Development and characterization of Iron-Cobalt (FeCo) based bulk metallic glass (BMG) materials

(PhD Thesis)

By

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Dedicated to my parents, wife, children and all those who have contributed towards the completion of this work
Abstract

Bulk metallic glass (BMG) is an important class of materials possessing unique set of properties. Iron Cobalt (FeCo) based BMGs have properties especially suited for applications where high strength and wear resistance is required like surgical tools and mechanical precision elements. These can also be used in electromechanical conversion devices.

The current thesis is aimed at the study of the mechanical properties of the FeCo based BMGs. Three FeCo-based BMGs with the compositions (Fe_{0.5}Co_{0.5})_{69-x}Nb_{6}B_{25+x} (x = 0, 2, 4) were cast using electric arc melting and suction casting technique. For each composition three samples were prepared, tested, and analysed in as-cast, annealed and partially crystalline conditions. The as-cast alloys possessed high hardness that was found to increase with annealing and partial crystallization. Hardness values approaching 1400 H\textsubscript{V} were obtained for partially crystalline BMG alloy having the maximum boron content.

In X-ray diffraction scans no peaks that indicate crystallinity in the BMG alloys were observed in the as-cast and annealed condition while small broad peaks were present in the diffraction patterns of partially crystalline alloy samples. Glass transition (T\textsubscript{g}) and crystallization (T\textsubscript{x}) temperatures of all the three BMG alloys in as-cast condition were above 800 K. Saturation magnetization (M\textsubscript{s}) has shown a decrease while magnetic coercivity (H\textsubscript{c}) increased with an increase in boron content of the alloy. The maximum value of M\textsubscript{s} (92 emu/g) was obtained for annealed BMG alloy with the maximum iron-cobalt content.

Indentation of the BMG alloys resulted in the formation of the deformation zone underneath the indents that consisted of shear bands. Annealing of the cast FeCo based BMG alloys resulted in a decrease in the size of the deformation zone as compared to as-cast amorphous alloys mainly because of increase in strength of the alloys. Plastically deformed zone size calculations through available models show an overestimation of the zone size. Indentation of partially crystalline alloys (intrinsic composites) produced corner cracks while no cracks were observed in case of as-cast and annealed alloys. Palmqvist crack morphology was observed for corner cracks at all the indentation loads used.

Indentation fracture toughness of intrinsic composites was obtained by calculations based on the measured corner crack lengths. Indentation fracture toughness values ranging in 1.85 MPa\textsubscript{\sqrt{m}} to 2.9 MPa\textsubscript{\sqrt{m}}, were obtained. Best mechanical properties and thermal stability was shown by the alloy with the highest boron content (29 at\%) while better magnetic properties were exhibited by the other two BMG alloys.
Acknowledgement

All praises to Allah the Almighty, who by His infinite mercy enabled me to complete this work. I am most indebted to Ghulam Ishaq Khan Institute (GIKI) for providing me this opportunity to work here as a research associate and graduate assistant and providing financial support. I am also thankful to higher education commission (HEC) Pakistan for their support through project no. NRPU 20-1814 to which I contributed as Co-PI. The project has been completed and the report submitted in June 2016. This research work would not have been possible without the assistance from many people and it is my pleasure to have the opportunity now to express my gratitude to them.

First of all, it gives me great pleasure to acknowledge the guidance, suggestions, and constructive criticism provided by my supervisor Prof. Dr Fazal Ahmad Khalid. The completion of this research work and the HEC project (as PI) was impossible without his worthwhile guidance, valuable suggestions and constant encouragement.

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Publications

The research work carried out for the completion of this thesis resulted in the following publications


**Structure of the thesis**

In Chapter 1, general introduction including background, applications, Fe and FeCo based bulk metallic glasses, problem statement, aim and objectives, is described.

Chapter 2 contains literature survey including topics of glass forming ability, structure, crystallization behavior, thermal analysis, production methods, physical and mechanical properties, magnetic behavior, and types of Fe and FeCo based bulk metallic glasses.

In Chapter 3, alloy production and characterization techniques are described. The bulk metallic glass alloy production includes cutting, cleaning, melting, casting, annealing etc. The characterization techniques include differential scanning calorimetry, X-ray diffraction analysis, microstructure analysis, microhardness measurement, vibrating sample magnetometer, tests of deformation behavior and indentation fracture toughness.

In Chapter 4, \((\text{Fe}_{0.5}\text{Co}_{0.5})_{69-x}\text{Nb}_6\text{B}_{25+x}\) (\(x = 0, 2, 4\)) have been characterized. The results obtained for the BMG alloys in the as-cast, annealed and partially crystalline condition through the techniques mentioned in chapter 3 are presented and discussed.

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Chapter 1

Introduction

This chapter is general introduction to bulk metallic glasses including background, applications, Fe and FeCo based bulk metallic glasses, problem statement, aim and objectives of this research.

Glass is an amorphous or noncrystalline solid formed on continuous cooling of a liquid to low temperatures till its viscosity becomes greater than $10^{12}$ Pa-s. Glass possess what is referred to as short range order. Metallic glass produces a limited number of diffuse halos in X-ray, electron and neutron diffraction patterns. No sharp diffraction contrast is obtained in high-resolution electron microscopy. The glass formability of materials varies widely. Some oxide glasses can form even at slow cooling rates of ~1K/min. Pure metals are difficult to obtain in amorphous form and with the possible presence of impurities in the melt, require cooling rates as high as $\sim 10^{10}$ K/s [1, 2].

1.1 Background

The first report of metallic glass appeared in 1960 for a Au$_{75}$Si$_{25}$ (at%) alloy using splat quenching technique [2]. These early glass forming alloys required an extremely rapid cooling rate (on the order of $10^6$ K/sec) to avoid crystallization. Early produced shapes were ribbons, foils, or wires in which one dimension was small enough to allow fast cooling rates to be achieved. As a result, metallic glass specimens were limited to thicknesses of less than one hundred micrometers. In 1976, thin ribbons of amorphous alloy (Fe-Ni-P-B) were developed by using water cooled fast-spinning wheel that allowed fast cooling rates to be achieved [3]. This material known as METGLAS had lower losses and was used in power distribution transformers. METGLAS-2605 (80% iron and 20% boron) is an amorphous alloy having a curie temperature ($T_c$) of 646 K and a saturation magnetization of 1.56 Tesla at room temperature [4].

In 1990s, however, new alloys based on zirconium and palladium systems were developed that formed glass at cooling rates as low as 1 K/sec thus making casting of metallic glass in bulk possible. These alloys having amorphous structure could be cast into parts of upto several centimeters in thickness (the maximum thickness depending on the composition of
the alloy) are known as bulk metallic glasses [5]. Many amorphous alloys have been prepared by making an alloy containing a number of elements through a phenomenon called the "confusion" effect [6]. The alloys exploiting this phenomenon contain many different elements that the amorphous structure is obtained due to difficulty in formation of an equilibrium crystalline state as the mobility decreases upon cooling at sufficiently fast rates, and eventually stopped at $T_g$. The first commercial bulk metallic glass, Vitreloy 1 ($\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$), was developed in early 1990s [7]. The first Fe-based BMG alloy (in the form of melt spun ribbons) was produced in 1995 with a composition $\text{Fe}_{72}\text{Al}_{5}\text{Ga}_{2}\text{P}_{11}\text{C}_{6}\text{B}_{4}$. This alloy had a wide supercooled liquid region of 61 K [8, 9]. The research on the Fe-based bulk metallic glasses increased and many other Fe-based BMGs were subsequently produced (See Table 1.1).

1.2 Applications

The soft magnetic Fe-based melt-spun amorphous alloy ribbons find applications in power distribution transformers and choke coils. The force generated and response time of Fe based BMG actuators is better than those using strontium ferrite permanent magnets in the frequency range of 20–45 Hz. In addition, the high relative permeability of the BMG allows the BMG actuators to be used at higher frequencies. Fe based BMGs are suitable for low-loss magnetic cores for choke coils due to their high permeability and low magnetic coercivity ($H_c$). FeCo based BMGs possess very low magnetostriction coefficient and suitable for high frequency devices and sensors. Further applications include X-Y positioning stage with fine accuracy and in microelectromechanical systems (MEMS) and nanoelectromechanical systems (NEMS) because of their multitude of properties and viscous formability. Excellent high frequency magnetic properties, as well as formability in supercooled liquid region (SLR), paved their way for being used as magnetic shielding sheets for laptop computers (Figure.1.7) [10-12].

Fe based BMGs are suitable for structural applications with amorphous diameters in excess of 10 mm obtained for certain alloys. Their hardness and wear resistance make them suitable for gears and coatings. Dies for microscale imprintability and formability can be formed from these BMG materials. These also have potential applications in knives, surgery tools, micro-parts for biomedics, precision mechanical elements, actuator springs, and machine structural elements. Another potential application is the use in kinetic energy penetrators. Water atomized powder of Fe based BMGs are used for making of noise reduction sheets, cell
phone sensors, and choke coil cores. Another application of Fe based BMGs is 
(Fe$_{44}$Co$_{5}$Ni$_{24}$Mo$_{2}$B$_{17}$Si$_{8}$ amorphous alloy) is manufacturing of shots having a diameter of about 80 μm for shot peening. These powders are produced through water atomization and then sieved to obtain the required size distribution. The shot peening performance of BMG balls is superior to those produced from the conventional steels used for shot peening [10, 13, 14].

![Fig. 1.1 (a) Fe based BMG magnetic shielding sheets for laptop computers [10] (b) Surgical tools from Zr based BMGs [14].](image)

Figure 1.2 shows potential applications of Fe and FeCo based BMGs. All the mentioned applications require good strength, hardness and even fracture toughness.

![Fig. 1.2 Potential applications of Fe and FeCo based BMGs. Images taken from [14]](image)
1.3 Fe and FeCo based bulk metallic glasses

There are number of iron based bulk metallic glass systems available with properties that can be adjusted with variation in composition. These alloys have been used in certain electromagnetic and sensor applications but the main impediment to their wider use is their low glass forming ability compared to Zr, Pd and Cu based bulk metallic glasses. Some of the Fe based alloys that can be cast into a bulk metallic glass are given in Table 1.1. Properties of some Fe based amorphous ribbons are also included in the table for comparison.

Table 1.1 Different parameters of Fe and FeCo based BMG alloy systems. Maximum diameter achievable as bulk metallic glass ($\phi_m$), glass transition temperature ($T_g$), saturation magnetization ($M_s$), magnetic coercivity ($H_C$), strength ($\sigma$) and percent strain ($\%\varepsilon$) values taken from literature.

<table>
<thead>
<tr>
<th>#</th>
<th>Fe based BMG alloys</th>
<th>Year</th>
<th>$\phi_m$ (mm)</th>
<th>$T_g$ (K)</th>
<th>$\Delta T$ (K)</th>
<th>$M_s$ (T)</th>
<th>$H_C$ (A/m)</th>
<th>$T_C$ (K)</th>
<th>$\sigma$ (MPa)</th>
<th>$%\varepsilon$</th>
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<td>1</td>
<td>Fe$<em>{80}$Nb$</em>{20}$B$_{14}$</td>
<td>1997</td>
<td>-</td>
<td>750</td>
<td>25</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>Fe$<em>{75}$Al$</em>{5}$Ga$<em>{5}$P$</em>{5}$</td>
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<td>750</td>
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<td>-</td>
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</tr>
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<td>3</td>
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<td>2002</td>
<td>2.7</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
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<td>4</td>
<td>Fe$<em>{65}$Cr$</em>{16}$Mo$<em>{14}$B$</em>{4}$</td>
<td>2004</td>
<td>5</td>
<td>820</td>
<td>50</td>
<td>-</td>
<td>-</td>
<td>692</td>
<td>4210</td>
<td>-</td>
</tr>
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<td>-</td>
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<td>[88]</td>
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<td>-</td>
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<td>-</td>
<td>-</td>
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<td>10</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
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<td>2007</td>
<td>3</td>
<td>751</td>
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<td>0.020</td>
<td>-</td>
<td>[65]</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>370</td>
<td>-</td>
</tr>
<tr>
<td>14</td>
<td>Fe$<em>{72}$B$</em>{20}$Si$_{1}$</td>
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<td>7</td>
<td>871</td>
<td>111</td>
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<td>1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
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<td>5</td>
<td>729</td>
<td>37</td>
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<td>-</td>
<td>3200</td>
<td>&lt;6</td>
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<tr>
<td>16</td>
<td>Fe$<em>{65}$Co$</em>{10}$Hf$<em>{5}$Mo$</em>{15}$B$_{15}$Y$_3$</td>
<td>2009</td>
<td>3</td>
<td>880</td>
<td>64</td>
<td>[57]</td>
<td>79.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>17</td>
<td>Fe$<em>{7}$Nb$</em>{17}$Y$_3$</td>
<td>2009</td>
<td>3</td>
<td>775</td>
<td>54</td>
<td>1.44</td>
<td>1.2</td>
<td>3700</td>
<td>2.3</td>
<td>-</td>
</tr>
<tr>
<td>18</td>
<td>Fe$<em>{7}$Nb$</em>{17}$Y$_3$</td>
<td>2009</td>
<td>4</td>
<td>850</td>
<td>78</td>
<td>1.08</td>
<td>1.6</td>
<td>-</td>
<td>3490</td>
<td>-</td>
</tr>
<tr>
<td>19</td>
<td>Fe$<em>{65}$Nb$</em>{17}$B$_{14}$</td>
<td>2009</td>
<td>Rod</td>
<td>845</td>
<td>31</td>
<td>-</td>
<td>550</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>20</td>
<td>Fe$<em>{7}$Nb$</em>{17}$B$_{14}$</td>
<td>2009</td>
<td>3</td>
<td>918</td>
<td>62</td>
<td>[106]</td>
<td>24</td>
<td>500</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>21</td>
<td>Fe$<em>{7}$Nb$</em>{17}$B$_{14}$</td>
<td>2009</td>
<td>4</td>
<td>842</td>
<td>83</td>
<td>[118]</td>
<td>24</td>
<td>524</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>22</td>
<td>Fe$<em>{7}$Nb$</em>{17}$B$_{14}$</td>
<td>2010</td>
<td>5</td>
<td>854</td>
<td>102</td>
<td>0.86</td>
<td>4.2</td>
<td>3854</td>
<td>1.5</td>
<td>-</td>
</tr>
<tr>
<td>23</td>
<td>Fe$<em>{7}$Nb$</em>{17}$B$_{14}$</td>
<td>2010</td>
<td>ribbon</td>
<td>-</td>
<td>[105]</td>
<td>1.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>24</td>
<td>Fe$<em>{7}$Nb$</em>{17}$B$_{14}$</td>
<td>2011</td>
<td>4</td>
<td>800</td>
<td>65</td>
<td>0.9</td>
<td>2.5</td>
<td>598</td>
<td>4160</td>
<td>0.2</td>
</tr>
<tr>
<td>25</td>
<td>Fe$<em>{7}$Nb$</em>{17}$B$_{14}$</td>
<td>2011</td>
<td>4.5</td>
<td>95</td>
<td>-</td>
<td>20</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Toughness is an important property of engineering materials and is of paramount importance for certain applications. The values of critical stress intensity (K_C), elastic modulus, and energy release rate are given table 1.2. These values provide a comparison of the toughness of different metallic glasses. From table 1.2 it is evident that most of the Fe based BMGs possess low value of fracture toughness compared to Pt, Pd and Zr based BMGs.
Table 1.2. Elastic modulus (E), critical stress intensity (K_C) and energy release rate (G_C) of some metallic glasses and window glass.

