, y and z-axis to fix it at proper location. One end of the quartz tube could be tuned to very small orifice with diameter 0.1-0.5mm. Initially the tube stays inside the coil to melt the ingots and then could be brought down to the vicinity of the wheel surface (0.1-0.5mm). A precise distance between the orifice of the tube and wheel surface is maintained to constrain the melt and to generate the stable melt flow by ejecting with low pressure of inert gas (argon). By controlling the chamber pressure, temperature of the melt, ejection pressure, diameter of the tube orifice and speed of wheel, ribbons of 20-50um thickness with few mm width and several meter length could be prepared with homogeneous dimensions. A schematic diagram of melt spinner with optical photograph of melt spinner used for the fabrication of sample is shown in the figure 3.2.

![Schematic diagram of melt spinner and optical image of melt spinner](image)

**Fig. 3.2.** A schematic diagram of melt spinner. An optical image of the melt-spinner used for the production of ribbon samples is also shown.

### 3.1.3 Cu-Mold casting

After the invention of complex multi component metallic glass systems which could be fabricated in monolithic amorphous phase even with very low critical cooling rates, it is now possible to fabricate BMGs with larger three dimensional shapes by pouring the melt into Cu-molds. There are two basic techniques by which melt could be inserted into molds. These are the inert gas pressure injection (utilized for present work) presented in figure 3.3 and piston injection. Inert gas (argon) is usually used to inject the melt into molds while in later case solid
piston shoots the melt into copper molds. In both cases, induction melting and inert gas plasma arc heating could be utilized for melting the ingots while quartz tubes with tuned nozzle orifice or boron nitride crucible could be utilized for keeping the master ingots.

Various models of Cu-mold casting have been designed by considering different conditions for different alloy systems. Anyhow, successful fabrication could be achieved by a particular casting technique. Tilt casting method could be used to prepare the samples with larger dimensions. In this method, one could melt the constituent elements with an inert gas plasma arc melting on a copper hearth and then pour the melt in-situ into Cu-mold by tilting the copper hearth. One of the advantages of this technique is that contamination of the master ingot could be reduced during the transferring process between the chambers. Also, the pouring position of melt in this technique is advantageous which reduces the chances of nucleation sites during the fabrication process. However in this melting method one should consider the precipitation of heterogeneous nucleation by incomplete melting at the bottom side contacted with copper hearth.

For Fe-based BMGs we utilized copper mold casting technique with inert gas injection pressure while titanium based BMGs were casted by tilt-casting method. Figure 2.3 represents the schematic diagram of the injection pressure Cu-mold casting method. An optical image of the Ti-based BMGs of 1cm diameter fabricated by tilt casting also presented in figure 3.3.

![Fig. 3.3. Schematic diagram of the injection pressure Cu-mold casting technique. Optical image of 1cm bulk metallic glass prepared by tilt casting method is also presented.](image-url)
3.2 Thin film technology and preparation techniques

Films prepared by the condensation of atomic and molecular entity irrespective of their thickness are called thin films [104]. Generally it takes three steps for the deposition process and these are I) production of atomic/molecular entities, II) their transport and III) condensation on substrate [105]. Deposition of the films starts with nucleation and growth process by making a network structure by giving rise to continuous films [106]. The initial growth of the films strongly depends upon the thermodynamic parameters of the deposited material, surface of the substrate and environment of the transport of material. It is reported that crystallization of the films occurs during the coalescence stage, and orientation of crystals and size of grains depends upon nucleation density [107]. The details of the numerous film deposition techniques are covered in the literature. Here we describe specific vapor phase deposition technique used for the present work.

3.2.1 Pulse Laser Deposition

Since the invention of Laser by 1965, it has been used to produce high temperature and dense plasma by evaporating the small amount of materials with high powered short laser pulses [108]. In 1987, the discovery of high Tc superconducting thin film by Venkatesan and his co-workers by using PLD with low oxygen pressure environment and low processing temperature opened the new horizons for the materials scientists to utilize the advantages of this technique by depositing even with complex compounds [108-111].

Pulse laser deposition technique has numerous advantages for thin film investigations. The stoichiometry of the target composition in the deposited films is quite easy to replicate and also reactive depositions are very advantageous by using this technique. In one way, it is very flexible to deposit multilayer and other way; the simple operation procedure makes it versatile technique [112]. Targets used for the depositions are relatively small and inexpensive and studies with compositional variation could be performed readily. The variety of films deposited by PLD ranges from high Tc superconductors to piezoelectric, ferroelectric films, semi conducting oxides and metallic films to study their tremendous properties. PLD technique itself has been paid great attention for understanding the deposition principles, the influence of various parameters such as laser density, laser pulse frequency, gas pressure etc. PLD is a highly versatile technique in the field of materials science. In the present thesis work, we utilized PLD deposition technique for the depositions of FeBNb/FeNiBNb thin films on Si substrates.
3.2.2 Experimental setup

Pulse laser deposition system consists of a laser, a chamber equipped with vacuum pumps, rotating target holder, and substrate heating holder. A schematic diagram of the PLD system with optical image of the system used for the deposition of films for the present work is shown in the figure 3.4.

![Schematic diagram of Pulse Laser Deposition (PLD) system. Optical photograph of the PLD system used for the deposition of films also presented.](image)

For the deposition of multilayer, the target holder is able to hold few targets at same time which could be fixed in front of laser beam for the depositions of different compositions. Usually, target rotates during deposition procedure otherwise laser could make a deep spot on material. The temperature of the substrate could be raised to 1000°C for the depositions at elevated temperatures. Focused laser beam hits the target at an angle of 45° to make the plume of laser normal to substrate surface. The distance between target and substrate can also be changed by changing the target position. Vacuum pumps attached with chamber can reduce the pressure down to 10⁻⁶ mbar. Also atmosphere inside the chamber is controllable by inserting the inert or reactive gasses.

3.2.3 Important growth parameters

Laser wavelength, pulse frequency, pulse energy, spot size of laser, and mode structure are the important parameters belongs to laser beam which may effects the growth of thin films during deposition. Also the substrate temperature, distance between target and substrate, pressure inside the chamber and deposition geometry such as on or off axis deposition also effects the quality of films. Parameters belong to the material of the target also effects the quality of films and these parameters are reflectance and absorption coefficient, specific heat of material, latent heat and thermal conductivity [113].

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3.3 Characterization techniques

3.3.1 X-ray diffraction

X-ray diffraction method is a non-destructive method to study the structure of the materials. It could provide information about the degree of crystallinity, lattice parameters, size of the crystallites and phases present in the material. Skin depth of the x-rays is quite large [114]. Samples with smaller thicknesses, like thin films, require longer time to count the signals otherwise substrate effect dominates. Bragg stated that if the atoms are arranged in a particular order inside the material then inter planer spacing between the atoms could be considered as grating for x-rays, because the wavelength is comparable to the spacing, and diffraction phenomenon could be observed. According to Brag’s law, \(2d\sin\theta = n \lambda\), where \(d\) is the spacing between the layers of atoms, \(\lambda\) is the wavelength of the X-rays and \(\theta\) is the angle between plane of the angle and source of the X-rays. If Brag’s law is satisfied, one could observe the strong diffraction peaks at particular angles which are a characteristic of a sample.

Opposite to crystalline materials, atoms inside amorphous and glassy solids do not possess long range periodicity. But they have affinity to order them in such a way that they are considerably tightly packed which gives statistical preferences for a particular inter atomic distance. In their diffraction pattern it is only possible to observe the one or two broad maxima which confirm their disordered structure [114]. For example, Fe-based glassy metals showed broad maxima in the range of \(2\theta = 40-50^\circ\) and for Ti-based glassy metals it is in the range of 30-50°. For structural investigation of our samples, we utilized Siemens’ diffractometer (D5000) with Cu-K\(\alpha\) as a source of radiation with \(\lambda = 1.54\text{Å}\) by using monochromatic detector to avoid background signals and is shown in figure 3.5. Metallic glassy ribbons were placed close enough to each other with area of at least 1cm\(^2\) while rod samples were prepared in thin slices with cross sectional area presented to x-ray source. Thin films investigations were carried out by grazing angle technique to reduce substrate effects.

![Fig. 3.5. Optical photograph of x-ray diffractometer (XRD) used for structural analysis of the samples.](image-url)
3.3.2 Electron microscopy and ion beam techniques

Electron microscopes transform an object into image by using the high energy electrons. The wavy nature of accelerated electrons is responsible for the diffraction phenomenon which could be applied to see the surface morphology as well as the internal structure of the materials depending upon the thickness. These energetic electrons could be excited by using high voltages applied to filaments or field emission guns and focused by electromagnetic lenses to several nanometer spot size to enlarge the image to several thousand times while bombardment of heavy ions on the surface of materials could be treated to manufacture different type of shapes or digging deep into the materials. These state of the art techniques made possible to look at the nanometer scale to understand the material at the very fundamental level. We have used scanning electron microscopy (SEM), focused ion beam (FIB) technique and transmission electron microscopy (TEM) for the analysis of surface morphology, film thickness measurement, and structural investigations for samples used in the study.

3.3.2.1 Scanning electron microscopy/ Focused ion beam

Scanning electron microscope is versatile technique which provides very useful information about the surface morphology, shape and size of grains, size of the particles of the samples at nanometer scale.

A beam of electrons, generated from the electron gun made of tungsten filament, accelerates toward an anode. The potential difference between electron gun (cathode) and anode is usually few tens of kilo volts depending upon the nature of material and type of analysis. This beam of electrons is collimated by electromagnetic condenser lens and then focused by second condenser lens (objective lens) on the surface of the sample. The electron beam raster on the surface of the sample with electromagnetic scanning coil. The interaction between electrons and surface of the sample generates variety of signals which provides very useful information for the sample. Imaging with secondary electron released from the surface is the primary method for the analysis. These secondary electrons are detected by scintillated photomultiplier system and resulting signal provides the image of the object.

Field emission gun SEM (FEG-SEM) provides better brightness as compare to the thermionic emission gun SEM. When an extremely high electrical field is subjected to the surface of metal (tungsten), there is a probability for the electrons to escape from the surface which is known as tunneling current. More electrons are drawn from metal as compare to the thermionic emission
which enhances the brightness to a great extent. Higher beam currents in small diameter of beam provide better resolution in imaging as compare to thermionic emission SEM.

Focused ion beam is a versatile tool for removal of material from the specimens. It could be used as a milling machine to prepare three dimensional shapes at nanoscale within short time and it is very convenient to measure the thickness of the thin films. Focused ion beam (FIB) microscope uses the heavy ions instead of electrons which could also be used for imaging. Where imaging is the only purpose, SEM is advantageous otherwise heavy ions may modify the surfaces. Because of the low melting temperature (30°C) and low vapor pressure, Ga based Liquid Metal Ion Source (LMIS) is usually used in FIB microscopes. By applying a high positive voltage to the liquid metal, it takes a conical shape and its apex continuous to grow till evaporation of the metal takes place.

A dual beam system consist of a SEM and FIB provides the facility to image the surface by using electrons of SEM while at the same time milling process by using heavy ions (e.g. Ga) could be carried out. This facility provides the quick measurement of surface analysis as well as measurement of film thickness. A schematic diagram of the dual beam SEM/FIB along with optical photograph of the instrument used for present work is presented in figure 3.6.

3.3.2.2 Transmission electron microscopy

Transmission electron microscope (TEM) consists of vertical column which contains electron gun (thermionic or field emission), electromagnetic lenses, few apertures and a sample holder. Electrons accelerate, due to the high potential difference, in a fine and very small tube (diameter is around millimeter) down to a very thin specimen. Interaction with thin specimen could cause transmittance, diffraction, and absorption. The transmitted electrons are focused by an objective
lens into an image which is usually 50-100 times enlarged. For further magnification a series of intermediate and projector lenses are used and finally it is projected on a fluorescent screen. A schematic diagram of TEM with different components is presented in figure 3.7.

![Schematic diagram of TEM](image)

**Fig. 3.7.** A schematic diagram of transmission electron microscope (TEM).

### 3.3.3 Atomic force microscopy

Atomic force microscope (AFM) is versatile technique to investigate the surface morphology of metallic, insulating and semiconducting samples. It consists of a sharp tip attached at the free end of a cantilever which could deflect or bend in vertical direction relative to the surface morphology of the sample. Force between tip and the surface of the sample is usually interatomic known as Van der Waals force. This force could be either attractive or repulsive depending upon the distance between tip and surface of sample. Figure 3.8 represents the behavior of force with the separation between tip and sample surface. A sharp laser beam reflects from the tip end of the cantilever and is detected by a calibrated position detector to measure the amplitude of deflection, and this is known as the contact mode. However, oscillating or tapping mode is most favorable to avoid damaging the surface of the sample and usually used for soft and elastic samples. The cantilever oscillates near the surface of the samples and the change or drop in resonance frequency provides the information about the tip contact with the surface.

![Interatomic force diagram](image)

**Fig. 3.8.** Interatomic force as a function of distance between tip and surface.
3.3.4 Magnetic force microscopy

Magnetic force microscopy (MFM) is used to study the magnetic domain structure in magnetic materials. Stray magnetic field at the surface of sample is detected by sharp tip coated with magnetic material. When a magnetic tip, attached with one end of cantilever, is close to the surface of the magnetic sample, then two type of interaction are possible and that are Vander wall interaction and magnetic interaction. Magnetic interactions are long range and weak interactions as compare to the Van der Waals and if the sample is at the distance of few tens of nanometer from the surface, it feels only the magnetic ones. In magnetic force microscopy, two-pass method is used to reduce the influence of topography. The fist one provides the information about the topography of the sample while other one, where the tip is lifted to some fixed distance, the magnetic interactions are only considered which provides the magnetic image. Figure 3.9 illustrate the MFM image of the magnetic domains performed on the sample surface.

![MFM signal](image)

**Fig. 3.9.** MFM image of the magnetic domains at the surface of the sample.

3.3.5 Differential scanning calorimetric and thermal analysis

Differential scanning calorimetry (DSC) and differential thermal analysis (DTA) are techniques in which a specimen undergoes a programmed temperature range and its thermal effect is analysed. In this way, any event either absorbs or releases heat could be examined which helps to measure the temperature of phase transitions, to investigate of disorder/order transitions, and to determine the heat capacity. In DTA, the sample and reference material are heated in a temperature range and the temperature difference is measured as a function of temperature. In DSC, the specimen and reference material are heated while the difference in their energy inputs is measured as a function of temperature.

Few milligram weights of the samples were used and all samples were analyzed in highly pure argon flow atmosphere with heating rate of 0.67K/s.
3.3.6 Magneto-thermo gravimetry

Magnetic thermo gravimetric analysis is an extremely sensitive method to determine the existence of magnetic phases as well as kinetics of magnetic grain growth with temperature in magnetic materials. The magnetic force exerted by a gradient magnetic field on the sample is measured by a sensitive balance. The balance consists of a small pan which sits inside the small furnace equipped with a thermometer. The magnetic force on the sample is

\[ F_z = \nabla_z (mB) \]

Where \( m \) is magnetic moment induced by the magnetic field. A sample of few milligrams is measured with temperature range from 50-950°C while different heating rates could be used. Although this method provides relative values of the magnetization but critical temperatures are readily measured.

3.3.7 Vibrating Sample Magnetometer

Vibrating sample magnetometer (VSM) works on the principle of Faraday law of induction. It consists of an electromagnetic that generates steady magnetic field; set of stationary pick-up coils (4 coils) for detection of induced voltage, and a sample holder in the centre of pick-up coils which is connected to mechanical vibrator. In the centre of pick-up coils, the sample vibrates vertically in the steady magnetic field produced by electromagnet. Stray field associated with sample oscillates through the pick-up coils and hence induced voltage could be generated which provides the information about the strength of magnetic material and its response in the presence of applied magnetic field.