<table>
<thead>
<tr>
<th>#</th>
<th>BMG Alloy</th>
<th>E (GPa)</th>
<th>K_C [MPa-m^{1/2}]</th>
<th>G_C (KJ/m^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Zr_{35}Ti_{30}Cu_{25}Be_{26.75}</td>
<td>86.9</td>
<td>85</td>
<td>96.1</td>
</tr>
<tr>
<td>2</td>
<td>Zr_{55}Nb_{3}Cu_{15.4}Ni_{12.6}Al_{10}</td>
<td>87.3</td>
<td>27</td>
<td>7</td>
</tr>
<tr>
<td>3</td>
<td>Zr_{60}Cu_{16.5}Ni_{12.8}Al_{7.9}Sn</td>
<td>81.9</td>
<td>37.6</td>
<td>14.6</td>
</tr>
<tr>
<td>4</td>
<td>Zr_{60}Cu_{16.5}Ni_{12.8}Al_{7.9}Sn_{2} (as-cast)</td>
<td>-</td>
<td>68</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>(Annealed for 45 min below T_g at 623 K)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Pd_{29}Ag_{3.5}P_{6}Si_{9}Ge_{2}</td>
<td>109</td>
<td>203</td>
<td>310</td>
</tr>
<tr>
<td>6</td>
<td>Pt_{34.7}Cu_{3}Ag_{0.3}P_{18}B_{4}Si_{1.5}</td>
<td>-</td>
<td>125</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>Pt_{37.5}Cu_{14.5}Ni_{3.6}P_{22.5}</td>
<td>98.4</td>
<td>84</td>
<td>90</td>
</tr>
<tr>
<td>8</td>
<td>Fe_{60}Mn_{10}Mo_{14}Cr_{14}B_{6}</td>
<td>200</td>
<td>2.0</td>
<td>0.02</td>
</tr>
<tr>
<td>9</td>
<td>Fe_{60}Cr_{15}Mo_{15}C_{15}B_{6}Er_{2}</td>
<td>192</td>
<td>12.7</td>
<td>0.72</td>
</tr>
<tr>
<td>10</td>
<td>Fe_{60}P_{15}C_{7}</td>
<td>[53]</td>
<td>137</td>
<td>77</td>
</tr>
<tr>
<td>11</td>
<td>Fe_{60}Cr_{15}Mo_{15}Er_{2}C_{15}B_{6}</td>
<td>[55]</td>
<td>[3.8]</td>
<td>-</td>
</tr>
<tr>
<td>12</td>
<td>Fe_{60}Co_{15}Cr_{15}Mo_{15}C_{15}B_{6}Y_{3}</td>
<td>[55]</td>
<td>225</td>
<td>[2.26]</td>
</tr>
<tr>
<td>13</td>
<td>Mn_{35}Fe_{25}P_{15}B_{3}C_{1}</td>
<td>[56]</td>
<td>169</td>
<td>[1.91]</td>
</tr>
<tr>
<td>14</td>
<td>Window glass</td>
<td>[54]</td>
<td>67</td>
<td>0.2</td>
</tr>
<tr>
<td>15</td>
<td>Toughened glass</td>
<td>[54]</td>
<td>87</td>
<td>0.5</td>
</tr>
</tbody>
</table>

[ ] indentation fracture toughness

Fe-Nb-B alloy system has been under considerable investigation since the past few years. Various compositions within the ternary system and different alloys with quaternary additions have been produced to investigate the effect on different properties of the amorphous alloys.

In Fe-B-Nb ternary alloy system presence of boron and niobium improves glass forming ability. Iron (Fe) is a transition metal of group VIII in the periodic Table while Nb (metal) and B (metalloid) belong to group V and XIII respectively. Addition of transition metals like Co in Fe-Nb-B system generally leads to an improvement in glass formability. Fe-Co-Nb-B alloys are marked for their good soft magnetic properties which they retain even at higher temperatures thus making them suitable for applications involving high temperatures.
1.4 Problem statement

BMGs possess many useful properties but their application is limited by the size and shape in which these BMGs can be produced. Another problem with BMGs is their poor toughness [53, 55] which hinders their use in structural applications [13, 14]. Fe based BMGs possess good strength and soft magnetic properties with possibilities of use in structural as well as soft magnetic applications [13, 14]. One of the reasons of their limited applications is their poor toughness [53, 54] and limited section thickness to which an amorphous structure can be produced [13, 14]. The maximum section thickness produced for an iron based BMG is 18 mm [57] while for non-iron based BMGs it is 80 mm for a Pd alloy [58]. Fe based BMGs having Nb and B as alloying additions have high strength as well as good soft magnetic properties [13, 44, 59-62]. Addition of cobalt to iron based BMGs improves the glass forming ability and decreases the magnetic coercivity [62-64]. (Fe\textsubscript{0.5}Co\textsubscript{0.5})\textsubscript{69-x}Nb\textsubscript{6}B\textsubscript{25+x} alloys have good glass forming ability but the physical, mechanical and magnetic properties of these has not been explored extensively especially in annealed and partially crystalline conditions.

1.5 Objectives and novelty

The objectives of this research work are given as follows

1. Melting and casting of (Fe\textsubscript{0.5}Co\textsubscript{0.5})\textsubscript{69-x}Nb\textsubscript{6}B\textsubscript{25+x} (x = 0, 2, 4) BMG alloys using arc melting and suction casting technique.
2. To investigate the thermal stability of the BMG alloys produced for selection of temperatures for annealing and partial crystallization treatment.
3. To observe the effect of the alloy composition and annealing on the soft magnetic properties of the BMG alloys produced.
4. To investigate the deformation behavior and fracture toughness of the BMG alloys produced in as cast, annealed and partially crystalline conditions.

Bonded interface technique used was to study the deformation behavior these BMG alloys. The deformation behavior of these BMG alloys through the use of bonded interface technique has not been reported in the literature. Fracture toughness of these BMG alloys is also calculated through indentation technique in partially crystalline condition. Indentation fracture toughness of these BMG alloys has also not been reported in the literature. Various models of indentation fracture toughness present in the literature have been employed for
calculation of indentation fracture toughness and the type of crack system formed due to indentation is observed.

1.6 BMG alloy system

The alloy system selected for investigation is composed of Fe, Co, Nb, and B elements. The BMG alloys are produced according to the composition scheme \((\text{Fe}_{0.5}\text{Co}_{0.5})_{69-x}\text{Nb}_6\text{B}_{25+x}\). Some of the properties of these elements used for BMG production are given Table 1.3.

Table 1.3 Some physical properties of iron, cobalt, niobium, gadolinium and boron elements [65].

<table>
<thead>
<tr>
<th>Element</th>
<th>Density (g/cc)</th>
<th>Melting point (K)</th>
<th>Boiling point (K)</th>
<th>Atomic number</th>
<th>Atomic weight</th>
<th>Atomic radius (pm)</th>
<th>Heat of fusion (J/g)</th>
<th>Specific heat capacity (J/g-K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron (Fe)</td>
<td>7.87</td>
<td>1812</td>
<td>3134</td>
<td>26</td>
<td>55.8</td>
<td>126</td>
<td>272</td>
<td>0.44</td>
</tr>
<tr>
<td>Cobalt (Co)</td>
<td>8.8</td>
<td>1768</td>
<td>3200</td>
<td>27</td>
<td>57</td>
<td>125</td>
<td>260</td>
<td>0.44</td>
</tr>
<tr>
<td>Niobium (Nb)</td>
<td>8.6</td>
<td>2750</td>
<td>5017</td>
<td>41</td>
<td>92.9</td>
<td>146</td>
<td>290</td>
<td>0.27</td>
</tr>
<tr>
<td>Boron (B)</td>
<td>2.6</td>
<td>2573</td>
<td>4200</td>
<td>5</td>
<td>10.8</td>
<td>90</td>
<td>2050</td>
<td>1.285</td>
</tr>
</tbody>
</table>

A set of criteria known as Inoue criteria gives the conditions for the formation of bulk metallic glass [66]. Fe-Co-Nb-B alloys are assessed by the Inoue criteria for their glass forming ability. According to the Inoue criteria, that consists of three empirical rules, this system satisfies all the conditions imposed in the criteria as discussed below:

1. According to the first criterion, there should be at least three elements in the system. This system consists of four elements namely iron, cobalt, niobium, and boron thus satisfying first criterion.

2. The second rule says that the atomic size difference should be greater than 12% for elements constituting the amorphous alloy. The percentage differences between the atomic radii of elements present in the alloy system are given in the Table 1.4. In this system, iron is partly replaced by cobalt which has an atomic radius about the same as iron. Also the properties are very much similar. Others have a radii difference of greater than 12% which is in accordance to this second rule.
3. This rule requires that the mixing enthalpies between the elements present in the alloy should be negative. Mixing enthalpies of the elements present in the alloy system are given in Table 1.5. This rule is satisfied as the mixing enthalpies between the elements of this system are negative.

Table 1.4 Percentage difference between the atomic radii of elements in the alloy system [67].

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Co</th>
<th>Nb</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>0</td>
<td>0.8</td>
<td>13.7</td>
<td>28</td>
</tr>
<tr>
<td>Co</td>
<td>0.8</td>
<td>0</td>
<td>14</td>
<td>28</td>
</tr>
<tr>
<td>Nb</td>
<td>13.7</td>
<td>14</td>
<td>0</td>
<td>38.4</td>
</tr>
<tr>
<td>B</td>
<td>28</td>
<td>28</td>
<td>38.4</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 1.5 gives the values of mixing enthalpies of the elements present in the selected system of FeCo based BMG alloys.

Table 1.5 Mixing enthalpies (kJ/mol) of the elements present in the alloy system [68].

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Co</th>
<th>Nb</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>0</td>
<td>-0.6</td>
<td>-15.7</td>
<td>-26.5</td>
</tr>
<tr>
<td>Co</td>
<td>-0.6</td>
<td>0</td>
<td>-24.5</td>
<td>-24.2</td>
</tr>
<tr>
<td>Nb</td>
<td>-15.7</td>
<td>-24.5</td>
<td>0</td>
<td>-53.9</td>
</tr>
<tr>
<td>B</td>
<td>-26.5</td>
<td>-24.2</td>
<td>-53.9</td>
<td>0</td>
</tr>
</tbody>
</table>
Chapter 2
Literature Survey

Bulk metallic glass is an important class of advanced engineering materials with certain unique properties. The structure is completely amorphous in a metallic glass. The extent of formation of amorphous structure in an alloy depends upon chemical composition and rate of heat removal. This chapter includes topics of glass formability, structure, crystallization behavior, thermal analysis, production methods, physical properties, mechanical behavior, magnetic behavior, corrosion behavior, types of Fe and FeCo based bulk metallic glasses and their properties.

2.1 Glass and glass formability
A metallic glass may be considered as a solid having the structure of liquid that is frozen. The structure is the same as the liquid and no change in spatial atomic configuration happens during the solidification. Metallic glass is not in an equilibrium state; therefore, it relaxes structurally to a more stable equilibrium state whenever atoms attain an appreciable mobility. A glass undergoes a nucleation and growth process to attain a crystalline state. A glass would transform to the liquid phase on heating provided that the rates of crystallization are slow enough to delay its initiation. The temperature at which liquid freezes to a solid without crystallization is called, glass transition temperature, \( T_g \). Thus, in amorphous metals long-range translational order is not present. There is a short-range order that may be similar to that present in the crystalline counterpart. Figure 2.1 shows a schematic free energy diagram for a system as a function of temperature. The alloys follow the path that results in greater decrease in free energy as a function of temperature, whether it is solid or liquid. The free energy follows the liquidus curve for high enough cooling rates thus avoiding crystallization down to glass transition temperature, \( T_g \). The frozen liquid possesses a free energy value that is in between the liquid state and crystalline state [10, 69].
Fig. 2.1 Free energy diagram as a function of temperature L and S refer to liquid and solid respectively [10].

Figure 2.2 shows the variation of specific volume (volume per unit mass) as a function of temperature. When the temperature of a liquid metal is reduced, its volume decreases with decreasing temperature up to the freezing/melting point, $T_m$. At the freezing temperature, there is a large drop in the specific volume of the metal till all the liquid crystallizes. Further decrease in temperature below $T_m$ results in a slow decrease of the volume of the metal, depending on its coefficient of thermal expansion.

Fig. 2.2 Variation of volume with decreasing temperature for glass formation and crystallization [10].

The glass forming liquid can be significantly undercooled, either because of the use of a higher cooling rate, or removal of heterogeneous nucleating sites. Its viscosity continues to increase even in the undercooled region. At some temperature, normally well below $T_m$, the
viscosity becomes so high that the liquid freezes without forming crystals. This noncrystalline frozen state of liquid is termed as a glass. The temperature at which the viscosity of the undercooled liquid reaches a value of $10^{12}$ Pa·s is called glass transition temperature. The supercooled liquid present between $T_g$ and $T_m$, is thermodynamically and kinetically metastable. A glass transition can be identified by a change in the thermodynamic properties, like specific heat and thermal expansion coefficient that happen during heating or cooling of the amorphous alloy. From the Figure 2.2 it is evident that the amorphous alloy would have a greater specific volume compared to the crystalline counterpart. This difference in the specific volume of an equilibrium cooled crystalline alloy and fast cooled amorphous alloy at a particular temperature is free volume [10, 69].

On heating, the supercooled liquid transforms into the crystalline phase(s) at a temperature $T_x$, which is greater than $T_g$. The temperature interval between $T_x$ and $T_g$ is the span $\Delta T_x$, of the supercooled liquid region (SLR), i.e., $\Delta T_x = T_x - T_g$. The size of this region is a measure of the thermal stability of the metallic glass. BMGs have large supercooled liquid regions and values greater than 120 K have been reported; the highest reported value is 131 K in a Pd$_{43}$Cu$_{27}$Ni$_{10}$P$_{20}$ BMG alloy [70].

Glass forming ability is the ease of forming of amorphous phase in a material by suppressing crystallinity during solidification. The minimum cooling rate at which a bulk metallic glass can form from the melt is called critical cooling rate ($R_c$). It is a measure of the glass forming ability (GFA) of the alloy. Higher the required $R_c$, lower is the GFA of the material and vice versa. Critical casting thickness ($D_{\text{max}}$) of an alloy is another measure and defined as maximum thickness in which a bulk metallic glass can be obtained [10, 69, 71].

Pure metals require an extremely high cooling rate $R_c (>10^{10}$ K s$^{-1}$) for glass formation. For metallic alloy liquids, the value of $R_c$ is in the range $10^4$–$10^6$ K s$^{-1}$ which can be achieved by rapid quenching. The value of $R_c$ can be further reduced with increasing the number of components of the metallic glass resulting in achievement of amorphous structure in bulk with a cooling rate of $10^3$ K s$^{-1}$ or less. Low $R_c$ is required to cast these multicomponent alloys into BMGs using water cooled metallic molds [10, 69, 71].

2.2 Criteria for glass formability

Various criteria for glass formability of alloys had been put forwarded during the development of these amorphous alloys. The criteria for the formation of BMGs are based on
glass transition temperature of glasses, structural and topological parameters, physical properties of alloys, and computational approaches. Some of the widely used criteria are given below:

1. **Inoue criteria**

   Three basic empirical rules for the formation of BMGs were formulated by Inoue et. al., based on the huge data available on the properties \[66, 72\]. These are stated as follows:

   1. The alloy must contain at least three elements. The formation of metallic glass becomes easier with increasing number of components in the alloy system.
   2. The atomic size of the three constituent elements of the alloy should be significantly different. This difference should be greater than 12% among the main constituent elements.
   3. The heat of mixing among the (major) constituent elements of the alloy system should be negative.

   The first Inoue criterion addresses the thermodynamic and kinetic aspects of glass formation; the second Inoue criterion is concern with the topological aspects like structure and packing of atoms. Figure 2.3 shows atomic diameters of various elements. Size of the elements is divided into three groups divided by the dotted lines. The third Inoue criterion deals with mixing of atoms (alloying) and homogeneous glass formation \[66, 72\].

2. **The \(\Delta T_x\) criterion**

   The large temperature span of the supercooled liquid region (\(\Delta T_x\) or SLR) in BMGs suggests that the amorphous phase obtained resists crystallization and is very stable. On this basis, it had been suggested that the GFA of alloys is directly related to \(\Delta T_x\) (crystallization temperature \(T_X\) – glass transition temperature \(T_g\)). Accordingly, it was noted that the critical cooling rate for glass formation decreases with an increase in the \(\Delta T_x\) \[5, 9\].

3. **The \(t_{max}\) criterion**

   Cooling rate greater than the critical cooling rate leads to formation of glass. Heat is extracted from the bulk to the surface during cooling; therefore, at any point cooling rate varies with the distance from the surface. The maximum amorphous diameter
achieved for a certain cooling rate is another parameter, known as $t_{\text{max}}$, for the evaluation of GFA. A decrease in the critical cooling rate for glass formation, $R_c$, results in an increase in $t_{\text{max}}$. [73].