VSM is highly sensitive instrument with capability of measuring magnetic moment of \( 10^{-5} \) emu. Maximum magnetic field of one Tesla (in our case) is possible to apply by the electromagnet. The size of the samples is limited because of small space between the pickup coils. We utilized VSM (Model 155 EG&G Princeton Applied Research) for the measurement of magnetic response of samples in the presence of external magnetic field at room temperature in the current thesis work. An optical image of VSM used for current work is given in the figure 3.10.
3.3.8 Super Conducting Quantum Interference Device

Superconducting quantum interference device (SQUID) is a magnetometer capable of measuring the magnetic response of material in external magnetic field $M(H)$ and temperature behavior of magnetism $M(T)$ in the range of 4-300K. In SQUID, magnetic field is generated by a superconducting magnetic in vertical direction around the sample which is surrounded by superconducting pick up coils. Sample moves up and down through the superconducting pickup coils situated in the centre of superconducting magnet and generates changes in magnetic flux in pickup coils. This changing magnetic flux induces electric signal proportional to the magnetic strength of the sample and transported to the SQUID detector. This detector consists of a ring of a superconducting material with a tunneling barrier, called Josephson junction, on each side of the ring. To keep the superconducting state, the components are always immersed in an evacuated vessel filled with liquid helium. A schematic diagram along with photograph of the SQUID (MPMS2, Quantum Design) used for current thesis work is presented in figure 3.11.

Fig. 3.11. Schematic illustration of the internal configuration of SQUID. Optical photograph of the SQUID used for magnetic properties measurement at low temperature is also shown.
3.3.9 Four probe setup for transport measurement

A conventional four probe electrical measurement setup is used for the transport measurement of the samples connected with a cryostat. Resistance of the sample could be measured from 800K down to 40K. To avoid from the contact resistance and artifact we used four probe terminals instead of two probes. The contacts were made by depositing the gold/platinum on the surface of the samples and then tin soldering or silver paste was utilized to make the contacts with the wires. All measurements were carried during the cooling of the samples. An optical image of the setup (Keithly 2400) is presented in figure 3.12.

![Image of four probe setup](image)

Fig. 3.12. An optical photograph of four probe setup used for resistivity measurements.

The resistance of the samples could be calculated by measuring I-V curves. According to Ohm’s law of resistance $V = IR$, where $V$ is the voltage drop across the terminals, $I$ is the current and $R$ is the resistance of the sample. When resistance is known, resistivity of the sample could be calculated by measuring the cross sectional area, and the length of the sample.

$$\text{Resistivity} = R \times (A/l)$$

3.3.10 Nanoindentation

Instrumented nanoindentation is a potential method for quantitative analysis of numerous mechanical properties. It is a depth or load sensing technique which is usually performed to measure the elastic modulus (E) and hardness (H) of a material possessing small dimensions like thin films and coatings and these load-displacement curves are the characteristics of material.

The nanoindenter consist of an optical microscope, the indenter system, moveable x-y table and a computer. Optical microscope is used to position the area of the sample where the indents should be performed. The indenter is mounted on a hollow aluminum tube, which is suspended by a system of leaf springs inside a housing head. The load is provided by a coil and magnet assembly located at the opposite end of the indenter column and inside the indenter housing head.
A typical load-displacement curve by nanoindenter is represented in figure 3.13 (a). This figure also represents some of the particular features which are used for the analysis of the mechanical properties and these are maximum depth of penetration ($h_{\text{max}}$), maximum load ($L_{\text{max}}$), the initial unloading contact stiffness ($S$) and the contact depth ($h_c$). Figure 3.13(b) is the representative schematic of these defined parameters.

Oliver and Pharr developed a method to measure the elastic modulus and hardness from the load displacement curve [115, 116]. The procedure is based on the observation that the unloading data is well described by a simple power law relation as

$$P = A (h - h_f)^m$$

where $h_f$ is the final displacement after unloading, $A$ and $m$ are fitting parameters. The initial unloading slope, measured at peak load and displacement, gives the stiffness of the contact as $S = dp/dh$, the contact depth ($h_c$) at the peak load is also calculated from load-displacement curve as

$$h_c = h_{\text{max}} - h_s = h_{\text{max}} - \frac{p_{\text{max}}}{S}$$

where $h_s$ is the amount of depression of the contact perimeter below the original unindent surface. For lower loads the geometric constant, $\varepsilon$, of Berchovich tip is 0.75.
CHAPTER 4

4- SUMMARY OF RESULTS

We briefly review the salient features of the detailed papers/manuscripts that are attached to this Thesis. The first paper is on a depth sensing nano-indentation investigation performed radially on a Fe$_{71}$B$_{23}$Nb$_6$ demonstrating that the hardness decreases towards outer most surface of a BMG due to surface softening, and indicating the role of rate of quenching on the variation of the local short range order of a BMG. The subsequent papers are on the consequence of Ni substitution for Fe in FeBNb, and FeBNbY alloys rendering it possible to grow bulk glassy rods when an otherwise ‘ribbon only’ situation prevails. This study is followed by exploiting the superior mechanical properties even in a thin film form which is magnetic, transparent, as well as exhibits various manifestations of spins involving anisotropy with film thickness. We then discuss fabrication and physical property studies of toxic elements free Ti-based alloys designed with the help of CALPHAD methodology obtaining BMGs of at least five compositions in range of upto 14mm diameter. These are the highest GFA materials to be reported and only preliminary selected results are presented herein.

4.1 FE-BASED BULK METALLIC GLASSES

4.1.1 The observation of surface-softening in Fe-based metallic glasses (supplement-1)

In order to investigate the effect of cooling rates on mechanical properties (hardness and elastic modulus) of Fe$_{71}$B$_{23}$Nb$_6$ bulk metallic glass, instrumented nanoindentation was performed along the radius of the half millimeter rod. Typical load displacement curves obtained at the central axis (reference line) of the rod and at the outer most surface from the central axis are presented in figure 4.1.
Fig. 4. 1. The typical load-displacement curve for the indents at reference line and at the outer most position of the rod.

Elastic modulus (E) and hardness (H) were found to be decrease along the radius from the reference line and presented in figure 4.2. In this study the value of H is the lowest at the surface, which can be considered as an indication of surface-softening of the material as reported for other systems [131]. The different values of E at different positions points out that the local atomic arrangements at different locations are probably not similar although overall structure of the sample is amorphous. The elastic modulus was found to decrease by about 15 % from the reference line to the outer surface of the sample.

Cooling rate during casting plays a vital role in the formation of BMG. During casting, even a small difference in cooling rate inside the material can lead to variation in local atomic arrangement resulting in change of mechanical properties. This phenomenon indicates that the local atomic arrangement is highly influenced by the cooling rate during casting process. This kind of surface softening would originate the ductility of the material [132].

Fig. 4.2. Variation of elastic modulus (E) and hardness (H) along the radius of the rod from the reference line. (a) Shows value of E before and after correcting contribution of pile-up material. (b) Shows value of H before and after correcting the contribution of pile-up material.
4.1.2 Soft magnetic Fe-Ni-B-Nb bulk metallic glasses (supplement-2&3)

The effect of partial substitution on Fe by Ni was investigated on glass forming ability, thermal stability, magnetic behaviors and electrical transport properties of Fe$_{72-x}$Ni$_x$B$_{24}$Nb$_4$ glassy alloy with $x \simeq 2-14$. We observe that substitution of Fe by Ni significantly improves the glass forming ability and, as a result, the fabrication of rods of half millimeter diameter can be possible which were rather impossible in the case of unsubstituted Fe$_{72}$B$_{24}$Nb$_4$ alloy [117]. Table I summarizes the effect of Ni addition on different transition temperatures along with glass forming parameters.

TABLE I. Glass transition temperature ($T_g$), crystallization temperature ($T_c$), supercooled region($\Delta T_c$), melting temperature ($T_m$), liquidus temperature ($T_l$), reduced glass transition temperature ($T_{rg}$), $\gamma$, and $\delta$ of Fe$_{72-x}$Ni$_x$B$_{24}$Nb$_4$ with different concentration of Ni as determined by thermal analysis by DSC and DTA.

<table>
<thead>
<tr>
<th>x</th>
<th>$T_g$ (K)</th>
<th>$T_c$ (K)</th>
<th>$\Delta T_c$ (K)</th>
<th>$T_m$ (K)</th>
<th>$T_l$ (K)</th>
<th>$T_{rg}$</th>
<th>$\gamma$</th>
<th>$\delta$</th>
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<td>1348</td>
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<td>0.379</td>
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<td>0.393</td>
<td>1.575</td>
</tr>
<tr>
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<td>1410</td>
<td>0.575</td>
<td>0.385</td>
<td>1.426</td>
</tr>
</tbody>
</table>

Existence of ferromagnetism in amorphous metals is due to the exchange interactions between the spins of unpaired electrons [118]. $T_c$ depends on interactions between magnetic atoms and increases if the exchange coupling among them becomes stronger. It was found that $T_c$ of the studied alloy linearly increased with substitution of Fe by Ni as shown inset of Fig. 4.3(a). Increase in $T_c$ with Ni content is not obvious, because $T_c$ of the Ni (~631K) is less than that of Fe (~1044K) and exchange coupling between Fe-Fe atoms is stronger than Fe-Ni atoms. It could be anticipated that rise in $T_c$ with substitution of Ni is due to the smaller size of Ni ($r \sim 0.162$nm) as compared to the Fe atoms ($r \sim 0.172$nm) [119]. This size difference reduced the distance between interacting atoms and enhances the exchange interactions by giving rise to $T_c$ with the addition of Ni content [119-121]. Low-field magnetic behaviors of as-quenched samples revealed minimum value of $H_c$ for 8% of Ni concentration and shown in Fig. 4.3(b). This lowest value of $H_c$ could be attributed to much higher packing density, higher degree of amorphicity and structural homogeneity of glassy alloy as particular composition reveals good glass forming ability by exhibiting highest values of glass forming parameters $T_{rg}$, $\gamma$ and $\delta$ [12, 122].
Fig. 4.3. (a) Temperature dependence magnetization of as-quenched glassy ribbons of Fe$_{72-x}$Ni$_x$B$_{24}$Nb$_4$ alloys where x~2-14. Inset of the figure represents the dependence of T$_c$ of as-quenched glassy ribbons with Ni concentration. (b) H$_c$ of Fe$_{72-x}$Ni$_x$B$_{24}$Nb$_4$ as-quenched glassy ribbons as a function of Ni concentration. Inset shows the saturation magnetization of same samples as a function of Ni concentration.

The effect of annealing temperature on evolution of different nanocrystalline phases and magnetic properties was investigated for Fe$_{60}$Ni$_{12}$B$_{24}$Nb$_4$ alloy (due to the large $\Delta T_c$) and presented in figure 4.4. Magnetic softening behavior was found for samples annealed at temperatures ~833K and attributed to structure relaxation due to the reduced elastic anisotropy [13, 123]. On further annealing at more elevated temperatures, initial crystallization of ribbons revealed development of bcc-Fe and fcc-FeNi phases as confirmed by XRD analysis and shown in figure 4.4(a). As a result, coercivity of the samples further reduced and could be explained by random anisotropy (RAM) model [inset of Fig. 4.4(b)] [124, 125]. According to this model, improved soft magnetic properties can be expected for grain sizes smaller than the exchange correlation length ($L_{ex}$) where the effective anisotropy ($K_{efl}$) overcomes the local magnetocrystalline anisotropy of the grains [124, 125]. Development of magnetic phase with annealing temperature could also be observed in MTG analysis of the annealed ribbons as presented in Fig. 4.4 (b). However, magnetic hardening was observed for samples annealed at more elevated temperatures (≥861K) and may be attributed to the magnetocrystalline anisotropy of large size grains developed during annealing [124, 125].
Fig. 4.4. (a) X-ray diffraction pattern of Fe$_{60}$Ni$_{12}$B$_{24}$Nb$_{4}$ glassy ribbons annealed at different temperatures. The pattern of as quenched glassy alloy is also shown for comparison. (b) Temperature dependence magnetization of as-quenched glassy ribbons of Fe$_{72-x}$Ni$_x$B$_{24}$Nb$_4$ alloys where $x \sim 2-14$. Inset of the figure represents the dependence of $T_c$ of as-quenched glassy ribbons with Ni concentration.

Low temperature electrical transport properties of various as-quenched glassy alloys were investigated in the temperature range of 77-300K and presented in figure 4.5 (a). All investigated compositions showed weak temperature dependent variation with positive temperature coefficient and satisfied the Mooij’s criteria [126, 127]. Addition of Ni decreased the resistivity of the samples appreciably. Room temperatures resistivity measurements of annealed samples of Fe$_{60}$Ni$_{12}$B$_{24}$Nb$_{4}$ alloy were investigated and shown in figure 4.5 (b). Initially it increased for 843K annealed sample and may be attributed to the interface energy between grains and phase boundaries. However, on further annealing it decreased in a similar manner to the polycrystalline materials wherein the resistivity is inversely proportional to the grain size [127].

Fig. 4.5. (a) Temperature dependence of resistivity of as quenched glassy ribbons of Fe$_{72-x}$Ni$_x$B$_{24}$Nb$_4$ with $x \sim 2, 6, 12, \text{and} 14$. (b) Room temperature resistivity as a function of annealing temperature of Fe$_{60}$Ni$_{12}$B$_{24}$Nb$_4$ ribbons.
4.1.3 Magneto-Thermo-Gravimetric technique to investigate the structural and magnetic properties of Fe-B-Nb-Y Bulk Metallic Glass (supplement-4)

The magneto-thermo-gravimetry (MTG) of ferrous \((\text{Fe}_{0.72}\text{B}_{0.24}\text{Nb}_{0.04})_{95.5}\text{Y}_{4.5}\) glassy ribbon and BMG samples have been studied in detail (Fig. 4.6) and the results were compared with the data from DSC measurement. In this study, thermal behaviors, including the \(T_c\), \(T_g\) and \(T_x\) of the ferrous \((\text{Fe}_{0.72}\text{B}_{0.24}\text{Nb}_{0.04})_{95.5}\text{Y}_{4.5}\) glassy ribbon and BMG were investigated by the MTG analyses sequentially to 1170 K. The results can be summarized as follows.

- The \(T_c\) decreases due to structural relaxation of the glassy ribbon sample, which means the internal stress caused by quenching process, can influence the magnetic property.
- Concomitant with structural amorphous phase there is a 2nd magnetic amorphous phase observed in the as-cast BMG sample, the temperature dependence of which does not change although \(T_c\) shifts to higher temperatures with annealing for longer times.
- Shift in \(T_c\) is a result of magnetic short range order (MSRO) changes that occur in the samples. Addition positive mixing enthalpy can enhance the GFA and thermal stability.
- The MTG measurement is the most effective and convenient method for determining structural and magnetic transition as well as the MSRO of the amorphous materials.

![MTG traces and DSC](image)

Fig. 4.6. (a) A DSC curve and MTG traces of the ferrous \((\text{Fe}_{0.72}\text{B}_{0.24}\text{Nb}_{0.04})_{95.5}\text{Y}_{4.5}\) (b) glassy ribbon and (c) low field magnetization of BMG as a function of temperature from RT to 1170 K.

4.1.4 Effect of Ni-substitution on glass forming ability, mechanical and magnetic properties of FeBNbY bulk metallic glasses (supplement-5)

It is well known that \(Y\) stabilizes FeNbB alloys to form more easily BMGs. The effect of substituting Fe with Ni should in principle enhance this property. To confirm this, a series of amorphous metallic glassy alloy of \((\text{Fe}_{0.72-x}\text{Ni}_x\text{B}_{0.24}\text{Nb}_{0.04})_{95.5}\text{Y}_{4.5}\), \(x \sim 0.02, 0.04, 0.06\) and 0.10 were prepared in the form of ribbons. The values of different parameters (\(\Delta T_s, T_{np}\) and \(\gamma\)) governing
the glass forming ability of a material were calculated and summarized in Table II. It was found that among the series of alloys of \((\text{Fe}_{0.72-x}\text{Ni}_x\text{B}_{0.24}\text{Nb}_{0.04})_{95.5}\text{Y}_{4.5}\) composition, the maximum values of glass forming parameters were found \((\Delta T_x = 94, T_{rg} = 0.644, \text{and } \gamma = 0.435)\) for \(x \sim 0.06\).