The GFA of a material is affected by intrinsic and extrinsic factors. Intrinsic factors include thermal parameters ($T_g$, $T_x$, $T_{rg}$, $T_L$), physical properties (heat capacity, thermal expansion, thermal diffusivity etc), presence of a deep eutectic, and topology like efficient packing. Extrinsic factors include non-metallic inclusions, mold surface quality and cleanliness, surface temperature and thermal conductivity of the mold, liquid metal superheat and turbulence on entry to the mold. Intrinsic and extrinsic factors are responsible for the homogenous and heterogeneous nucleation in the liquid melt respectively. No single factor can truly predict the glass forming ability of alloys but knowing the limitation of these is the way forward to obtaining a better GFA [10, 69, 71].

2.3 Structure of bulk metallic glasses

BMGs are classified into three types, namely, metal–metal-type alloys, metal–metalloid type alloys and the Pd–metalloid-type alloys. The atoms in these BMGs are arranged in different configurations. In metal–metal amorphous alloys [65], the structure consists of icosahedral clusters. The critical size for a transition from icosahedral cluster to icosahedral phase is around 8 nm. Icosahedral quasicrystalline phase (I-phase) is produced by annealing the amorphous alloy in the supercooled liquid region. Icosahedral clusters acts as nuclei for the precipitation of the I-phase and are considered as the fundamental structural unit in these amorphous alloys. Nucleation of I-phase requires lesser activation energy than the nucleation of stable crystals in the supercooled alloy liquid [74].

The I-phase formed possesses a five-fold rotational symmetry and it is incompatible with the crystalline phase having translational symmetry. Therefore, the icosahedral clusters present in the amorphous state impede the nucleation of the crystalline phases. The redistribution of atoms across the icosahedral liquid is hindered by the dense amorphous phase thus decreasing their mobility. Suppression of the nucleation and growth results in excellent GFA due to this structural discontinuity between amorphous and crystalline states [74].
A network atomic structure consisting of trigonal prisms exists for metal-metalloid-type of amorphous alloys as shown in Figure 2.3. Atoms like Zr, Nb, Ta or Lanthanides act as joining point of these prisms. Fe and Co occupy similar positions in this configuration [74].

![Fe-TM-B system (TM=Zr,Nb,W, etc.)](image)

Fig. 2.3 Atomic configuration in transition metal containing Fe-TM-B BMGs [75]

These supercooled liquids are highly dense having small free volumes and high values of viscosities. Their viscosities are several orders of magnitude greater than those of pure metals or crystalline alloys. Supercooled bulk metallic glass possess high packing density and short range order and compared to other metallic melts are closer to crystalline state. All these factors leads to slow crystallization kinetics and high glass-forming ability of the alloys [74]. The ability of metals to form amorphous structure by fast cooling is enhanced by the dominance of icosahedral short-range order (ISRO) in melts. The existence of ISRO in the supercooled liquid state brings about an extremely small interfacial free energy between an icosahedral quasicrystalline phase (I-phase) and a metallic glass of the same composition. Consequently the nucleation of the I-phase during annealing of BMGs is easier than the formation of the more stable crystalline phases [76].

### 2.4 Crystallization behavior of BMGs

Metallic glasses crystallize at or above the crystallization temperature; \( T_x \). \( T_x \) provides an upper limit to the safe use of metallic glasses without losing their interesting combination of properties. For example, the magnetic behavior of metallic glasses and the crystalline
counterpart is different. It is possible to obtain a composite consisting of a fine crystalline phase precipitated and dispersed in the amorphous matrix. This composite formed by the partial crystallization of glass may result in the improvement of various properties. The properties can be optimized by proper understanding of the crystallization procedure. The commonly used techniques to monitor and study this behavior are DSC, DTA, XRD, and electron microscopy. Crystallization temperature is the temperature at which crystallization begins in an amorphous alloy on heating. The driving force for crystallization is the free energy difference between the glass and the appropriate crystalline phases. The crystallization temperature ($T_x$) of a metallic glass is kinetic value not a thermodynamic parameter like melting temperature of a metal. The metallic glasses are metastable and these can transform into a stable crystalline phase(s) if sufficient time is allowed at any temperature. Metallic glasses can be considered as “stable” indefinitely at room temperature for all practical purposes. Higher value of $T_x$ implies easier glass formation and better thermal stability amorphous phase formed. Many studies relating to thermodynamics and kinetics of crystallization from amorphous phase are present in the literature [70, 77-80]

2.5 Thermal analysis of BMGs

Glass transition temperature ($T_g$) is a measure of the thermal stability of the metallic glass. $T_g$, $T_x$ (crystallization temperature) and $T_L$ (liquidus temperature) can be obtained through the use of differential scanning calorimetry (DSC). Activation energies of nucleation and growth stages of the transformation can be evaluated. Full information about the transformation temperatures, the number of stages involved in transformations, details about the phases produced in each individual transformation, and the activation energy required for the transformation can be obtained through techniques like DSC, X-ray diffraction (XRD), and Transmission electron microscopy (TEM) [77].

A number of different reactions can happen in a BMG when it is heated above room temperature. At temperatures below $T_g$, this may be structural relaxation, phase separation (around $T_g$) and finally crystallization (at $T_x$).
2.6 Production techniques of BMGs

BMGs have been produced by a number of techniques including copper mold casting, mechanical alloying, high pressure die casting, tilt casting, zone refining, etc. Some of the techniques are discussed below:

2.6.1 Copper mold casting

Copper mold casting is widely used technique for the production of BMGs. Copper is good thermal conductor and it rapidly extracts heat from the liquid poured in it to facilitate glass formation. Two techniques are commonly used namely induction melting and casting and arc melting and suction casting. Both of these techniques require a water cooled copper mold. In the first technique, the pure elements or master alloys are induction melted together in a ceramic tube and then pushed through a small hole present at the bottom of the tube into a water cooled copper mold using inert gas pressure. In the second technique, pure elements or master alloys are melted together through arc melting in a water cooled copper crucible. The molten alloy is then sucked into a water cooled copper mold through an opening in the copper crucible using vacuum. An inert gas environment is used in both the cases for melting and casting. Repeated melting of the alloy before casting in suction casting technique ensures proper homogeneity. The temperature of the molten metal is maintained such that it remains molten during the ejection filling of the mold cavity. The casting can be done in air, vacuum or inert atmosphere in case of induction technique [10, 81-84].

2.6.2 High-pressure die casting

In high pressure die casting method an alloy is melted by an induction melting method and bottom filled in a water-cooled copper mold utilizing a hydraulic press. The pressure is maintained even after complete filling of the mold, until the liquid alloy completely solidifies. In this method the surface finish of the casting depends upon the surface finish of the die and show a bright metallic luster.

The casting solidifies in a few milliseconds, thus making it possible to achieve high productivity. Also, the application of high pressure ensures good contact between the melt and the copper mold. The casting defects are removed and relatively complex shapes can be cast [85, 86].
2.6.3 Mechanical alloying

Amorphous phase in a powdered form can also be produced through mechanical alloying. This amorphous powder can be consolidated through a suitable process that retains its amorphous structure. Amorphous structure can also be produced in those alloys that are difficult or impossible to obtain in amorphous form through melting and casting techniques. A mixture of elemental powders is filled into a milling container along with a particular size and weight ratio of grinding medium (hard materials). An inert atmosphere is produced in the container by using an inert gas. This container is then fixed inside the mill and violently agitated for certain desired length of time. The powder is subjected to shear, impact, or other types of mechanical forces by the agitation. Continuous milling flattens the soft particles while hard particles are comminuted and particle size reduces. The flattened/layered soft particles convolute and the layers get thinner along with an increase in the defect density. The rise in the temperature during milling leads to diffusion which is aided by high defect density and shorter diffusion distances resulting in an alloy of constituent elemental or alloy powders. Amorphous powders of Fe, Zr, and Mg based alloys had been produced by this method [10, 87-89].

2.7 Bulk metallic glass alloys

BMGs are noncrystalline solids having a diameter or section thickness ≥ 1 mm that are produced by continuous cooling from the liquid state.

BMGs have the following four characteristics [10]:

1. These are multicomponent systems having at least three components. The alloy system should have a minimum of three components; more commonly the number is greater than three and that is why they are frequently referred to as multicomponent alloy systems.
2. These can be produced at a cooling rate that is less than $10^3$ K.s$^{-1}$.
3. BMGs can be produced in large section thickness or diameter with a minimum of 1 mm. The largest diameter of a BMG rod so far produced 72 mm in a Pd$_{40}$Cu$_{30}$Ni$_{10}$P$_{20}$ alloy [58].
4. These alloys exhibit a large supercooled liquid region. This SLR could be as large as a few tens of degrees. The highest reported value so far is 131K in a Pd$_{43}$Cu$_{27}$Ni$_{10}$P$_{20}$ alloy [70].
2.7.1 Comparison of bulk metallic glasses and melt-spun ribbons

Bulk metallic glasses are metastable like melt-spun ribbons. A comparison of the properties of bulk metallic glasses and melt-spun ribbons is given in Table 2.1.

<table>
<thead>
<tr>
<th>#</th>
<th>Melt spun ribbons</th>
<th>Bulk metallic glasses</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Higher critical cooling rates (10^5 - 10^6 K/sec)</td>
<td>Lower critical cooling rate (10^2 – 10^3 K/sec)</td>
</tr>
<tr>
<td>2</td>
<td>Number of components can be any</td>
<td>Number of components ≥ 3</td>
</tr>
<tr>
<td>3</td>
<td>Thickness in micrometers</td>
<td>Thickness in millimeters/centimeters</td>
</tr>
<tr>
<td>4</td>
<td>Lower density</td>
<td>Higher density</td>
</tr>
<tr>
<td>5</td>
<td>Difference in cooling rates on both sides</td>
<td>Cooling rate symmetric</td>
</tr>
<tr>
<td>6</td>
<td>Greater departure from equilibrium</td>
<td>Closer to equilibrium</td>
</tr>
<tr>
<td>7</td>
<td>Faster kinetics of crystallization</td>
<td>Slower kinetics of crystallization</td>
</tr>
</tbody>
</table>

Table 2.1 Comparison of melt-spun ribbons and bulk metallic glasses

Figure 2.4 illustrates some differences in conventional amorphous alloys and bulk metallic glasses. The crystallization temperature (T_X) and glass transition temperature (T_g) coincide while in BMGs these two are separated by a supercooled liquid region.

Fig. 2.4 Schematic diagram that shows the differences between conventional amorphous alloys and bulk metallic glasses [90].

Atoms in crystalline materials are arranged periodically in three dimensional lattices and X-ray diffraction patterns of these metals exhibit sharp diffraction peaks that confirms the presence of long range order of the atoms. BMGs on contrary do not possess any long range
order in structure and are termed amorphous. The atomic distribution in BMGs results in a very broad peak or hump in diffraction patterns and is attributed to the short range order of the atoms. Some amorphous metals possess order over a length scale that is larger than short range. This kind of order is known as medium range order (MRO), and it does not exhibit any periodicity [91].

In contrast to crystalline materials, amorphous metals and alloys do not possess any microstructural features (i.e. grain boundaries, dislocations, etc.).

2.8 Physical properties of BMGs

A measurement of physical properties like density, viscosity, specific heat, electrical resistivity add to the understanding of the structural relaxation and the crystallization processes occurring in metallic glasses and their effect on various properties like corrosion resistance, mechanical and magnetic properties.

2.8.1 Density

Archimedes principle has been used in the measurement of densities of ribbons and BMG alloys. Alloy ribbons produced through rapid solidification possess higher free volume and are about 2%-3% less dense than their crystalline counterparts [92].

The free volume is expected to be lower in the bulk metallic glasses because these are produced at a lower solidification rates than melt-spun ribbons. The density of the BMG alloys is about 0.5% lower than that of the crystalline alloy of the same composition.

Free volume within an amorphous alloy will depend upon cooling rate and therefore it varies with the technique used to produce the amorphous alloy. Densities of the amorphous samples obtained by different techniques could be different due to difference in the free volume of these alloys. This difference in the densities between BMGs produced by different methods is expected to be small. An increase in the free volume results in an increase in strength and hardness but brittleness may also increase [93].

2.8.2 Thermal expansion

Useful information is obtained about the structural relaxation behavior through thermal expansion measurements. Coefficient of thermal expansion of BMGs can be obtained through
dilatometric measurements. BMGs possess higher CTE as compared to crystalline counter parts and their constituent pure metals [94].

The CTE of a BMG remains constant upto $T_g$, after which it increases due to structural relaxation. In case of externally applied load, the CTE remains constant to a temperature lower than the $T_g$ but increases and assumes a large value in the supercooled liquid region. CTE is again reduces to value near to that of the glassy alloy after crystallization [95].

### 2.8.3 Viscosity

Viscosity determines the flow behavior and glass forming ability of the liquid alloy. An increase in viscosity of the supercooled liquid to a very high level such that the mobility of atoms ceases, results in glass formation and marks the $T_g$ of the alloy. At the melting point the viscosity of the liquid alloy is about $10^{-3}$ Pa-s and it increases to $10^{12}$ Pa-s at $T_g$. Any liquid whose viscosity reaches a value of $10^{12}$ Pa-s on cooling without crystallization is called a glass, irrespective of the alloy system and composition. Liquids can be classified into two types (i) strong and (ii) fragile depending upon the rate of change of viscosity with temperature. If a liquid has a high viscosity near the melting point and it increases gradually with a decreasing temperature then the liquid is termed as “strong”. On the other hand, if a liquid has low viscosity at the melting temperature, and it increases slowly with a decreasing temperature and rises abruptly near the glass transition temperature, $T_g$, then it is termed as “fragile” [1, 96].

### 2.9 Mechanical behavior of BMGs

Metallic glasses are elastically isotropic bodies. These possess high strength and high hardness. Elastic moduli of BMGs provide a macroscopic view of a material’s stiffness. It is a reflection of interatomic bonding energies and the connectivity of atoms or groups. Generally BMGs have Young’s modulus (E) values between 25 GPa and 250 GPa, and shear modulus (G) values between 9 GPa (CaLi-based BMGs) and 88 GPa (Fe-based BMGs) [53]. Cobalt based BMGs have shown high strengths (> 5 GPa) and high elastic moduli in excess of 250 GPa. The maximum value of elastic moduli (> 350 GPa) has been observed in tungsten based bulk metallic glasses. The ratio of elastic to shear modulus has an approximate value of 2.61 for most of the bulk metallic glasses [53]. The value of poison’s ratio ($\nu$) of the various BMGs is close to that of their base metals. Iron ($\nu = 0.29$) and rare
earth elements have low values of poison’s ratio ($\nu$), therefore, iron and rare earth based BMGs also have low values of $\nu$. For isotropic materials, the shear ($G$) and bulk ($K$) moduli can be calculated from the elastic modulus and Poisson’s ratio as given in equations 2.3 and 2.4 [97].

\[
G = \frac{E}{2(1 + \nu)} \quad (2.3)
\]
\[
K = \frac{E}{3(1 - 2\nu)} \quad (2.4)
\]

The shear modulus of Fe based BMGs can be related to the bulk modulus using equation 2.5. This relation provides an approximate value of the bulk modulus for Fe based glasses [53].

\[
K = \frac{5}{3} G \quad (2.5)
\]

Metallic glass with higher density has higher bulk modulus. BMGs possess high strength but they are limited by low room temperature ductility. These fail at low value of strain. At higher temperatures, BMGs behaves differently.

2.9.1 Deformation behavior

Bulk metallic glasses deform inhomogeneously at low temperatures and high stresses and strain rates, and homogeneously at higher temperatures and low strain rates. These deform by formation of shear bands at temperatures below $T_g$. These shear bands form approximately on the planes of maximum resolved shear stress i.e., close to 45° to the loading axis. The unstable deformation behavior of BMGs at high stresses is due to this inhomogeneous deformation. This results into catastrophic failure of metallic glass.