**TABLE II.** Glass transition temperature \((T_g)\), crystallization temperature \((T_c)\), supercooled region \((\Delta T_x)\), melting temperature \((T_m)\), liquidus temperature \((T_l)\), supercooled region \((\Delta T_x = T_c - T_g)\), reduced glass transition temperature \((T_{rg} = T_g / T_l)\), and the \(\gamma \left[ T_x / (T_l + T_g) \right]\) parameter of as-quenched ribbons of \((\text{Fe}_{0.72-x}\text{Ni}_x\text{B}_{0.24}\text{Nb}_{0.04})_{95.5}\text{Y}_{4.5}\) alloy with different concentration \((x)\) of Ni determined from thermal analysis by DSC and DTA. Critical diameter \((D_{\text{max}})\) of cylindrical rods obtained for different alloys is also summarized in table.

<table>
<thead>
<tr>
<th>(x)</th>
<th>(T_g) (K)</th>
<th>(T_c) (K)</th>
<th>(\Delta T_x) (K)</th>
<th>(T_m) (K)</th>
<th>(T_l) (K)</th>
<th>(T_{rg})</th>
<th>(\gamma)</th>
<th>(D_{\text{max}}) (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td>808</td>
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<td>1348</td>
<td>0.599</td>
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</tr>
<tr>
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<td>842</td>
<td>924</td>
<td>82</td>
<td>1295</td>
<td>1332</td>
<td>0.632</td>
<td>0.425</td>
<td>3</td>
</tr>
<tr>
<td>0.06</td>
<td>850</td>
<td>944</td>
<td>94</td>
<td>1284</td>
<td>1319</td>
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<td>0.435</td>
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</tr>
<tr>
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<td>882</td>
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<td>1285</td>
<td>1320</td>
<td>0.604</td>
<td>0.416</td>
<td>3</td>
</tr>
</tbody>
</table>

Substitution of Fe by Ni in FeBNbY alloy has indeed significantly improved the glass forming ability. As a consequence, BMG rods were fabricated with the largest diameter of 4.5mm of \((\text{Fe}_{0.66-x}\text{Ni}_x\text{B}_{0.24}\text{Nb}_{0.04})_{95.5}\text{Y}_{4.5}\) composition. The XRD-patterns of the critical diameters of rods for particular compositions are shown in figure 4.7.

![XRD patterns of the cross sections critical diameter of the rods](image)

**Fig. 4.7.** XRD patterns of the cross sections critical diameter of the rods \((\text{Fe}_{0.72-x}\text{Ni}_x\text{B}_{0.24}\text{Nb}_{0.04})_{95.5}\text{Y}_{4.5}, x \sim 0.02, 0.04 0.06 and 0.10.**

The soft magnetic properties of the alloys were investigated and found that \((\text{Fe}_{0.66}\text{Ni}_{0.06}\text{B}_{0.24}\text{Nb}_{0.04})_{95.5}\text{Y}_{4.5}\) exhibits the lowest coercivity among the studied alloys and can be attributed to its high glass forming ability [12, 128]. By considering the lowest coercivity and the maximum glass forming ability with appreciable large supercooled region \((\Delta T_x)\), effect of structural relaxation on the soft magnetic properties of \((\text{Fe}_{0.66}\text{Ni}_{0.06}\text{B}_{0.24}\text{Nb}_{0.04})_{95.5}\text{Y}_{4.5}\) glassy ribbons were investigated. Figure 4.8 presents the values of \(H_c\) as a function of annealing temperature. Coercivity was found to decrease with the annealing temperature. The lowest value of \(H_c \sim 0.06\) Oe was found for the ‘as quenched’ sample annealed at 823K. However, further annealing above 823K drastically increased the coercivity. Magneto thermo gravimetry (MTG)
patterns of the annealed samples are presented as inset of figure 4.8. It is obvious that temperature dependent behavior of magnetization of the annealed samples is very similar to that of as quenched samples by confirming that there is no magnetic phase separation on thermal treatment. Extremely low coercivity of the glassy metals is due to the dense packed glassy structure which further improved on annealing. [12, 128-130].

Fig. 4.8. Coercivity of (Fe_{0.66}Ni_{0.06}B_{0.24}Nb_{0.04})_{95.5}Y_{4.5} glassy ribbons as a function of annealing temperature. Ribbons were annealed for 600 sec. For comparison, H_c of as-quenched glassy ribbon is also shown. Inset: magneto thermo gravimetry of the ribbons annealed samples.

4.2 THIN FILM STUDY

One of the great exploitation of the superior mechanical properties of the BMGs is the possibility of designing them for low dimensions, i.e. thin films. In the next section we discuss manifestations of magnetic properties on producing films of thickness as low as 8nm when the films is really transparent with a high transmission coefficient and yet remains strongly magnetic! We discuss some of the changes that occur as a function of film thickness in the range 8 to 400nm.

4.2.1 Exchange bias in Fe-B-Nb thin films (supplement-6)

Amorphous thin films of Fe_{77}B_{17}Nb_{6} alloy prepared by Pulse Laser Deposition (PLD) have been studied to investigate their magnetic properties. Films of different thicknesses (200-400nm) were cooled from room temperature down to 5K at remnant state of magnetization (M_r) and inplane magnetic hysteresis loops were measured. Figure 4.9 represents the inplane magnetic hysteresis loop of the 400nm film performed at 300K and 5K. Rom temperature hysteresis loop revealed a typical feature of soft magnetism of Fe-based amorphous alloys with coercivity of \(~0.1\)Oe and could be explained by random anisotropy model (RAM) of amorphous alloys [11, 12, 128, 142-144]. For low temperature investigations, sample was cooled from 300K down to 5K with positive sate of remnant magnetization (+M_r) in the absence of any applied magnetic field.
A shift in hysteresis loop toward negative magnetic field axis with asymmetric shape was observed which clearly indicates the effect of exchange bias. This finding in an amorphous matrix is indeed new and needs to be understood in detail.

Fig. 4.9. Inplane magnetic hysteresis loop of 400nm film performed at room temperature and 5K. For low temperature measurement the sample was cooled from positive remnant state of magnetization (+M₀).

In this preliminary study we have used film of ~200nm thickness for further investigation. Figure 4.10 represents the in-plane magnetic hysteresis loops of 200nm thick film performed at as a function of temperature (5-50K). For these measurements, sample was zero field cooled to 5K and the M-H loop was measured in fields upto 150Oe. It is clear from the Fig. 4.10(a) that the shift in the hysteresis loop performed at 5K indicates the effect of exchange bias with typical values of exchange bias force (H_{EB}) ~ 19Oe and coercivity (Hc) ~23Oe. On increasing temperature from 5K, H_{EB} begins to decrease continuously and magnetization reversal became fully symmetric at 30K temperature. In Fig. 4.11 we plotted the temperature dependences of H_{EB} for the samples of thickness 200nm and 400nm. The value of H_{EB} decreased exponentially with increasing temperature, as expected for thermally activated behavior.

Fig. 4.10. Inplane magnetic hysteresis loop of 200nm thin film at different temperatures (5-50K) performed after cooling the sample from negative remnant state of magnetization (-M₀). (a) Represents the shift of the hysteresis loop from origin. (b) Hysteresis loops do not show any shift above 20K.
Fig. 4.1. Exchange bias field ($H_{EB}$) as a function of temperature after cooling the sample from negative state of remnant state of magnetization ($-M_R$).

Temperature dependence of zero field cool (ZFC) and field cool (FC) magnetization was performed for the film of thickness $t \sim 200\text{nm}$ under probe fields in the range of $5\text{-}20\text{Oe}$ and presented in Fig. 4.12. The most obvious feature of the ZFC curve is the inflection point $T_f$ at the low temperatures. Above $T_f$, magnetization curve follows a smooth evolution characteristic of a ferromagnetic state up to room temperature. On the other hand, the FC curves remains roughly constant with increasing temperature and overlaps the ZFC curve at higher temperatures. This behavior is typically known for glassy systems and suggests that the system probably enters into a spin-glass-like state at low temperatures, or at least a spin freezing phenomena is occurring that can be easily overcome by the application of increasing magnetic field [145, 146].

Fig. 4.12. ZFC (solid symbols) and FC (open symbols) temperature dependence of magnetization $M (T)$ with different probe fields from $50\text{e}$ to $200\text{e}$ of $\sim 200\text{nm}$ thin film.
Low temperature spin-glass-like disorder has been recently experimentally confirmed at the surface layer of various nano-sized magnetic particles and it was attributed to be an origin of observed low temperature anomalies in different crystalline systems [147, 148]. While exploring the mechanism behind exchange bias anisotropy, one can suggest that there might be chemical heterogeneity between the constituent elements at the sub-nanometer regime, produced due to the multiphase target, which gave rise to regions of different disorder in the material, very similar to the case of two phase nanocrystalline alloys [149, 150]. Highly disorder regions between different phases are the most probable candidate for occurrence of frustration and subsequent spin freezing effects in the investigated material. At temperatures below $T_f$ the presence of surface frozen spins favor the regions of strong ferromagnetic phases to be magnetize in the direction of remnant magnetization ($\pm M_R$ or $M_R$), resulting in the observed shift in the hysteresis loops. For the deep understanding of the phenomenon, further investigations are currently in progress.

4.2.2 Magneto optical properties of amorphous Fe-B-Nb thin films (supplemet-7)

Thin films of Fe$_{77}$B$_{17}$Nb$_6$ alloy thickness 8 and 11nm were deposited by using PLD to investigate the magneto-optical properties. Films were found fully amorphous by x-ray analysis. Spectroscopy of the films reveals that films were continuous. Curie temperature of the films is appreciably high (~842K) and is therefore useful for application at high temperatures. Films were found more than 60% transparent in visible regime. Figure 4.13 represents the Faraday rotation angle ($\theta_f$) of both films measured at $\lambda$=590nm. Saturation Faraday rotation angle found to increase with the thickness of the films. It is as high as 11.8deg/$\mu$m for 11nm thick film and as low as 3 deg/$\mu$m for 8nm measured at 611nm wavelength. Also, magnetic field saturating the Faraday rotation angle increased with the thickness of the film. It is 3kOe for 8nm and 4.8kOe for 11nm thick film.

![Fig. 4.13. Faraday rotation as a function of applied magnetic field (perpendicular to the plane) for 8 and 11nm films measured at 611nm wavelength.](image)
Figure 4.14(a) represents the Verdet constant ($V$) of films as a function of wavelength. It increased for both films and a linear relation was observed between $V$ and $\lambda$. At smaller wavelengths, Verdet constant of studies films are almost similar. As the $\lambda$ increases, $V$ of 11nm film increases sharply as compare to thinner film. For example at $\lambda=611\text{nm}$, 11nm film exhibits 21.4 deg/Oe-cm and dropped to 9.8 deg/Oe-cm for 8nm thin film. Values of $V$ are considerably high as compare to the other reported material used for magneto-optical applications. For example, it is one order of magnitude higher than the FeCoNiBSi amorphous films and two orders of magnitude more than YIG films which are often used in fiber optic sensors [151-153].

Figure 4.14(b) represents the saturation Faraday rotation angle as a function of wavelength for 8 and 11nm films. The $\theta_f$ increased linearly as a function of wavelength for both films. Similar to Verdet constant, $\theta_f$ is considerably higher for 11nm thick films. Faraday rotation angle of the present amorphous films is significantly higher than what is reported in the literature for iron oxide films [154]. Faraday rotation angle measured at $\lambda=645\text{nm}$ for iron oxide films of different thickness deposited by PLD is 4 deg/$\mu$m [154]. However, for the present case, it is 11.8 deg/$\mu$m for 11nm film at similar wavelengths. It is also observed that rise in Faraday rotation as a function of wavelength for 11nm thick film is more prominent in comparison to the 8nm film.

There are not many reports about the magneto-optical properties of Fe-based amorphous films. Considerably high values of Verdet constant and saturation Faraday rotation of the present amorphous films as compare to the iron oxide films and Yttrium garnet group may open new possibilities to explore materials for magneto-optical applications which could also be fabricated with the state of art fabrication techniques [151].

![Graph](image-url)  
Fig. 4.14. (a) Verdet constant and (b) saturation Faraday rotation angle of 8 and 11nm film as a function of wavelength for both (8, 11nm) films. Solid line represents the linear fit of the results.
4.2.3 Spin-Reorientation Transition in Fe-Ni-B-Nb thin films (supplement-8)

Spin-reorientation transition (SRT) was observed in thin films of Fe$_{62}$Ni$_{6}$B$_{24}$Nb$_{4}$ alloy deposited by PLD as a function of film thickness where spins align themselves from an in-plane to perpendicular to surface as the thickness of film increases from few tens of nanometer (~27nm) to several hundred nanometer (~408nm) and represented in figure 4.15(a). Magnetic force microscopy (MFM) performed on the thicker film (~408nm) showed stripe magnetic domain pattern by manifesting the presence of perpendicular magnetization for the thicker films and presented in figure 4.15(b) [133-135].

![Image](image_url)

**Fig.4.15.** (a) Inplane magnetic hysteresis loops of as-deposited films of different thickness (27, 258 and 408nm). Inplane magnetic hysteresis loop amorphous ribbon (thickness ~ 20um) of same composition is also shown for comparison. Inset represents out of plane magnetic field dependence of 258nm thick film. (b) Magnetic force microscopy (MFM) image performed on the surface of as-deposited 408nm thick film at remanence state of magnetization.

Temperature dependent magnetization $M$ (T) of the thick film (~408nm) showed a sharp transition at ~225K for zero field cooled (ZFC) and field cool (FC) state of magnetization and presented in figure 4.16(a). Inplane hysteresis loop performed at different temperatures (100-300K) revealed that special type of transcritical loops could not be observed below the transition temperature [Fig. 4.16(b)]. This spontaneous perpendicular magnetization was attributed to the competing magnetic interaction of nanocrystals embedded in weak ferromagnetic amorphous matrix. Weak ferromagnetic amorphous matrix gets magnetically order-disorder as a function of temperature by giving rise to different global magnetic behaviors.
Effect of thermal annealing on the magnetic properties was also studied and presented in figure 4.17. Hysteresis loop and temperature dependent magnetization (Fig. 4.17) manifested that annealing of the samples changed the state of the system and hysteresis loop started to disappear with reduced values of coercivity and perpendicular component of magnetization. However, hysteresis loops fully transformed to square type after annealing at 200°C. A very different behavior of temperature dependent magnetization M (T) was also found for annealed films and presented in figure in 4.17 (b). Divergence between ZFC and FC curves increased significantly with annealing temperature. These studies clearly manifests that heat treatment of the films radically modified the overall structure by giving rise to inplane magnetization for the films annealed at 200°C.

Fig. 4.16. (a) Temperature dependence of magnetization M (T) in field cool (FC) and zero field cool (ZFC) state of magnetization in the presence of 10Oe probe field of as-deposited film (t ~408nm). It shows a sharp transition at ~225K. (b) Inplane hysteresis loop of 408nm thick film performed at different temperatures (100-330K). Film was cooled in the absence of applied magnetic field.