Metallic glasses show viscous flow with distributed plastic strain at a temperature of about 0.5$T_g$. In this regime every volume element contributes to strain, that is known as homogeneous deformation.

Two hypotheses exist about the formation of shear bands. The first hypothesis suggests that the localized decrease in resistance to deformation is a consequence of decrease of viscosity in shear bands due to creation of free volume. The second hypothesis suggests that the
resistance to deformation decreases due to decrease in viscosity as a result of local adiabatic heating that occurs in the shear bands.

Homogeneous deformation as viscous flow of supercooled liquid happens in SLR. Plastic forming of metallic glass can be done in the supercooled liquid state [98]. Partial crystallization of metallic glass often results in a homogeneous flow. Normally crystallization is accelerated by presence of pressure (in tension, compression, and complex loading conditions).

The deformation behavior of most bulk metallic glasses in the inhomogeneous regime result in an elastic strain of about 2%, followed by catastrophic failure without plastic flow. The strain tends to localize into shear bands, during deformation of the metallic glass. This behavior is due to free volume accumulation ahead of an advancing shear band. This causes the structure to dilate, leading to strain softening. This can also result into failure through a single shear band [99].

A tin coated bulk metallic glass has shown melting of tin on the shear bands which supports the idea of local adiabatic heating due to shear band formation [100]. Other view related to the formation and propagation of shear band due to shear induced density fluctuation has produced more realistic predictions of the size of the shear band [99, 101].

Shear bands in metallic glasses had been observed by microscopy to have a thickness of approximately 10 nm [101]. Shear transformation zone (STZ) consists of groups of atoms (up to a few hundred) that move collaboratively to enable deformation via inelastic shear. An STZ is an event that happens in a local volume and not a feature of the metallic glass. A shear transformation zone (STZ) is defined by its short-term existence; it is not a permanent defect like a dislocation in a crystal [99].

The STZ has been described as a local cluster of atoms (upto 100) that undergoes an inelastic shear distortion from one relatively low energy configuration to another low-energy configuration, crossing an activation barrier. Sear transformation zone that consists of a free volume site with adjacent atoms is the basic shear unit. These atomic scale STZs collectively deform under an applied shear stress to produce macroscopic shear deformation [99].
Operation of an STZ means a local dilatation of the structure, resulting in higher free volume that may be retained by the structure [99, 103]. Plastic deformation in metallic glasses is essentially an accumulation of the atomic movement accrued through STZ operation. STZ forms in weak areas in the structure (local density fluctuations, stress concentrations, etc). The local density must decrease to accommodate the transient state of deformation, and does not necessarily return to its original state afterwards [103].

STZ operation makes further activation of deformation easier. Regions where STZs activate become weak points and reach a percolation threshold thus allowing deformation to occur along the band that forms due to collective action of a large number of STZs [104]. Either the STZs activate throughout the structure and shear bands form when they reach percolation threshold, or a region of STZ action act as stress concentrator and causes adjacent regions to activate [53].

STZ operation can be considered anelastic. It is plastic locally, but can be reversible and does not provide large-scale plasticity. Therefore, STZs activate before macroscopic plastic yielding [105].

Inhomogeneous flow in metallic glasses has been attributed to local decrease in viscosity in shear bands. Local adiabatic heating leads to an increase in temperature. The temperature rise in the shear band could not be measured directly due to practical limitations of temperature measurement but it is expected to be several hundred degrees Kelvin. Shear band operation due to adiabatic heating is not likely due to quick dissipation of heat to the surrounding materials. A Zr based BMG alloy sample with 50nm thick tin coating was observed after deformation (three point bending). Frozen droplets of tin were present at the places where shear bands intersected the coating indicating local rise in temperature at least above the melting point of tin due to band formation. It has been suggested that the temperature rise could be a few thousand of degrees for nanoseconds [100]. Rise in temperature could lead to crystallization. Nanocrystallization had been observed in the shear bands of the deformed BMG alloys [106] whereas formation of nanovoids within the shear bands prevented the nanocrystallization [107, 108].

Shear bands can also be observed as semicircular pile-ups around the hardness indents. These appear as overlapping layers of upwardly displaced material. The deformation in elastic-
plastic materials, as BMGs are elastic-plastic, occur as pile-up against the walls of the indent due to volume conservation. These pile-ups are observed as discrete steps due to inhomogeneous deformation of the material [109]. The included angle observed in these shear bands is less than 90° that indicates pressure sensitivity to plastic deformation of these materials [110].

2.9.2 Indentation behavior

Indentation tests are an excellent means of conducting studies on elasto-plastic behavior of materials, for gaining insights into the micromechanisms of plastic deformation, as well as developing an understanding of the material’s response to multiaxial loading. Indentation is easier to perform and it is not so particular about the sample size. This constrained deformation test, unlike the uniaxial tests, does not lead to catastrophic failure and it is possible to study the deformation process beyond the elastic domain.

The hemispherical plastic deformation zone produced beneath the indent contains shear bands. These shear bands represent the plastic deformation that has been produced as a result of indentation. An expanding cavity model (ECM) proposed in [111] had been employed to study the indentation behavior under the hardness indent in many investigations [109, 112-114].

Figure 2.5 shows a semi-spherical cavity formed due to the indentation with a Vicker’s indenter. In this elastic – plastic indentation model (ECM), when the pressure beneath the indenter reaches a critical value, given by the equation 2.6, the material shows uncontained deformation behavior.

\[ P_m = cY \]  

(2.6)

The value of \( c \) depends upon the indenter geometry and friction at the interface, \( P_m \) is the pressure, \( Y \) is the yield strength.
The transitional range of contact pressure lies between $Y$ and $3Y$, where the plastic flow is contained by the elastic material and the mode of deformation is radial expansion [111].

The three ranges of loading are

(i) purely elastic,
(ii) elastic-plastic (contained) and
(iii) fully plastic (uncontained).

In this simplified cavity model of elastic-plastic indentation, it is considered that the contact surface of the indenter is encased in a hemi-spherical ‘core’ of radius “a”. The assumption made is that within the core hydrostatic component of stress $p$ is present. It is further assumed that radial symmetry in terms of stresses and displacements is present outside the core. These are the same as in an infinite elastic, perfectly plastic body containing a spherical cavity under a pressure $p$. The boundary between the elastic and plastic part lies at a radius $c$, where $c > a$. The radial component of stress in the external zone and the hydrostatic component of stress in the core are equal at the interface. Therefore, the volume displaced by the indenter (neglecting compressibility of the core) during an increment of penetration $dh$ must be accommodated by the radial displacement of atoms lying on the boundary $r = a$. [111].

The stresses in the plastic zone $a \leq r \leq c$ are given by,

$$\sigma_r / Y = -2\ln(c/r) - 2/3 \quad (2.7)$$
In the elastic zone $r \geq c$,

\[ \frac{\sigma_r}{Y} = -\frac{2}{3}(c/r)^3 \quad (2.9) \]

\[ \frac{\sigma_\theta}{Y} = -\frac{2}{3}(c/r)^3 \quad (2.10) \]

At the boundary of the core, the core pressure is given by equation 2.11.

\[ \frac{p}{Y} = -[\frac{\sigma_r}{Y}]_{\text{eval}} = \frac{2}{3} + 2\ln(c/a) \quad (2.11) \]

The elastic – plastic boundary is given by the equation 2.12.

\[ E \tan \beta / Y = 6(1-v)(c/a)^3 - 4(1-2v) \quad (2.12) \]

Where $\beta$ is the inclination of the face of the cone to the surface ($\beta = \pi/2 - \alpha$). $v$ is the poison’s ratio.

Substituting in equation 2.12 in 2.11 for $c/a$ gives the pressure in the core. For an incompressible material a simple expression is obtained,

\[ \frac{p}{Y} = \frac{2}{3} \left[ 1 + \ln\left\{\frac{1}{3}(Etan\beta/Y)\right\}\right] \quad (2.13) \]

The stress in the material immediately below an indenter is not purely hydrostatic. If $p$ denotes hydrostatic component, the normal stress will have a value

\[ \sigma_z \approx -(p + 2Y/3) \quad (2.14) \]

and the radial stress,

\[ \sigma_r \approx -(p - Y/3) \quad (2.15) \]

The best estimate for the indentation pressure $p_m$ for the spherical cavity would therefore be $(p + 2Y/3)$.

The pressure in the hydrostatic core beneath the indenter is a function of the single non-dimensional variable $E\tan\beta / Y$, which may be interpreted as the ratio of the strain imposed by the indenter ($\tan\beta$) to the elastic strain capacity of the material $(Y/E)$.

The simplified model above was used obtain an equation below using FeSi single crystals by Zielinski [115].
\[ R = \frac{3P}{2 \pi \sigma_y} \]  

(2.16)

Where \( R \) is the plastic zone size, \( P \) is the applied pressure, and \( \sigma_y \) is the yield strength.

A similar equation was obtained by Giannakopoulos by instrumented indentation [116],

\[ R = \sqrt{\frac{0.3P}{\sigma_y}} \]  

(2.17)

Bulk metallic glasses are pressure sensitive materials. Incorporating the pressure sensitivity, Narsimhan proposed the following equation for the size of the plastically deformed zone beneath the indenter [117].

\[ R = \left[ \frac{3P}{2 \pi \sigma_o} c \left( 1 - \frac{tana}{3} \right) \right] \]  

(2.18)

\( \alpha \) is the pressure sensitivity index.

Ramamurty et. al., found that the zone size matched well with the square root of indentation load and fits the equation 2.19 [109].

\[ R = CP^{0.5} \]  

(2.19)

\( C \) is the constant of proportionality related to the intrinsic characteristics of the material.

Using the expanding cavity model of Johnson, Zhang obtained the following equation to predict the size of the plastically deformed zone [112].

\[ R = \sqrt{\frac{P}{\pi H_y}} \left[ \frac{E}{6(1-v)} \tan \beta + \frac{2(1-2v)}{3(1-v)} \right]^{1/3} \]  

(2.20)

2.9.3 Indentation fracture toughness

Indentation of brittle materials produce corner cracking that can be used to measure the toughness known as indentation fracture toughness of the material. Bulk metallic glasses are brittle material with the exception of few BMGs known as tough BMGs [55, 118]. Initiation and propagation of a crack requires creation of two new surfaces with surface energy \( \gamma \). For
brittle materials surface energy is related to the critical energy release rate \( (G_C) \) as \( G_C = 2\gamma \). In terms of \( E \), \( K_C \), and \( v \), \( G_C \) is obtained as shown in equation 2.21.

\[
G_C = \frac{K_C^2}{E(1-v^2)}
\]  

(2.21)

Indentation with a sharp indenter like the Vickers will result in an elastic/plastic stress field that governs the propagation of the crack. As shown in Figure 2.6, cracks produced by the elastic/plastic stress field can be divided into two categories (i) half-penny crack system (ii) Palmqvist cracks. Half-penny cracking system is associated with highly brittle material as compared to Palmqvist cracks formed in lesser brittle materials [119, 120].

Fig. 2.6 (a) Schematic diagrams showing plan view of Vickers hardness indent and the formation of corner cracks (b) Side view of radial (Palmqvist) cracks (c) Side view of half-penny cracks (d) side view of median and penny crack [121].

The ratio hardness to elastic modulus (H/E) is considered as a controlling parameter in the extension of a crack and formation of cracking system [122]. The cracks that are visible on the surface are shown in Figure 2.7. The cracks formed on the application of load extends further during unloading under the action of residual stress fields [123]. Penny shaped median cracks turns into a fully developed half-penny crack on unloading that is visible at the surface and also extending any lateral cracks that are formed [124]. The ratio between surface radial crack length \( c \) and half diagonal length \( a \) was related to the fracture toughness and an equation incorporating \( c \) and \( a \) was obtained empirically [122]. Hardness provided the magnitude of tensile stress on the advancing cracks as contact pressure. Plastic zone ahead of the advancing crack front increases with decreasing hardness [125]. The sharp indenter produces a wedging action to introduce a penny-shaped crack [119]. Elastic modulus was introduced into the equations through fracture mechanics analysis where fracture toughness was related to the energy release rate. In indentation testing, the applied load on the indenter
acts to plastically deform material that in turn drives the crack propagation. Crack is assumed to initiate from either the flaws already present in the material or from the interactions of the plastic deforming material during indentation. Nucleation of crack is thought to be material specific. During loading, the elastic contact stresses and the residual stresses due to plastic deformation are two contributions at the crack tip but upon unloading only residual stresses act. These residual tensile stresses arise due to elastic accommodation of the plastically deformed material. It was observed that the residual stresses upon unloading provided a greater contribution to crack extension compared the elastic contact stresses during loading. The contributions from these two components were considered and empirical relations were obtained [126, 127]. More equations were obtained by curve fitting the data of different materials [128-132]. These equations provide fracture toughness in terms of crack length, hardness, elastic modulus and applied load and had been reviewed in the literature [133]. Table 2.2 presents various models present in the literature for the calculation of indentation fracture toughness of the materials. Load below which corners cracks are not observed is called “critical or threshold load”. Indentation fracture toughness measurement is a quick method to evaluate fracture toughness. It also requires a smaller test piece and provides a number of measures from one sample. The advantages of the technique can be offset by a number of reasons including: (i) crack length measurement requires accuracy (ii) the great variety of indentation fracture toughness equations given in the literature, and (iii) the variation in fracture toughness values obtained through indentation of a material and those measured by conventional methods, such as the single edge notched beam (SENB) test (iv) lateral cracking, chipping and inhomogenieties in the material [127, 133]. The indentation technique has widely been used for fracture toughness evaluation of ceramics and glasses.

Most of the iron based BMG alloys possess low fracture toughness with indentation toughness values even below 10 MPa√m [53, 55, 56].

Table 2.2 Models for the calculation of indentation fracture toughness (IFT).

<table>
<thead>
<tr>
<th>Model</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. $K_c = \frac{(1-2\nu)}{2\pi^{2.5}} \left(\frac{HP}{c}\right)^{0.5}$</td>
<td>[120] Lawn &amp; Swain (M)</td>
</tr>
<tr>
<td>2. $K_c = 0.45 \left(\frac{H\nu(a^{0.5})}{\Phi}\right)^{1.5}$</td>
<td>[125] Charles &amp; Evans (M)</td>
</tr>
<tr>
<td>3. $K_c = \left[\frac{1}{(\pi)^{1.5}(\tan\theta)}\right] \left[\frac{P}{c^{3/2}}\right]$</td>
<td>[124] Lawn &amp; Fuller (M)</td>
</tr>
<tr>
<td>Model</td>
<td>Reference</td>
</tr>
<tr>
<td>-------</td>
<td>-----------</td>
</tr>
<tr>
<td>4. (K_c = 0.085 \frac{P}{a^{1.5}} \left[ \log \left( \frac{4.5a}{c} \right) \right] )</td>
<td>[122] Evans &amp; Wishaw (M)</td>
</tr>
<tr>
<td>5. (K_c = 0.016 \left( \frac{E}{H_V} \right)^{\frac{1}{2}} \frac{P}{c^{3/2}} )</td>
<td>[127] Anstis (M)</td>
</tr>
<tr>
<td>6. (K_C = 0.129 \left( \frac{hv}{\Phi} \right)^{0.5} \left[ \frac{Ef}{H_V} \right]^{0.4} \left( \frac{c}{a} \right)^{1.5} )</td>
<td>[126] Niihara (M)</td>
</tr>
<tr>
<td>7. (K_c = 0.014 \left( \frac{E}{H} \right)^{0.5} \left( \frac{P}{c^{1.5}} \right) )</td>
<td>[119] Lawn &amp; Evans (M)</td>
</tr>
<tr>
<td>8. (K_C = 0.142 \left( \frac{hv}{\Phi} \right)^{0.5} \left[ \frac{Ef}{H_V} \right]^{0.4} \left( \frac{c}{a} \right)^{1.56} )</td>
<td>[128] Lankford (M)</td>
</tr>
<tr>
<td>9. (K_C = 0.035 \left( \frac{E}{H_V} \right)^{0.25} \left( \frac{P}{c^{3/2}} \right) )</td>
<td>[132] Tanaka (CF)</td>
</tr>
<tr>
<td>10. (K_C = 0.022 \left( \frac{E}{H_V} \right)^{0.4} \left( \frac{P}{c^{1.5}} \right) )</td>
<td>[129] Laugier (M)</td>
</tr>
<tr>
<td>11. (K_c = 0.0285Hv^{0.6}E^{0.4}a^{0.5}\log \left( \frac{8.4a}{c} \right) )</td>
<td>[134] Blendell (CF)</td>
</tr>
<tr>
<td>12. (K_c = 0.0089 \left( \frac{E}{H_V} \right)^{0.4} \left( \frac{P}{a^{c/0.5}} \right) )</td>
<td>[126] Niihara (CF)</td>
</tr>
<tr>
<td>13. (K_c = \alpha \left( \frac{H_P}{\tau} \right)^{0.5} )</td>
<td>[135] Shetty (PQ)</td>
</tr>
<tr>
<td>14. (K_c = 0.035 \left( \frac{hv}{\Phi} \right)^{0.5} \left[ \frac{Ef}{H_V} \right]^{0.4} \left( \frac{1}{a} \right)^{-0.5} )</td>
<td>[126] Niihara (PQ)</td>
</tr>
<tr>
<td>15. (K_C = 0.015 \left( \frac{E}{H_V} \right)^{0.67} \left( \frac{1}{a} \right)^{-0.5} )</td>
<td>[131] Laugier (PQ)</td>
</tr>
</tbody>
</table>

\( K_c = \text{Indentation fracture toughness}, \ H = \text{Hardness} \ (P/2a^2), \ H_V = \text{Vickers hardness} \ (MPa), \ P = \text{Indentation load}, \ a = \text{Half diagonal length}, \ l = \text{Crack length}, \ c = a + \ell, \ \Phi = \text{Constraint factor}. \ PQ = \text{Palmqvist}, \ M = \text{Half-penny/Median}, \ CF = \text{Curve fitting}. \)

2.10 Magnetic behavior of BMGs

The magnetic properties of BMGs have been investigated mostly in Fe-based BMGs, and a few investigations have also been reported on Co-based BMGs. The most desirable soft magnetic properties of the material include high saturation magnetization, electrical resistivity and magnetic permeability and low magnetic coercivity. Good corrosion resistance and high mechanical strength with reasonable ductility are also useful. It should be kept in mind that it is not always easy to achieve a good combination of all the desired features in one alloy composition. A set of properties can be chosen which can perform the desired function properly. For example, improvement in GFA by alloying additions may lead to a
decrease in the value of saturation magnetization. On the other hand, if we wish to attain the highest saturation magnetization, for example, in case of Fe based BMGs, Fe or other ferromagnetic elements have to be in the highest quantity and it can be achieved if the alloying elements are maintained at a low level. This may as a result lower the glass forming ability [69].

Co-based metallic glasses not only are marked by very low saturation magnetostriction constant of the order of $1 \times 10^{-7}$ ppm but these also possess low magnetic coercivity values ($< 1 \text{ A/m}$). These are considered zero-magnetostriction alloys. Fe-based BMGs show a higher saturation polarization compared to Co-based BMGs, but they possess coercivity values that are an order of magnitude higher. Magnetostriction constant of Fe-based BMGs can reach $10 – 20 \times 10^{-6}$ ppm [20].

**2.11 Development of Fe and FeCo based BMGs**

The first Fe-based BMG alloy (in the form of melt spun ribbons) was produced in 1995 with a composition Fe$_{72}$Al$_5$Ga$_2$P$_{11}$C$_6$B$_4$ [8]. Many other Fe-based BMGs were subsequently produced. The components of the Fe based bulk amorphous alloys can be grouped into four categories as shown in Figure 2.7.

![Fe based BMG construction](image)

**Fig. 2.7 Fe based BMG construction [136].**

The FM elements provide the magnetic properties, the EM and ML elements act as glass-formers and grain refiners, and the LM elements act as nucleation agents in forming the nanocomposite state [136].

Early transition metal additions (Nb, Ta, Cr, and Mo) influence the stability of the amorphous
phase as well as promote casting without excessive oxidation. Cr substitution for ferromagnetic metals reduces the amorphous phase’s Curie temperature and allows study of the decoupling of nanoparticles/nanophase above the amorphous phase’s Curie temperature. Variation of the Fe:Co ratio in alloys optimize the amorphous phase curie temperature, magnetic inductions, and magnetostriction coefficient [136].

Some of the important Fe and FeCo based BMG alloy systems are discussed in 2.11.1 to 2.11.4

2.11.1 Fe-Cr-Mo-Ga-P-C-B BMGs

This is iron-metal-metalloid type of system. In this system bulk metallic glass of a few millimeter diameter is possible to cast and the critical cooling rate required is of the order of hundreds K/s. Presence of Ga improves the glass formability and soft magnetic properties by increasing the density and dissolving into the bcc grains [137]. Three of the typical compositions are \( \text{Fe}_{65.5}\text{Cr}_4\text{Mo}_4\text{Ga}_4\text{P}_{12}\text{C}_5\text{B}_{5.5} \), \( \text{Fe}_{69.5}\text{Cr}_4\text{Mo}_4\text{P}_{12}\text{C}_5\text{B}_{5.5} \) and \( \text{Fe}_{71.5}\text{Cr}_2\text{Mo}_2\text{Ga}_2\text{P}_{12}\text{C}_5\text{B}_{5.5} \) [19, 20, 24]. The iron content is normally kept above 65at%. Increasing the iron content leads to a decrease in the GFA. The supercooled liquid region also decreases with an increase in the iron content. These alloys have a \( T_g \) ranging in 720 K to 760 K and crystallization temperature in the range 780 K – 820 K. The reduced glass transition temperature (\( T_{rg} \)) of these alloys fall in the range 0.55 – 0.57. The values of crystallization enthalpy range from 50 – 70 J/g [24].

The cooling rate required to obtain an amorphous structure lies in the range \( 10^2 - 10^3 \) K/min. The values of the reduced glass transition temperature \( T_{rg} = T_g / T_1 \) and the extension of the supercooled liquid region \( \Delta T_x \) are high. These high values are as a result of compliance with the Inoue criteria of glass formation. [24].

The atomic size ratios for transition metal/metalloid in this system are in the range 0.57- 0.73. The fracture stress of these alloys is in the range 2.8 – 3.2 GPa with a maximum fracture strain of 2.3% in compression. The hardness values range from 880 – 900 Hv [24, 138]. The Fe-(CrMoGa)-PCB amorphous alloys exhibit good soft magnetic properties, characterized by a low magnetic coercivity and a high magnetic permeability because of the absence of crystalline anisotropy. The magnetic coercivity values in these alloys range from 5 A/m to 75 A/m. There is an abrupt increase in magnetic coercivity of these samples after crystallization with the values reaching 10 kA/m whereas annealing below \( T_g \) leads to a decrease in the values of coercivity (approaching 1 A/m). The curie temperatures of these alloys range in 400
K - 450 K. The saturation magnetization values are the range 85 – 90 Am²/Kg. The value of saturation magnetization increases with decreasing test temperature approaching a value of 110 Am²/Kg at 100 K. The critical diameter of the amorphous rod can be enhanced by the addition of metals like yttrium, and rare earth elements like lanthanum but at the cost of some of the desired magnetic properties. The largest diameter of 12 mm was obtained by the addition of erbium [10].

In Fe₅₃Ni₁₅Mo₅P₁₀C₁₀B₅ alloy shows good formability. The value of viscosity in the supercooled liquid region range between 10⁷ Pa-s and 10¹⁰ Pa-s. Critical diameter is 4 mm with good magnetic properties [139].

2.11.2 Fe-Si-B-Nb BMGs

Boron imparts glass formability to these alloys. Presence of Nb also improves glass formability. Upto 1.5 mm cylindrical rods have been cast by the addition of 4 at% Nb. The addition of Nb results in an increase in the supercooled liquid region (ΔTₓ) in this system. These alloys have high saturation magnetization (> 150 Am²/Kg) that decreases with a decrease in the iron content especially below 80 at%. Their glass transition temperatures (T₉) fall in the range 800K – 850K with their crystallization temperatures (Tₓ) existing within 850K – 900K. The Curie temperature (Tₐ) of the alloy Fe₇₅Si₁₀B₁₅ is near 700K [140].

Annealing of Fe–Si–B–M glassy alloys containing small amounts of (up to 1.5 at%) of M (M = Cu, Nb, Mo, W, Ta, etc) results in the precipitation of fine (10nm in size) α-Fe(Si,B) crystalline particles. Since Cu and Fe have a positive heat of mixing, segregation occurs forming Fe-rich, Cu-rich and Nb-rich regions. Fe-rich regions become the nuclei for the α-Fe solid solution. Cu-rich and Nb-rich regions do not crystallize as these have a higher crystallization temperature. Therefore, the microstructure consists of fine α-Fe grains dispersed in an amorphous matrix. These partially crystalline alloys exhibit low saturation magnetostriction, low coercivity, and low core losses as compared to the fully amorphous alloys [61, 140].

Over 1.3T saturation magnetization has been shown by Fe-rich Fe–Co–B–Si–Nb alloys that decrease with an increasing Co and Ni contents. Low value of coercivity (<2.5 A.m⁻¹) is shown by all the alloys that decreases gradually with an increasing Co content. The alloys rich in cobalt have shown values ≤1 A.m⁻¹ [61].
In (Fe\textsubscript{72}Nb\textsubscript{4}B\textsubscript{20}Si\textsubscript{4})\textsubscript{100-x}Y\textsubscript{x} \,(x = 0 – 5) BMGs, addition of yttrium improves the glass formability \((D_{\text{max}} = 4\,\text{mm for } x = 3)\), thermal stability of the alloy by increasing \(\Delta T_x\) (56 K for \(x = 3\)) and \(T_g\) \((\text{from 842 K for } x = 0, \text{to 905 K for } x = 4)\) of the alloy. Yttrium is an oxygen scavenger that can reduce oxygen concentrations. In a study 1 at\% addition of Y reduced the oxygen concentration from 1250 ppm to 170 ppm in the BMG alloy [22].

In (Fe\textsubscript{0.75}Si\textsubscript{0.10}B\textsubscript{0.15})\textsubscript{100-x}Dy\textsubscript{x} \,(x = 0, 0.5, 1 and 2) alloys, dysprosium additions resulted in an improvement of glass formability and thermal stability of the BMG. A large supercooled liquid region (56 K) is obtained by the addition of 2at\% dysprosium. Dy has a negative heat of mixing with all the constituent elements in the alloy [141].

### 2.11.3 Fe-Nb-B BMGs

This is an iron - transition metal - metalloid type of system. In these metallic glasses, the amount of intermediate transition metals in alloys is normally kept greater than 5 at\% for bulk glass formation [142]. Niobium causes slowing down of diffusion which increases the crystallization temperature of the amorphous alloy [143]. The upper limit to retain good magnetic properties after crystallization is 10 at\% for Nb and 15 at\% for B in the BMG alloy [34]. Decrease in the iron content of the alloy results in a decrease of saturation magnetization. Curie temperature increases with an increase in the boron content and decreases when niobium replaces iron [15, 144].

Various compositions in this alloy system have been produced in the ribbon form owing to the low glass formability of these alloys. In Fe\textsubscript{77}Nb\textsubscript{6}B\textsubscript{17} alloy, 45 µm thick ribbons were produced with \(T_g = 797\,\text{K},\ T_x = 814\,\text{K},\ \Delta T_x = 17\,\text{K},\ T_S = 1398\,\text{K} \) and \(T_L = 1424\,\text{K}\). This alloy has a saturation magnetization value of 0.735 T with \(H_C\) value of 22 A-m\textsuperscript{-1}. The permeability is good with a value of 4300 [21]. In Fe\textsubscript{79}Nb\textsubscript{7}B\textsubscript{14} thin ribbons with a thickness of 20 µm, the value of saturation magnetization was \(\sim 65\,\text{emu/g at 294 K and it increased to } \sim 90\,\text{emu/g at 260 K. The curie temperature is } \sim 370\,\text{K for this composition [25]}.\) In Fe\textsubscript{79}Nb\textsubscript{3}B\textsubscript{15}Cu\textsubscript{1} ribbons formed through melt spinning, high saturation magnetization value of 150 A-m\textsuperscript{2}/kg is obtained after annealing above \(T_g\) but below \(T_x\). It formed nano sized (< 10 nm) \(\alpha\)-Fe crystals in an amorphous matrix. A low value of magnetic coercivity (<10 A/m) is also obtained after annealing [34]. The Fe\textsubscript{80}Nb\textsubscript{6}B\textsubscript{14} has low glass formability thus only forming thin ribbons. The glass transition temperature is \(\sim 750\,\text{K and crystallization temperature is } \sim 775\,\text{K. In Fe}_{86-x}\text{Nb}_xB_{14} \,(x = 0 – 10) alloys, upon primary crystallization,
mean grain size decreases with an increase in the Nb content, becoming less than 20 nm for Nb content of 5 at% or more. The apparent activation energy increases and reaches a value of 4 eV or more for the Nb content of 5 at% or more [15, 143]. Nb plays an important role in the formation of nanostructure through accelerated nucleation. B generates strong intergranular magnetic coupling by increasing the $T_c$ of the residual amorphous phase [15]. It increased from 299K to 419K in Fe$_{93-x}$Nb$_7$B$_x$ alloy system with x changing from 9 to 20 [25]. In Fe$_{65+x}$Nb$_{10}$B$_{25-x}$ ($x = 0, 5, 10$), the metallic glass has shown good thermal stability and that increases with B/Fe ratio. The 1st crystallization product changes from Fe$_{23}$B$_6$ metastable phase to bcc-Fe with increase in x. Soft magnetic properties are deteriorated after precipitation of the large size (~14 nm) metastable boride grains [34].

Bulk amorphous alloys have been produced in high boron compositions with the best glass formability obtained for a boron content greater than 20 at% [145]. In Fe$_{66}$Nb$_3$B$_{30}$ alloy, a combination of a high thermal stability against crystallization with a low coercivity (1.5 A/m) and a high saturation magnetization (105 Am$^2$/Kg), makes this glass an excellent material for application as soft magnetic material. This alloy requires very high activation energy for crystallization (~760 kJ/mol) and has a supercooled region of around 31K with a reduced glass transition temperature $T_{ig}$ value of 0.55. It shows a high glass transition temperature (845K), crystallization temperature (876K and 1067K) and curie temperature (550K for amorphous and 900K for nanocrystalline), thus making it suitable for applications which require a continuous operation at high temperatures. Annealing between $T_g$ and $T_x$ forms Fe$_{23}$B$_6$ phase in the glass matrix while annealing above $T_x$ forms $\alpha$-Fe, Fe$_2$B, Fe-Nb-B phases. The coercivity is reported to increase with crystallization [31].

In Fe$_{77-x}$Nb$_3$B$_{17}$Y$_x$ ($x = 0 - 4$) BMGs, addition of yttrium improves the glass formability, thermal stability, fracture strength and elastic modulus. The saturation magnetization increased by 10% for $x = 3$ [21].

In (Fe$_{0.72}$B$_{0.24}$Nb$_{0.04}$)$_{100-x}$Y$_x$ ($x = 0 - 6$), addition of Y improves the glass formability with the maximum diameter reaching 7 mm with $x = 4.5$. This alloy has shown good thermal stability as the amorphous structure is retained even after 6 hours of heat treatment at $T_g$. It has also shown good soft magnetic properties. The largest supercooled liquid temperature region is shown by the alloy without yttrium i.e., $x = 0$ [26].
In (Fe\(_{0.72-x}\)Ni\(_x\)B\(_{0.24}\)Nb\(_{0.04}\))\(_{95.5}\)Y\(_{4.5}\) system substitution of Fe by Ni has resulted in improvement in the glass formability of the alloy (critical diameter increased from 0.5mm to 4.5 mm). The supercooled region enhanced to 94 K with \(x = 0.06\) in this system. This alloy has a low coercivity that is less than 0.25 oersted [146].