Fig.4.17. (a) Room temperature hysteresis loop of film (t~408nm) annealed at different temperatures (100-200°C) in high vacuum for 1 hour. Hysteresis loop of as-deposited film is also shown for comparison. (b) Temperature dependence of magnetization in FC/ZFC state of magnetization with 100e probe field of 408nm thick film annealed at 125°C and 200°C.
Figure 4.18 represents the temperature dependence of AC susceptibility measurement of the 408nm thin film with 2Oe applied magnetic field oscillating at 181Hz frequency. Results of these measurements also revealed the sharp transition for both real and imaginary parts. The real part of ac susceptibility ($\chi_r$) showed a thermal evolution very similar to ZFC and FC curves of $M(T)$ by showing clear dispersionless Curie-Weiss type decay. However, $\chi'$ decreased very sharply to zero at 225K which is the clear manifestation of the magnetic phase transition with a Curie temperature due to exchange interactions. The inset of figure 4.18 represents the inverse of $\chi'$ as function of temperature which showed a sharp transition from ferromagnetic to paramagnetic phase.

![Fig.4.18. Real $\chi'$ and imaginary $\chi''$ AC magnetic susceptibility component of thin film (t~408nm) as a function of temperature performed by applying by oscillating magnetic field of 2Oe at 181Hz frequency. Inset represents the relation between $1/\chi'$ and temperature.](image)

From above analysis, it was concluded that amorphous matrix between the nanocrystallites play a vital role for the global magnetic behaviors of the sample observed at different temperatures. Amorphous matrix gets magnetically ordered/disorder as a function of temperature acting as a barrier for intergranular magnetic coupling. Below the spin reorientation transition temperature (225K), interface region is magnetically ordered and enables direct exchange interactions between nanocrystallites by giving rise to ferromagnetic–like behavior characterized by a smooth and roughly constant $M(T)$ curve. Magnetic hysteresis loops performed below transition temperature also showed very small coercivity which is the characteristic of the nanocrystalline Fe-based soft magnetic materials [11, 12, 53, 128, 136, 137]. Above transition temperature (225K), the amorphous matrix becomes paramagnetic and as a consequence, suppresses the ferromagnetic exchange interactions between nanocrystallites by decaying the global magnetization of the system and give rise to the perpendicular magnetization [138, 139].
4.2.4 Low temperature magnetic hardening in Fe-Ni-B-Nb thin films (supplement-9)

Two phase nanocrystalline thin films (nanocrystals embedded in an amorphous matrix) of Fe$_{66}$Ni$_{6}$B$_{24}$Nb$_{4}$ composition were grown on Si-substrate by PLD for the investigation of magnetic properties. The temperature dependence of magnetization $M$ (T) of zero field cool (ZFC) and field cool (FC) state of magnetization probed with applied magnetic field ranging from 1-10Oe showed that system enters into different states of magnetization with the evolution of temperature. There are two transitions at different temperatures denoted by $T_{SRT}$ (spin-reorientation transition temperature) and $T_{f}$ (spin-freezing temperature) which gave rise to different global magnetic behaviors [133, 140]. For the case of 10Oe field, ZFC curve exhibited that magnetization is increased from 5K to $T_{f}$ and then continued smoothly with almost constant magnetization up to $T_{SRT}$. On further increasing temperature, it dropped continuously by attaining its minimum value at 300K. Contrary to that $M$ (T) of FC remained almost constant over the range of 5K-$T_{SRT}$. However, after crossing $T_{SRT}$ it followed the path of ZFC up to room temperature. It is obvious from figure 4.19 that higher transition temperature ($T_{SRT}$) remained constant while splitting between the ZFC-FC curves increased by lowering the field. However, ZFC curve could be divided into three regions: I) where magnetization is increased from 5K-$T_{f}$, II) the region of almost constant magnetization i.e. $T_{f}$-$T_{SRT}$, and III) where it decayed from $T_{SRT}$ to 300K. It is clear from figure 4.19 that magnetization of the film for higher temperature region ($T_{SRT}$-300K) is unaffected by the variation of probe field. However, the other two regions are field dependent and ZFC-FC curves are mostly overlapped for stronger fields.

Fig. 4.19. ZFC (solid symbols) and FC (open symbols) temperature dependence of magnetization $M$ (T) with different probe fields from 1Oe to 10Oe for the film of thickness ~408nm
Inplane magnetic hysteresis loops were performed at different temperatures (5-300K) and coercivity was measured and presented as a function of temperature in figure 4.20.

![Image](image.png)

Fig. 4.20. Threefold temperature dependent behavior of $H_c$ measured by inplane M (H) loops. Inset represents the normalized remanence, $M_r/M_s$, as a function of temperature for the same sample.

Splitting between the ZFC-FC magnetization curves clearly revealed the difference between randomly frozen moments and fully aligned state which was obtained even with very weak fields [141]. On cooling the film in the absence of applied magnetic field, spins on the interfacial regions between nanograins and amorphous matrix were frozen randomly and it is considered that system enters into a spin-glass like state near cryogenic temperatures. These randomly frozen spins at the interfaces reduces the interparticle magnetic coupling between the grains giving rise to local anisotropy at low temperatures. Similar phenomenon of magnetic hardening was observed in PLD deposited thin films of Fe-Ag granular alloys and nanocrystalline FeBNb ribbons samples prepared by amorphous precursors [138, 139, 141]. According to RAM model, anisotropy and exchange constant of the crystalline and amorphous matrix do not depend strongly on the measuring temperature [141]. However, low temperature magnetic hardening is essential governed by spin-glass like behavior of the film at low temperatures.

### 4.3 BIOCOMPATIBLE Ti-BASED BULK METALLIC GLASSES

We briefly present some features of Ti-based alloys that have been designed and proposed by Dr. Mao under the Hero-M sponsorship. A more detailed presentation will be made in a future publication along with the theoretical basis of this research effort. Here we discuss the features of distinct plasticity observed in one of the studies. A communication on this study is now under review at the journal Applied Physics letters (2012).
4.3.1 Distinct Plasticity of Biocompatible Ti-Zr-Cu-Pd-Sn Bulk Metallic Glass (supplement-10)

Glassy metal of Ti$_{41.5}$Zr$_{10}$Cu$_{35}$Pd$_{11}$Sn$_{2.5}$ alloy without toxic elements (Ni, Be and Al) was developed to investigate the mechanical properties. Uniaxial compression tests exhibited distinct plasticity (~12.63%) by revealing strain hardening before failure (Fig 4.21). Specimens performed under compression tests do not show any crystalline phases which usually enhance the plasticity by branching or restricting the rapid propagation of shear bands [92-94]. Distinct plasticity along with strain hardening which is not commonly seen in monolithic bulk metallic glasses is attributed to the structural heterogeneity produced due to the positive heat of mixing between Cu-Sn (7kJ/mole) [155-158]. A propagating shear band reaching a region of different compositions might be forced to branch by giving rise to large plasticity in this particular sample.

Fig. 4.21. Uniaxial compressive stress-strain curve of Ti$_{41.5}$Zr$_{10}$Cu$_{35}$Pd$_{11}$Sn$_{2.5}$ bulk metallic glass of 3mm cylindrical rod by exhibiting high plastic strain of 12.63% along with strain hardening.

Along with excellent mechanical properties, the alloy also reveals appreciably high bulk forming ability with large supercooled region (~56K), the reduced glass transition temperature ($T_g$~0.61) and the $\gamma$ parameter of 0.41 and as a consequence, cylindrical rods of at least 7mm were fabricated directly by Cu-mold casting. Figure 4.22 represents the thermal analysis and XRD-pattern of the glassy samples. The combination of high glass forming ability, excellent mechanical properties of present alloy without toxic elements make it a potential candidate for biomedical applications point of view [158-162].
Fig. 4.22. (a) DSC trace of the studied alloy performed at 0.67K/s which exhibits glass transition ($T_g$) temperature followed by supercooled region ($\Delta T_g$) and crystallization temperature ($T_x$). (b) X-ray diffraction pattern of cross-sections of as-casted 5-7mm cylindrical rods. Presence of broad halo peak confirms the amorphous structure of the samples.

4.3.2 Excellent bulk forming ability and high plasticity of Biocompatible Ti-based bulk metallic glasses (supplement-11)

Series of Ti-based glassy metals of Ti-Zr-Cu-Pd-Sn composition were synthesized in bulk form without containing toxic elements Ni, Be and Al for biomedical applications. These glassy metals have revealed excellent glass forming ability and high thermal stability by exhibiting large supercooled region $\Delta T_x \geq 56\,$, reduced glass transition temperature $T_{rg} \geq 0.56$, and the $\gamma$ parameter $\geq 0.39$. Alloy compositions, transition temperature ($T_g$, $T_x$, $T_l$, and $T_m$) along with different glass forming parameters are summarized in Table III. We have produced up to 14 mm rods of a family of Ti$_{38.5}$Zr$_{11.2}$Cu$_{33.2}$Pd$_{14.3}$Sn$_{2.8}$ (Ti15) type BMGs. Detailed report on these will be published in the near future.

Table III. Thermal properties of Ti$_{39.1}$Zr$_{10.9}$Cu$_{33.6}$Pd$_{14.0}$Sn$_{2.4}$ (Ti11), Ti$_{40.5}$Zr$_{9.8}$Cu$_{34.8}$Pd$_{12.9}$Sn$_{2.0}$ (Ti12), Ti$_{36.4}$Zr$_{12.7}$Cu$_{34.3}$Pd$_{13.5}$Sn$_{2.7}$ (Ti13), Ti$_{39.3}$Zr$_{10.6}$Cu$_{33.1}$Pd$_{14.5}$Sn$_{2.8}$ (Ti14), and Ti$_{38.5}$Zr$_{11.2}$Cu$_{33.2}$Pd$_{14.3}$Sn$_{2.8}$ (Ti15) alloys: where glass transition temperature $T_g$, crystallization temperature $T_x$, supercooled region $\Delta T_x$, melting temperature $T_m$, liquidus temperature $T_l$, reduced glass transition temperature $T_{rg}$, and the $\gamma$ parameter.

<table>
<thead>
<tr>
<th>Name</th>
<th>Composition (at. %)</th>
<th>$T_g$ (K)</th>
<th>$T_x$ (K)</th>
<th>$\Delta T_x$ (K)</th>
<th>$T_m$ (K)</th>
<th>$T_l$ (K)</th>
<th>$T_{rg}$ (K)</th>
<th>$\gamma$</th>
<th>$D_{max}$ (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti11</td>
<td>Ti$<em>{39.1}$Zr$</em>{10.9}$Cu$<em>{33.6}$Pd$</em>{14.0}$Sn$_{2.4}$</td>
<td>701</td>
<td>759</td>
<td>58</td>
<td>1135</td>
<td>1235</td>
<td>0.568</td>
<td>0.392</td>
<td>10</td>
</tr>
<tr>
<td>Ti12</td>
<td>Ti$<em>{40.5}$Zr$</em>{9.8}$Cu$<em>{34.8}$Pd$</em>{12.9}$Sn$_{2.0}$</td>
<td>684</td>
<td>740</td>
<td>57</td>
<td>1128</td>
<td>1227</td>
<td>0.557</td>
<td>0.387</td>
<td>10</td>
</tr>
<tr>
<td>Ti13</td>
<td>Ti$<em>{36.4}$Zr$</em>{12.7}$Cu$<em>{34.3}$Pd$</em>{13.5}$Sn$_{2.7}$</td>
<td>704</td>
<td>760</td>
<td>56</td>
<td>1121</td>
<td>1223</td>
<td>0.576</td>
<td>0.394</td>
<td>10</td>
</tr>
<tr>
<td>Ti14</td>
<td>Ti$<em>{39.3}$Zr$</em>{10.6}$Cu$<em>{33.1}$Pd$</em>{14.5}$Sn$_{2.8}$</td>
<td>712</td>
<td>769</td>
<td>57</td>
<td>1141</td>
<td>1235</td>
<td>0.577</td>
<td>0.395</td>
<td>10</td>
</tr>
<tr>
<td>Ti15</td>
<td>Ti$<em>{38.5}$Zr$</em>{11.2}$Cu$<em>{33.2}$Pd$</em>{14.3}$Sn$_{2.8}$</td>
<td>694</td>
<td>764</td>
<td>70</td>
<td>1140</td>
<td>1247</td>
<td>0.557</td>
<td>0.394</td>
<td>14</td>
</tr>
</tbody>
</table>
We synthesized the alloys in different diameters. Figure 4.23 represents XRD patterns of the critical diameters of rods for particular compositions.

Fig. 4.23. X-ray diffraction pattern of critical diameters of rods of Ti$_{39.1}$Zr$_{10.9}$Cu$_{33.6}$Pd$_{14.0}$Sn$_{2.4}$ (Ti11), Ti$_{36.4}$Zr$_{12.7}$Cu$_{34.3}$Pd$_{13.0}$Sn$_{2.7}$ (Ti13), Ti$_{39.3}$Zr$_{10.6}$Cu$_{33.1}$Pd$_{14.2}$Sn$_{2.8}$ (Ti14), and Ti$_{38.5}$Zr$_{11.2}$Cu$_{33.2}$Pd$_{14.3}$Sn$_{2.8}$ (Ti15) alloys. X-ray pattern of melt spun ribbons are also presented for comparison.

Fig. 4.24. Compressive stress-strain curves of Ti$_{39.1}$Zr$_{10.9}$Cu$_{33.6}$Pd$_{14.0}$Sn$_{2.4}$ (Ti11), Ti$_{39.3}$Zr$_{10.6}$Cu$_{33.1}$Pd$_{14.2}$Sn$_{2.8}$ (Ti14), and Ti$_{38.5}$Zr$_{11.2}$Cu$_{33.2}$Pd$_{14.3}$Sn$_{2.8}$ (Ti15) BMG samples at room temperature.

In addition to high bulk forming ability, all samples exhibited good plasticity ($\geq 5.5\%$) and high specific strength ($\geq 2070$MPa) under compressive tests. Figure 4.24 represents large plasticity exhibited by different compositions under uniaxial compressive tests. Large supercooled region ($\Delta T_x \approx 70$K) and excellent plasticity (6.8\%) of Ti$_{38.5}$Zr$_{11.2}$Cu$_{33.2}$Pd$_{14.3}$Sn$_{2.8}$ (Ti15) alloy without the presence of toxic elements make it a potential candidate for biomedical application point of view [158-162].

We thus have successfully implemented the capabilities of a powerful technique based on CALPHAD formalism in producing high quality BMG rods based on toxic element free Ti based alloys. Further studies of establishing the toxicity factors of each element in the formulation is currently under experimental observation in cooperation with an experienced group and will be the topic of our communication in the near future.
CHAPTER 5

5- CONCLUDING REMARKS

This thesis work resulted out in different aspects of glassy metals. Without compromising with the magnetic properties of Fe-based glassy metals, it is possible to improve the glass forming ability by the substitution of Ni in Fe-based glassy metals. It not only improves the glass forming ability, but also the conductivity of Fe-based alloys which is advantageous in many applications. Addition of Ni improved the supercooling region and hence thermal stability of the Fe-based alloys. By considering the same alloys for thin films application point of view, very interesting phenomenon related to spins were found which are very important for technological application point of view. FeBNb alloy when deposited in thin film form appeared with exchange bias at liquid helium temperatures while at room temperature they behave simply like soft magnetic amorphous metals. Thin films of these alloys resulted as a soft ferromagnetic material with high optically transparency and significant saturation Faraday rotation angle. When thin films of Ni substituted alloys were deposited, they were grown with perpendicular anisotropy which just disappeared for thinner films and at lower temperatures. However magnetic hardening was observed at liquid helium temperatures and attributed to the spin glass like state of the interfacial region of the amorphous matrix with nanocrystals.

In this work biocompatible Ti-Zr-Cu-Pd-Sn were studied and resulted in improved bulk forming ability and mechanical properties. Among the series of alloys, Ti_{38.5}Zr_{11.2}Cu_{33.2}Pd_{14.3}Sn_{2.8} scaled up to the 14mm diameter of rods with large plasticity (6.8%). One of the glassy alloys composition resulted in distinct plasticity (12.6%) under compression tests with Strain hardening before failure which is not commonly seen in monolithic glassy metals.

Bulk metallic glasses exhibit a rich group of mechanical, electrical and magnetic properties with many a surprise to be exploited for specialized applications.
Bibliography