In (Fe\(_{0.72}\)B\(_{0.22}\)Y\(_{0.06}\))\(_{98}\)M\(_2\) series alloys, Nb or Ta addition enlarges supercooled region from 50 K for ternary alloy to \(~62\) K for Nb or Ta additions, and slightly increases reduced glass transition temperature (\(T_{g}\), from 0.56 to 0.58); therefore, making it possible to cast a 3 mm diameter BMG rod. The saturation magnetization and Curie temperature reduces (from \(~550\) K to \(~500\) K) due to the magnetic dilution as a result of the addition of these nonmagnetic elements. The substitution elements (Ti, Ta, Nb, Hf) improves the GFA of the alloy, thus making it possible to cast a rod of bulk amorphous alloy with a critical diameter of 3mm for Ti or Hf substitution and 4mm for Ta or Nb substitution. The expansion of the supercooled region in these bulk amorphous alloys is responsible for increase in maximum diameter. \(Y_4Fe_{72}B_{22}Ta_2\) has shown the optimal glass forming ability in terms of the critical diameter (4mm) achieved, and also good soft magnetic properties of \(M_s = 123\) emu/g, \(H_C = 0.2\) Oe, and \(T_C \sim 550\) K [32].

Addition of element/s with positive heat of mixing with the major alloying element (e.g., Cu addition) aids in the crystallization of the phases in the amorphous alloy. In the Fe\(_{75+y}\)Nb\(_y\)B\(_{15}\)Cu\(_1\) (\(y= 0, 2, 4\)) alloys, the effect of adding Cu and replacing Nb by Fe has been studied. Nanocrystallization behavior was changed to a single step from a complex two step process with the addition of Cu. It also resulted in a more refined microstructure with smaller grain size that reduces magnetic coercivity. Enhancement in saturation magnetization (from \(~100\) Am\(^2\)/Kg to \(~150\) Am\(^2\)/Kg) and curie temperature (from \(~350\) K to \(~425\) K) was observed with an increase in Fe/Nb ratio although thermal stability of the amorphous phase decreased. [34].

Addition of rare earth elements in Fe-Nb-B alloys improve glass formability and formation of nanocrystals [147]. In Fe\(_{82}\)Nb\(_2\)B\(_{14}\)RE\(_2\) (Gd, Tb, Dy), the magnetism of the rare earth alloying additions resulted in a decrease of the crystallization temperature (by 4–7 K), an increase of activation enthalpy (by 0.6–0.7 eV) and an increase of the heat of the first crystallization stage (by 3–6 J/g). Addition of rare earth also resulted in an increase in the curie temperature of the alloy. Diffusion process is slowed down by the activation enthalpy. Usually an increase in the crystallization temperature is noted with an increase in activation enthalpy [148].
Addition of Nd in the Fe-Nb-B system produces soft magnetic material if amorphous structure is obtained. Appearance of hard magnetic phases during cooling or after crystallization annealing render's it magnetically hard [149].

In quinary Fe$_{73-x}$Nb$_4$Hf$_3$Y$_x$B$_{20}$ alloys with Y addition not only the glass formability of the alloy is enhanced, but also the soft magnetic (H$_c$ = 1.6 – 3.6 A/m) and mechanical properties are improved ($\sigma_f$ > 3200 MPa) [30].

2.11.4 Fe-Co-Nb-B BMGs

Addition of cobalt in Fe-Nb-B alloys improves the glass forming ability, mechanical and soft magnetic properties. It also increases the supercooled liquid region (SLR).

Addition of transition metals generally leads to an improvement in glass formability. In (Fe$_{0.5}$Co$_{0.5}$)$_{71-x}$Nb$_6$B$_{23+x}$ (x = 0, 2, 3, 4 and 5) alloys, presence of Co improves glass formability. The plastic strain in amorphous alloys has increased from 1.4% to 3.7% with the addition of 0.4% copper in the alloy. The formation of proper size and amount of clusters result in significant improvement of plasticity. These alloys have a compression yield strength that is greater than 4800 MPa [44]. Cu and Ni additions result in 4.5% and 4.2% plastic strain respectively [40].

[(Fe$_{0.9}$Co$_{0.1}$)$_{0.72}$B$_{0.24}$Nb$_{0.04}$]$_{95.5}$Y$_{4.5}$ bulk metallic glass has shown low thermal expansion with a CTE (\(\alpha\)) close to kovar alloy (Fe-29Ni-17Co) in the range 100K to 300K [94].

For (Fe$_{0.5}$Co$_{0.5}$)$_{67.5}$Nb$_4$Gd$_{3.5}$B$_{25}$, the maximum diameter achieved is 5.5 mm with good soft magnetic properties. This is the largest diameter that has been achieved in Fe-Co based systems with rare earth presence. A large \(\Delta T\) value of 102 K has been reported for this alloy. The value of strength is 3854 MPa but the strain to failure in compression is low (<1%) [33].

In Fe$_{77-z}$Co$_2$Nb$_7$B$_{15}$Cu$_1$ (z = 2, 4, 8) alloys, the nanocrystallization kinetics and phases formed do not change with Co addition as it only substitutes Fe atoms in the bcc structure. However it shifts the crystallization peak to lower temperatures. Co addition enhances the saturation magnetization and curie temperature without significantly increasing the coercivity [34].
Chapter 3

Alloy production and characterization techniques

This chapter provides detailed information about alloy development, equipment employed, and experimental procedures adopted. The development and characterization techniques are discussed in detail.

3.1 Casting and characterization plan

The FeCo based BMGs were cast and characterized in the as-cast, annealed and partially crystalline conditions.

Pure elements in the form of small pieces were cleaned and weighed according the composition required. These elements are then loaded in controlled atmosphere arc furnace where these were melted together and then cast into amorphous strips. One third of the strips were annealed at temperature that was below $T_g$ while one third were partially crystallized by heating at the crystallization temperature. The remaining one third of the amorphous strips were used as-cast. The strips in the three conditions were characterized for their structure, hardness, thermal stability, and magnetic properties. The deformation behavior was also studied by using bonded interface technique.

3.1.1 Equipment and materials used

The equipment and materials required for the development and characterization of these BMG alloys is given in sections 3.1.1.1 and 3.1.1.2.

3.1.1.1 Equipment

Following equipment have been used for the completion of the research work.

1. Digital weighing balance
2. Electric arc melting furnace with copper mold for BMG casting
3. Ultrasonic bath for cleaning of materials
4. Electrical resistance heating horizontal tube furnace
5. Electric discharge machine (EDM)/Diamond precision cutter.
7. Differential scanning calorimeter (DSC)  
8. X-Ray diffractometer  
9. Optical microscope (OM) with fitted camera  
10. Vickers microhardness tester  
11. Scanning electron microscope (SEM)  
12. Vibrating sample magnetometer.  

### 3.1.1.2 Materials

Following materials have been used for completion of the research work.

1. Iron in the form of small lumps or cylindrical pieces (purity 99.99 at%).  
2. Cobalt in the form of small lumps or cylindrical pieces (purity 99.99 at%)  
3. Niobium in the form of small lumps or cylindrical pieces (purity 99.99 at%)  
4. Boron in the form of small lumps (purity 99 at%)  
5. Epoxy resin and hardener for joining.  

### 3.2 Alloy development

High purity elements were cut into small pieces having a size suitable for melting in an arc furnace. These small pieces were then put in separate beakers for each element. These beakers were then filled with acetone such that the pieces are completely dipped in the liquid. These are then placed in an ultrasonic cleaning bath for half an hour for surface cleaning. The pieces were dried and weighed according to the required compositions using an electronic balance with 1 mg least count made by Schimadzu Corporation.  

#### 3.2.1 Melting and casting of BMG alloys

Highly pure Fe (99.99%), Co (99.99%), Nb (99.99%) and B (>99%) were cleaned, dried and weighed according to the calculations for the production of the alloys (Table 3.1). The melting points of Fe, Co, Nb and B are 1808 K (1535 °C), 1766 K (1493 °C), 2741 K (2468 °C) and 2573 K (2300 °C) respectively [67]. Melting was carried out in a water cooled copper crucible in mini-arc melter (MAM1) of Edmund-Buehler GmBH in an argon atmosphere. Figure 3.1 shows a schematic diagram of the melting and casting technique for making the BMG alloys. The melting chamber of the furnace was purged with 99.999% pure argon three times and pure titanium was used as a getter before melting the metals. The elements were
melted together to produce a button shaped sample that was remelted four times to ascertain good homogeneity. These button shaped sample was cleaned and then cast into a rectangular strip in a hollow cavity made of copper in the same furnace. A number of strips were produced from one alloy button. All the BMG alloys were produced using the same procedure. Water cooled tungsten electrodes with a sharp tip were employed to produce an electric arc for melting of the metals. The cast strips were trimmed, cleaned and cut into parts by using abrasive diamond cutter. The cut samples were cleaned in acetone with the help of ultrasonic bath before characterization.

Table 3.1 shows alloy compositions produced by arc melting and casting in water cooled copper mold. Composition was determined through the use of inductively coupled plasma technique.

Table 3.1 Aim and actual compositions of the BMG alloys cast.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Co</th>
<th>Fe</th>
<th>Nb</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>42.5</td>
<td>40.3</td>
<td>11.6</td>
<td>5.7</td>
</tr>
<tr>
<td>A2</td>
<td>42</td>
<td>39.9</td>
<td>11.9</td>
<td>6.2</td>
</tr>
<tr>
<td>A3</td>
<td>41.6</td>
<td>39.5</td>
<td>12.1</td>
<td>6.8</td>
</tr>
<tr>
<td>A1</td>
<td>47</td>
<td>41.3</td>
<td>8.1</td>
<td>3.6</td>
</tr>
<tr>
<td>A2</td>
<td>45</td>
<td>44</td>
<td>6.1</td>
<td>4.9</td>
</tr>
<tr>
<td>A3</td>
<td>43.4</td>
<td>41.5</td>
<td>8</td>
<td>7.1</td>
</tr>
</tbody>
</table>
Fig. 3.1 Schematic diagram of the suction casting technique used to make the BMG samples.

Figure 3.2 (a) shows the mini-arc melter (MAM1) used for the production of BMG alloys. It is a single electrode arc furnace that is used for melting and casting of small quantity (maximum 10 g) of an alloy in controlled atmosphere. Figure 3.2 (b) shows water cooled copper plate with a copper die in the middle. This die is inserted into a hole in the plate. The walls of the plate hole are in contact with the outer surface of the die. The hole in the die that is visible at the top is the inlet for the molten alloy into the die cavity. The molten alloy rapidly cools and solidifies when it comes in contact with the die walls.

Figure 3.3 shows two BMG alloy samples cast using the mini-arc melter shown in Figure 3.2. BMG alloy strips can be produced to a length of approximately 15 mm. The width of the BMG alloy strips produced varies between 4 to 5 mm. The thickness of the BMG alloys produced is 1 mm.
Fig. 3.2 Suction casting setup (a) Mini-arc melter (b) Copper plate and die for suction casting

Fig. 3.3 FeCo based BMG alloy as-cast samples
Table 3.2 contains information related to the melting and casting of these BMG alloys in the mini-arc melter (MAM1).

Table 3.2 Parameters used for melting and suction casting

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Atmosphere (gas purity)</th>
<th>Power source</th>
<th>chamber purge (No. of times)</th>
<th>Getter type</th>
<th>Chamber pressure used for suction casting (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>Argon (99.999%)</td>
<td>Electric arc</td>
<td>03</td>
<td>Titanium</td>
<td>0.8</td>
</tr>
<tr>
<td>A2</td>
<td>Argon (99.999%)</td>
<td>Electric arc</td>
<td>03</td>
<td>Titanium</td>
<td>0.8</td>
</tr>
<tr>
<td>A3</td>
<td>Argon (99.999%)</td>
<td>Electric arc</td>
<td>03</td>
<td>Titanium</td>
<td>0.8</td>
</tr>
</tbody>
</table>

3.2.2 Annealing treatment of BMG alloys

Two types of annealing treatments have been carried out on the alloys. Annealing at temperature below the glass transition temperature (T_g) referred to as sub-T_g annealing and annealing at temperature higher than glass transition temperature (T_g) referred as post-T_g annealing (Partial crystallization treatment). Sub-Tg annealing was carried out 723 K for 30 minutes while post-Tg annealing was carried out at their respective crystalline start temperatures (T_x) for 1 minute to produce partial crystallinity. These temperatures were 853 K, 863 K and 903 K for A1, A2 and A3 respectively. These heat treatments were carried out in an evacuated quartz tube with vacuum of the level \(10^{-6}\) mbar. These tubes containing the samples were purged three times with high purity (99.999%) argon gas before maintain the high vacuum level. These thermally treated alloys were then characterized using DSC, XRD, SEM and VSM.

The chemical composition of the BMG alloys produced was obtained through inductively coupled plasma technique.
3.3 Differential scanning calorimetry (DSC)

The transition temperatures of the amorphous alloys are important to determine the thermal stability of the metallic glasses. The precise determination of these temperatures is therefore, important for their use in various applications. The transformation temperatures of the Fe-Co-Nb-B alloys were determined by Netsch DSC model-404 differential scanning calorimeter. Glass transition temperature ($T_g$), supercooled liquid region (SLR), crystallization start temperature, and crystallization finish temperature were determined using forward scans within the temperature range of 30°C to 1000°C at a scan rate of 10°C /min.

3.4 X-Ray diffraction analysis

X-ray diffraction scans were obtained at room temperature by using Philips PW3710 X-ray diffraction equipment. The rectangular strip samples in the as-cast, annealed and partially crystalline conditions were scanned from 30° to 60° at 20-angle with a step size of 0.01° and a time of 1.0 sec/step.

3.5 Microstructural analysis

Microstructural features like hardness indents, plastically deformed zone etc were observed using a scanning electron microscope (SEM). Philips XL 30 scanning electron microscope was used for imaging of the BMG alloy samples. Tescan Mira 3 SEM was also employed for imaging certain of the microscopic features.

Microstructure and other micron features of the samples were studied using Philips XL-30 (Figure 3.4) and Tescan Mira 3 electron microscopes.

3.6 Microhardness test

Microhardness of the samples was measured by using Tukon Vickers microhardness testing machine of Wilson Instruments. Load in the range 0.1 kg to 1.2 kg was applied with a step size of 0.1 kg. The load was applied for a time of 20 seconds.

The diagonals of the indent were measured using an optical microscope at a magnification of 800x. Figure 3.4 shows a schematic diagram of the indent and the length of the diagonals. The formula employed to calculate the hardness value is as follows:
\[ H_V = 1.854 \frac{F}{d_1 d_2} \]  \hspace{1cm} (3.1)

\[ H_V \] = Vickers hardness number

\[ F \] = Load (Kg)

\[ d_1 \] = Length of Vicker’s indentation diagonal 1 (mm)

\[ d_2 \] = Length of Vicker’s indentation diagonal 2 (mm)

Fig. 3.4 Schematic diagram of the hardness indent showing the diagonals lengths

3.7 Magnetic properties

The vibrating sample magnetometer (VSM) is one of the most common instruments used for the measurement of magnetization. It is an induction technique, which detects the magnetic field produced by an oscillating magnetic moment. The sample oscillates at a low frequency and induces a signal proportional to magnetization. Saturation magnetization (\(M_S\)), magnetic remanance (\(M_R\)), and magnetic coercivity (\(H_C\)) are determined from the magnetization curves.

3.8 Deformation behavior

The deformation behavior of the BMG alloys was studied by using bonded interface technique to view deformation zone beneath the microhardness indent (Figure 3.5). Two adjacent surfaces of the sample of a BMG alloy were ground and polished to obtain smoothness and straight edges. Two of these polished samples of the same BMG alloy were bonded together by joining the flat polished sides through a strong polymeric adhesive. This polymeric bonding agent was subsequently dissolved in acetone to separate the polished surfaces after hardness indents were made at the interface with 0.2, 0.5, and 1.0 kg loads. The thickness of adhesive layer was maintained at 6 μm ± 2 μm. Images of the hardness indents and the deformed zone in the BMG alloy, beneath the hardness indents were taken.
3.8 Indentation fracture toughness

Indentation fracture toughness was calculated by measuring the length of the crack produced at corner of the Vickers microhardness indent and substituting the values in the relations given in Table 2.2. Only indents with clean cracks were included. Crack length “l” and half diagonal length “a” is measured as shown in the Figure 3.5.

Fig. 3.5 Schematic diagram of a bonded interface also showing an impression of a hardness indent.

Fig. 3.6 Schematic diagram of a hardness indent with corner cracks. Crack length “l” and half diagonal length “a” is also marked.
Chapter 4
Results and Discussion

(Fe$_{0.5}$Co$_{0.5}$)$_{69-x}$Nb$_6$B$_{25+x}$ (x = 0, 2, 4) BMG alloys designated as A1, A2 and A3 respectively has been produced and characterized in the as-cast, annealed and partially crystalline conditions. The results are presented and discussed in this chapter.

4.1 X-ray diffraction analysis

X-ray diffraction is performed to detect any crystalline phases present in the samples. Absence of these crystalline phases is confirmed by the very broad peak or hump present in the diffraction scan of the samples. Figure 4.1 presents X-ray diffraction scan of the (a) as-cast, (b) annealed and (c) partially crystalline BMG alloys. No peak is present in the XRD scans of the as-cast and annealed samples thus confirming the amorphous nature of the structure. However, it is rather difficult to rule out the existence of a small volume fraction of nano-crystalline precipitates, which may be present in the glassy matrix.

Crystals of α-FeCo has been shown to form as first crystallization product in similar compositions [59, 62, 80, 150, 151] but there also are reports of the formation of borides along with α-FeCo solid solution [80, 152, 153]. X-ray diffraction patterns of these partially crystalline BMG alloys, shown in Figure 4.1 (c), contain low intensity broad peaks suggesting the presence of nanometer sized crystals within amorphous domains.

X-ray diffraction scans of A1, A2 and A3 have not shown presence of any crystalline phase for as-cast and annealed conditions. In the partially crystalline condition, a small broad peak can be observed in the scans of all the alloys indicating the presence of crystalline phase. Scherrer’s formula was used to calculate the size of the crystals formed in the BMG alloy after partial crystalline heat treatment. The crystal sizes obtained were 21.5 nm, 18.8 nm and 22.5 nm for A1, A2 and A3 respectively.
Fig. 4.1 XRD scans of the BMG alloys in (a) as-cast, (b) annealed and (c) partially crystalline conditions. Peaks are shown by arrows.
4.2 Thermal analysis and comparison of BMG samples

The influence of the composition on the glass forming ability and thermal stability can be evaluated from measurements performed through differential scanning calorimetry. For all the BMG alloys, the DSC scans have shown a glass transition followed by a supercooled liquid region and crystallization as shown in Figure 4.2 and Figure 4.3. The crystallization start ($T_x$) and crystallization peak ($T_p$) temperatures are also marked on the respective curves.

![DSC scans of BMG alloys A1, A2, and A3 in the as-cast condition showing transformations at different temperatures.](image)

**Fig. 4.2** DSC scans of BMG alloys A1, A2, and A3 in the as-cast condition showing transformations at different temperatures.

Figure 4.2 shows the DSC scans of the three alloys in the as-cast condition. Peaks in the scans represent the crystallization events that are marked as 1, 2, 3 etc. The first crystallization event, marked as 1, results in the formation of $\alpha$-FeCo solid solution. Crystallization at higher temperatures, marked as 2, 3 and 4 relate to the formation of various borides. At higher boron contents ($\geq$30 at%), the first crystallization event produces a boride rather than $\alpha$-FeCo solid solution [31, 37, 154, 155]. Figure 4.3 shows $T_g$ and $T_x$ of the BMG alloys in the as-cast condition. The chemical composition of these alloys is given in Table 3.1.
Fig. 4.3 DSC scans of the as-cast alloys. $T_g$ (glass transition), $T_x$ (crystallization start), and $T_p$ (crystallization peak) temperatures are marked for alloys.

The characteristic temperatures were measured as the onset of the events ($T_g$, and $T_x$ respectively) upon heating at a constant rate. Tangent intersection method was used for the purpose. The values of $T_g$, $T_x$, SLR and $T_p$ are given in Table 4.1.

Table 4.1 $T_g$, $T_{x1}$, $T_{x2}$, $T_p$, and SLR [$\Delta T$] of as-cast samples obtained from DSC scans

<table>
<thead>
<tr>
<th>#</th>
<th>Alloy</th>
<th>$T_g$ (K)</th>
<th>$T_x$ (K)</th>
<th>SLR (K)</th>
<th>$T_p$</th>
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<tr>
<td>1</td>
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<td>815</td>
<td>853</td>
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<td>2</td>
<td>A2</td>
<td>820</td>
<td>863</td>
<td>43</td>
<td>883</td>
</tr>
<tr>
<td>3</td>
<td>A3</td>
<td>840</td>
<td>905</td>
<td>65</td>
<td>935</td>
</tr>
</tbody>
</table>

DSC scans of these BMG alloys reveal that the $T_g$ and SLR increases with an increase in the boron content of the alloy. This is shown in the graphical form in Figure 4.4.

$T_g$ and $T_x$ temperatures have shown an increase when boron replaces iron-cobalt in the alloy composition i.e., with increasing $x$. The highest values have been exhibited by A3. $T_g$ and $T_x$ of all the three BMG alloys was above 800 K thus indicating a range of thermal stability. The supercooled liquid region also increases with an increase in the boron content (Figure 4.4).
Fig. 4.4 Change of $T_g$ and SLR with boron content

A large supercooled liquid region (36 - 65 K) indicates the stability of the glassy liquid, another parameter related to good glass forming ability. SLR is the region in which the BMG can be plastically deformed/shaped without being crystallized.

4.3 Mechanical properties and their comparison

The mechanical properties of the BMG alloys have been deduced from the indentation hardness values obtained for as-cast, annealed and partially crystalline BMG alloys.

4.3.1 Hardness of bulk metallic glass

The indentation hardness, $H_V$, is the resistance of a material to a permanent indentation. It is the average pressure under the indenter in fully developed plasticity, where the hardness $H_V$, is the ratio of the applied load to the remnant contact area of the plastic indentation.

4.3.1.1 Surface indentation characteristics

In Figure 4.5 (a), a hardness indent has been shown in which material from the edges of the hardness indent is displaced upwards and can be seen as pileups in discrete steps due to inhomogeneous deformation of the elastic-perfectly plastic solid also given in [109]. These shear bands formed at the indent edges show that the plastic deformation of the BMG takes place through the formation of shear bands. These bands are a common feature in BMGs but may not be present around all the indents as shown in the Figure 4.5 (b). Some of these bands are fully formed while others are only partially visible. Shear bands also intersect other shear bands and it seems that their radii are smaller than the
radii of the bands, these are intersecting. This type of intersection is shown in Figure 4.5 (a).

![Shear bands](image1)

![Corner cracks](image2)

Fig. 4.5 Hardness indents (a) as-cast A2 with shear bands formed at the edges. (b) Annealed A2 without any bands forming at the edges (c) partially crystalline A2 with cracks originating from the corners.

In partially crystalline alloys, cracks emanate from the corners of the indent as shown in Figure 4.5 (c). Formation of corner cracks indicates a decrease in toughness of the alloy on
partial crystallization as no cracks were observed for the as-cast and sub-$T_g$ annealed BMG alloys.

4.3.1.2 Variation of hardness with applied load

Plots of Vickers hardness values of the BMG alloys at different loads in different conditions are shown in Figure 4.6. The as-cast as well as annealed BMG samples have shown an increase in hardness with an increase in load initially. Then there is a decrease in the rate of increase at loads greater than 2.94 N (0.3 kg) with the hardness values remaining within a small range. The higher hardness of the annealed alloys is due to an increase in the atomistic friction. The relative motion of randomly packed atoms in a metallic glass is analogous to that of randomly packed particles in a granular solid. Thus decrease in free volume is therefore the cause of this increase in the hardness [156]. This tendency of hardness change has been reported in the literature [113, 114, 157]. The greater increase in hardness in partially crystalline alloy is possibly because of the presence of small crystals of hard boride.
Fig. 4.6 Hardness of the BMG alloys in different conditions (a) A1 (b) A2 (c) A3

The brittle nature of partially crystalline samples was revealed by formation of cracks that seems to emerge from the corners. Alloys A1 and A2, in partially crystalline condition, have also shown semi-circular cracks formed around the edges. These semi-circular cracks/chipping appeared at loads higher than 0.5 kg and 0.6 Kg for partially crystalline alloys A1 and A2 respectively as shown in Figure 4.7.
Fig 4.7 SEM micrograph showing hardness indent on the surface of partially crystalline A1. Also visible are cracks formed around indent edges.

In partially crystalline alloy A1, the hardness decreased to the level of hardness of the same alloy in as-cast condition. The microcracks were formed at all loads above the critical load. Critical load is the load used for the indentation at which corner cracks first observed in the SEM micrograph. Formation of microcracks could possibly be the reason behind the drop in hardness to lower levels. In partially crystalline alloys A2 and A3, the hardness values remained above those of the same alloy in annealed condition even after the decrease.

Hardness of the as-cast A1, A2 and A3 increased with annealing and increased further with partial crystallization treatment. Corner cracks appeared on indentation of partially crystalline samples after a certain critical indentation load. This increase can be attributed to increase in atomistic friction in case of annealing and nucleation of crystals in case of partial crystallization.

4.3.2 Deformation Behavior
Deformation behavior underneath the hardness indenter has been studied using bonded interface technique. Two pieces of a BMG alloy having smooth and straight edges were joined using a high strength polymeric adhesive. A good bond was formed between the BMG samples and the adhesive. It resulted in a thin layer of adhesive between the two pieces. The size of the Vickers hardness indent produced in the middle of this layer was considerably larger than the thickness of the adhesive layer as shown in the Fig 4.8.
Fig. 4.8 Hardness indent at the bonded interface.

Figure 4.9 illustrates the deformation region beneath the hardness indent for the as-cast samples. Shear bands are observed all around the indent in the form of semi-circular bands (primary shear bands) that appear to emanate from the edge of the indent. In addition to semi-circular shear bands some radial shear bands (secondary shear bands) were also observed as shown and indicated in Figures 4.9 & 4.10. In the annealed BMG alloys, as shown in Figure 4.10, more radial shear bands are present as compared to the as-cast BMG alloys. This observation is a reconfirmation of the behavior reported in [112, 158-160].

Two distinct deformation zones can be identified in the deformation region underneath the hardness indents formed in bonded interface technique. One with semi-circular shear bands is the plastic deformation zone while a small portion just under the indenter tip is the elastic zone that does not contain any shear bands. It is also argued that it might contain very small shear bands that could not be imaged through SEM techniques. Formation of these two zones has been reported in the literature [114, 161]. The elastic zone can be seen at the tip of the indent in some of the micrographs e.g., Figure 4.9 (f). The layered bulges produced due to presence of a non-rigid interface (adhesive layer) are a common feature of these glassy alloys as shown in Figures 4.9 & 4.10. The binder used to bond the surfaces, kept the two samples intact even under high loads of 1000 g but is not rigid enough to prevent the material from flow in the lateral direction. This is visible in the Figure 4.8, where a slight deformation of the material in the lateral direction can be seen in the indent. In the annealed samples, this elastic zone has diminished, as evident in Figure 4.10. This decrease in the size of the elastic zone is due to lesser amount of elastic strain the annealed samples can withstand upto yield.
The size of the deformation zone comprising of shear bands increases with an increase in the load.

Fig. 4.9 Deformation zone produced in BMG alloys beneath the hardness indent by bonded interface technique in the as-cast condition. (a), (b) and (c) are A1 loaded with 1.96 N, 4.9 N and 9.8 N respectively (d), (e) and (f) are A2 loaded with 1.96 N, 4.9 N and 9.8 N respectively. (g), (h) and (i) are A3 loaded with 1.96 N, 4.9 N and 9.8 N respectively.
Rough and serrated semicircular shear bands can be seen in the region beneath the indenter as shown in Figure 4.10 (b). It indicates that the deformation resulting from these bands took place after the formation of the smoother primary shear bands [114].

Fig. 4.10 Deformation zone produced in BMG alloys beneath the hardness indent by bonded interface technique in the annealed condition. (a), (b) and (c) are A1 loaded with 1.96 N, 4.9 N and 9.8 N respectively (d), (e) and (f) are A2 loaded with 1.96 N, 4.9 N and 9.8 N respectively. (g), (h) and (i) are A3 loaded with 1.96 N, 4.9 N and 9.8 N respectively.
These BMG alloys were embrittled by partial crystallization resulting in the formation of cracks and fragmentation during indentation as shown in Figure 4.11.

Fig. 4.11 Deformation zone produced in BMG alloys beneath the hardness indent by bonded interface technique in the partially crystalline condition. (a), (b) and (c) are A1 loaded with 1.96 N, 4.9 N and 9.8 N respectively (d), (e) and (f) are A2 loaded with 1.96 N, 4.9 N and 9.8 N respectively. (g), (h) and (i) are A3 loaded with 1.96 N, 4.9 N and 9.8 N respectively.
At low loads of 1.96 N a small overflow region can be clearly seen in the micrographs of the deformation zones while there is extensive microcracking and fragmentation at higher loads. Radial shear bands are mostly observed in the annealed alloys according to Figure 4.10. Radial shear bands were formed after the semicircular shear bands and are visible mostly in annealed alloys at higher loads. A radial shear band clearly dissecting the previously formed semi-circular bands is shown in Figure 4.12.

Hydrostatic component of stress plays an important role in the indentation of the BMGs. Pressure sensitivity index is a measure of the contribution from the hydrostatic stress and an increase in the hardness of the BMG alloy with an increase in load is due to an increase in the value of this index [162]. In annealed BMGs, pressure sensitivity increases due to an increase in the friction within atoms because of lesser free volume that is available [156]. Partial crystallization results in an increase in hardness due to interaction of shear bands with crystals [152]. The decrease in hardness to lower levels in A1 is due to excessive cracking as shown in Figure 4.6 that happened at loads higher than 4.9 N. Cracking of partially crystallized samples due to brittleness has also been reported in the literature [114].

Hardness in metallic materials can be related to yield strength through the relation [109, 163],

\[ H = C \sigma_y \]  \hspace{1cm} (4.1)

In equation 4.1, \( H \) is hardness in MPa, \( \sigma_y \) is compressive yield strength in MPa, and \( C \) is the constraint factor (also referred to as the normalized hardness) that depends on the \( \sigma_y/E \) and \( H/E \) ratios as well as the shape of the indenter (indenter half angle). From the data related to FeCo-based BMGs present in the literature, the value of \( C \) can be taken as 2.5 [44, 163]. The values of compressive yield strength calculated from the hardness data using equation 1 is given in Table 4.2. A constraint factor (C) value of 2.5 is used for the calculation.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>As-cast (MPa)</th>
<th>Annealed (MPa)</th>
<th>Partially Crystalline (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>4638</td>
<td>4776</td>
<td>4715</td>
</tr>
<tr>
<td>A2</td>
<td>4368</td>
<td>4604</td>
<td>5087</td>
</tr>
<tr>
<td>A3</td>
<td>4562</td>
<td>4665</td>
<td>5447</td>
</tr>
</tbody>
</table>
The values of calculated strength for partially crystalline alloys are exaggerated as cracking is visible in their micrographs showing hardness indents. So a value of C equal 2.5 is not really applicable to partially crystallized alloys.

The shear bands formed underneath the indents seem to be confined in a semicircular region within the diagonals of the indent as shown in Figures 4.9 and 4.10. Semicircular (Primary) shear bands are formed under the action of radial component of stress produced during indentation while shear stress components are responsible for radial (secondary) shear bands [112]. The radial component of stress responsible for the formation of primary shear bands decreases quickly as the surface is approached, therefore, only few shear bands could emerge out of the surface that are viewed around the hardness indents [112].

The secondary shear bands intersect primary shear bands as shown in Figures 4.9 (f) and 4.10 (f). The number of secondary shear bands seems to increase with increasing deformation load and annealing treatment. Increasing number of secondary shear bands originating from the surface can also be seen in Figure 4.10 at higher loads. These surface originating shear bands are also mentioned in [112, 113, 159, 162, 164].

Relaxation in BMGs can result in loss in elasticity [165]. Slight increase in Young’s modulus of BMG alloys on annealing has been reported [166]. The Young’s modulus of the BMG alloys increases with an increase in temperature. There is a sharp decrease in the Young’s modulus after \( T_g \) in the supercooled liquid region [53]. The as-cast BMG alloys have higher elastic deformation limit than the annealed ones. In annealed BMG alloys, formation of radial shear bands occurs in addition to semicircular shear bands to accommodate the deformation and release the local stresses. Under the same conditions of indentation, the local stress underneath the indent may be lower than the yield stress of the as-cast specimens, but larger than that of the annealed one thus producing deformation in the annealed alloys [114].

Presence of small crystalline domains in the amorphous matrix is expected to hinder the propagation of shear bands thus resulting in better mechanical properties [75, 152, 167]. In these BMG alloys, cracking and fragmentation underneath the indent, as shown in Figure 4.11, happened due to embrittlement as result of partial crystallization. Formation of cracks and fragmentation underneath the indents reveal a brittle behavior. A similar behavior has been reported in [114] but the difference is absence of shear bands and more fragmentation in the partially crystalline alloys in this study. This brittleness could be due to the change in
chemical composition of the remaining matrix. Formation of distributed nano-sized (a few nanometers) crystalline clusters in an amorphous phase is expected to improve toughness but the presence of larger crystals may lead to embrittlement [44]. Similarly the volume fraction of the crystals formed in the amorphous matrix is important. Volume fraction of crystalline phase greater than about 15% is expected to increase brittleness of the BMG alloy [150]. Crystals ranging in size from 18 to 23 nm were found in the X-ray diffraction analysis of the partially crystalline BMG alloys.

In as-cast and annealed BMG alloys, shear localization and stable growth of shear bands occurred, due to their lower hardness and lesser brittleness. Lower activation energy barrier to shear bands formation allowed stable growth of the deformation zone without cracking [114].

Fig. 4.12 (a) Semicircular and radial shear bands formed in the deformed zone beneath the indent. (b) Semicircular and radial shear bands at higher magnification.

Considering the hardness trends and deformation zone under the indent, an expanding cavity model proposed in [168] seems to be appropriate for as-cast and annealed BMGs. The partially crystalline BMGs formed microcracks on indentation. Modified expanding cavity model proposed for the estimation of the size of the deformation zone beneath the indent is given by the equation 4.2 [112].

\[
R = \sqrt{\frac{P}{\pi H_y}} \left[ \frac{E}{6(1-\nu)} \tan \beta + \frac{2(1-2\nu)}{3(1-\nu)} \right]^{\frac{1}{3}}
\] (4.2)
R is the shear band zone size, $H_V$ is the Vickers hardness, $E$ is the Young’s modulus, $\nu$ is the Poisson’s ratio, $\sigma_y$ is the compression yield strength, $P$ is the load and $\beta$ is the included angle of the Vickers indenter.

In another model, the deformation zone under an instrumented indentation is estimated [116],

$$R = \sqrt{\left(\frac{0.3P}{\sigma_y}\right)} \tag{4.3}$$

Another relation for the estimation of the size of the deformation zone based on the deformation of single crystals is given as [115].

$$R = \sqrt{\frac{3P}{2\pi \sigma_y}} \tag{4.4}$$

Figure 4.13 shows plots of the size of plastic deformation zones at different loads. The values of the size of the plastic deformation zone are calculated by using equations 4.2, 4.3, and 4.4 representing different models. Measured values are also plotted so that a comparison can be made between measured and calculated values. The value of $\nu$ is taken as 0.3 and $\sigma_y$ is calculated from hardness data.

Fig. 4.13 Comparison of experimentally measured deformed zone size of BMG alloy A1 in as-cast condition with different models
The models used for calculation as shown in Figure 4.13 have overestimated the size of the shear band zone. This discrepancy in the shear band zone size may be due existence of thin shear bands beyond the visible ones that are not visible in the techniques like SEM. Another reason for overestimation could be the pressure sensitivity of the BMGs that was not incorporated in any of the models used for comparison in Figure 4.13 [109, 112]. The model by Zielinsky et. al., produced reasonably good results for Fe-Si single crystals and the model by Giannokopolous et. al., was validated on high strength steel through instrumented hardness [115, 116].

Figure 4.14 shows plots of shear band zone size (SBZS) Vs load of these BMG alloys in as-cast and annealed conditions. Partially crystalline BMG alloys had undergone microcracking on indentation and no shear bands were observed in them (Figure 4.11). SBZS is measured as distance from the tip (center) of the indent to the outer most shear band.

The size of SBZS increases with an increase in load and is given by the equation 4.5 [109, 114],

\[ SBZS = K(P)^n \]  \hspace{1cm} (4.5)

K, the proportionality constant, is related to the intrinsic characteristics of the material, P is the load applied, and n is the exponent of P.

Higher value of K means larger SBZS and greater fracture toughness. Figure 4.14 shows plots of SBZS measured experimentally. A curve fit is obtained that is of the form shown by equation 4.5. The values of n obtained by curve fitting are close to the predicted value of 0.5.
Vicker’s indentation used in bonded interface technique resulted in the formation of plastically deformed zone consisting of semicircular and radial shear bands in as-cast and annealed alloys. Cracking and fragmentation was observed in the zone while no shear bands were present. The size of the shear band zone has shown a decreasing trend with annealing.
and increase of the cobalt content. The size of the shear band zone has been under estimated by the different models as compared to the measured value as shown in Figure 4.13.

4.3.3 Fracture Toughness

The resistance to fracture of a crack containing materials is given by a property called fracture toughness. BMGs are normally brittle and the knowledge of their fracture toughness is important.

4.3.3.1 Estimation of fracture toughness of BMGs

BMGs possess high strength and hardness but the Achilles heel is their poor room temperature toughness [13, 14, 169]. Some Pd and Zr based BMGs possess high fracture toughness whereas other BMG materials are brittle, some of them with fracture toughness values that tend to approach toughness of highly brittle materials like soda-lime glass as reported in [53, 118]. Testing of fracture toughness using ASTM standard (E399) requires bulk samples of a suitable size and shape [118]. Nevertheless indentation is one method that allows measurement of fracture toughness of brittle smaller samples through indent corner crack measurement [55, 56, 133, 160, 170]. For tougher materials, where microcracks do not form at the indent corners and the size of the sample is small for standard fracture toughness testing, an estimate can be obtained by considering plastically deformed zone produced by the hardness indenter. The size of the zone (R) is supposed to be comparable to the size plastic zone present ahead of an advancing crack and the indent tip is considered as a tip of the crack.

Figure 4.15 (a) shows an indent produced in the BMG alloy at a load of 9.8 N while Figure 4.15 (b) shows an indent produced at the interface with the same load in the bonded interface technique. No microcracks were observed in and around the hardness indents for all the hardness loads employed with a maximum value of 9.8N whereas shear bands can be seen around the indent in Figure 4.15 (a).
Fig. 4.15 (a) Hardness indent on the as-cast A2 also showing shear bands around edges (b) Hardness indent at the interface of the bonded polished edges of two BMG samples of the same alloy.

Figure 4.16 shows the plastically deformed zones beneath the indents as obtained through the bonded interface technique. The length of the line shown in Figure 4.16 (a) is a measure of the size (R), in micrometers. Similarly, size of all the plastic zones of all the alloys were measured through SEM. Semicircular shear bands are visible in both the samples as shown in Figure 4.16. These shear bands result from the localized deformation of the BMG under the applied load [109, 112]. No microcracks were observed within or originating from the deformation zone, an indication of better toughness of the BMG. Microcracking and fragmentation happens in case of brittle BMG materials [114, 171].

Equation 4.6 has been used to estimate the fracture toughness ($K_C$) using the zone size.

\[
R = \frac{1}{6\pi} \left[ \frac{K_C}{\sigma_y} \right]^2 \quad \text{(4.6)}
\]

Where

- $R$ is the plastic zone size,
- $\sigma_y$ is the yield strength,
- $K_C$ is fracture toughness.
Fig. 4.16 Deformation zones in the alloys that are formed beneath the hardness indent at the interface. Semicircular shear bands are visible (a) in as-cast condition (b) in sub-$T_g$ annealed condition.

The fracture toughness values obtained from equation 4.6 are only estimates, which, reveal that these alloys are considerably tough, with values better than Fe based BMG alloys reported in previous work [53-56, 160] and closer to tough bulk metallic glasses such as Zr, Pt and Pd based BMGs [55, 56, 118, 160]. The $K_C$ values are given in table 4.3.

Table 4.3 Hardness, yield strength and fracture toughness of the as-cast and annealed BMGs.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Condition</th>
<th>$H_V$ (MPa)</th>
<th>$H$ (MPa)</th>
<th>$\sigma_y$ (MPa)</th>
<th>$R$ (μm)</th>
<th>SD</th>
<th>$K_C$ (MPa√m)</th>
</tr>
</thead>
<tbody>
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<td>12440</td>
<td>4614</td>
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<td>Annealed</td>
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<td>4763</td>
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<td>0.62</td>
<td>93</td>
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<td>87</td>
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<td>0.36</td>
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<td>11731</td>
<td>12652</td>
<td>4692</td>
<td>17.4</td>
<td>0.42</td>
<td>85</td>
</tr>
</tbody>
</table>

$H_V$ = Vickers hardness, $H$ = load/area, $\sigma_y$ = Compressive yield strength, $R$ = Deformed zone size, SD = Standard deviation of the deformation zone size, $K_C$ = Fracture toughness.

Estimated fracture toughness has revealed a decreasing trend with a replacement of iron and cobalt with boron. The Poisson’s ratio of boron is low ($\nu = 0.21$) and an increase in the boron content of the BMG alloy decreases its Poisson’s ratio which in turn decreases the toughness [54, 98, 118].
Sub-\(T_g\) annealing is expected to decrease the free volume of the BMG alloys and, therefore, results in an increase in fracture toughness as shown in Figure 4.17. The decrease in toughness, according to equation 4.6, is due to a decrease in the size of plastically deformed zone (R) formed under the hardness indent, that is also given in the Table 4.3.

Increase in the boron content increases the tendency to compound formation thus reducing the toughness of the BMG alloys. There is a large negative difference in the mixing enthalpy values of B with Fe, Co and Nb (Fe-B= -26.5 kJ/mol, Co-B= -24.2 kJ/mol, Nb-B= -53.9 kJ/mol) that is an indication of its compound forming tendency [172].

### 4.3.3.2 Indentation fracture toughness behavior of BMGs

FeCo-based BMGs are strong but brittle. Their brittleness can be attributed to their low poison’s ratio [98]. The low poison’s ratio of these BMGs is a direct result of the low poison’s ratio of Fe, Co and B [53, 160]. Increase in brittleness of these BMGs on partial crystallization can be due to changes in the chemical composition of the matrix material on
formation of crystals. These partially crystalline BMG alloys can also be called BMG intrinsic composites or more commonly just BMG composites. Both shear banding and cracking can happen on indentation of the alloy. Cracking in the partially crystalline BMG alloys (BMG intrinsic composites) A1, A2 and A3 seems to be dominant as no shear bands were observed in the micrographs. This has happened in case of all the BMG composites A1, A2 and A3. Corner cracks were present in all of these alloys at an indentation load of 3.92 N and above. Indentation fracture toughness (IFT) of the BMG composites has been evaluated for the indentation loads at which the cracking system at the surface was clean. There is a critical load below which no cracks were observed. Figure 4.18 shows these two types of hardness indents, one without corner cracks (a), and the other one (b) with corner cracking. The lowest indentation loads at which corner cracking was observed in SEM were 1.96 N, 2.94 N, and 3.92 N for the alloys A1, A2, and A3 respectively.

Fig. 4.18 SEM images of the hardness indents on BMG composites (a) load less than critical load, no corner cracks present (b) load greater than the critical load, corner cracks observed.
Two of the most encountered cracking systems formed as a result of indentation are Palmqvist cracks and half-penny cracks (See Figure 2.16). The cracks visible at the surface emanating from the indent corners belong to any of the mentioned two systems.

Fig. 4.19 Hardness indents. (a), (c) & (e) A1, A2, and A3 at loads that produced corner cracks but without chipping. (b), (d) & (f) A1, A2, and A3 at loads that caused chipping.

The crack system can also change from Palmqvist to half-penny at a certain value of load. Some of the studies on BMGs have considered this change to happen at a c/a value of 2.5
(Figure 2.7) [56, 160], however, observation of cracking system is important for the calculation of IFT.

The loads used for the calculation of fracture toughness were those at which chipping and spalling of the sample did not happen. For alloys A1, A2, and A3, the maximum loads used for the indentation fracture toughness calculation were 6.86 N, 7.84 N and 9.8 N respectively. Above these loads chipping of the BMG composites was observed along with indents. Secondary cracks were also observed at these high loads.

Figure 4.19 (a), (c) and (e) show hardness indents with corner cracks. Chipping can be clearly seen along the indents at higher loads in Figure 4.19 (b), (d), and (f).

Fig. 4.20 Variation of (a) c/a ratio (b) l/a ratio with change in the indentation load. (See Figure 3.7)
The c/a (c is corner crack length plus half diagonal length while a is half diagonal length) ratio shown in Figure 4.20 has an increasing trend with the increase in indentation load. The c/a value for A1 and A2 increases beyond the value of 2.5 that is considered as the value of the ratio where a change in the crack system from radial to half-penny happens [56, 160]. So considering a changeover at 2.5, either of the crack type should exist for these two alloys within the loading range used for indentation. In case of A3, the ratio remains below 2.5 and the alloy can be considered to contain Palmqvist cracks. The observation of the change in crack morphology would confirm the system present and would allow selecting a suitable relation for the calculation of IFT.

Figure 4.21 shows indentation fracture toughness values of the BMG composites A1, A2 and A3. These values are calculated by the relations mentioned in Table 2.3. The value of E used in the calculation was taken as 225 GPa, which was the least value obtained from the hardness data using relation $E/H_V \approx 20$ [53]. P is the indentation load and $H_V$ is the Vickers hardness. The value of $\Phi$ has been taken as 2.5 [44, 163, 171]. Parameters c, l, and a are measured from the indent micrographs.

![Indentation Fracture Toughness vs. Boron Content](image)

Fig. 4.21 Indentation fracture toughness of the BMG alloys with different boron content.
Different values were obtained from the various relations used that span a range of 2.2 MPa√m for A3. A1 and A2 possess lesser IFT than A3 and the range is less. The values of c/a are less than 2.5, in case of A3, and it suggests a Palmqvist cracking system. For A3, the relations based on Palmqvist cracks, as shown in Figure 7, give a maximum IFT value 4.4 MPa√m. The toughness values for A3 is comparable to and in some cases are better than some Fe based BMGs mentioned in the literature [53, 55, 56, 160, 173]. One reason for better IFT of A3 is its higher compressive strength. IFT values of A1 and A2 are similar to other brittle Fe based BMGs given in the literature [55, 56, 170] but better than ceramic glasses [54, 121]. K_C values for different BMGs are given in table 1.2. Presence of small crystals in an amorphous matrix is expected to result in an improvement in toughness. One of the proposed mechanism is the interaction of the crack front with the crystalline domains that hinders the crack propagation [174] but in this case the brittleness of the matrix seems to overcome the expected improvement in IFT. Volume fraction and size of the crystals also effect the fracture toughness [150]. Smaller crystalline domains may result in an improvement in ductility. To really confirm the type of cracks formed during indentation, and to check any change in the crack morphology with load, observation of the cracking system is necessary.

![Fig. 4.22 BMG alloys A1 and A3 after polishing of indents (a) A1 having c/a > 2.5 (b) A3 having c/a < 2.5](image)

The crack morphology formed around the hardness indents was observed by polishing the indents and imaging the material below to reveal the morphology of cracks formed. All the indents in A1, A2 and A3 revealed Palmqvist crack morphology. Figure 4.22 (a) and (b) shows this behavior. It can be concluded from the observation of micrographs that the Palmqvist crack morphology prevails in the composition range explored in these BMG
composites Therefore, relations for Palmqvist type cracks would give appropriate values of fracture toughness.

Fig. 4.23 Variation of indentation fracture toughness with boron content. The relations used to calculate IFT represent Palmqvist type cracking system (a) Average IFT values (b) IFT values for all the indents. PQ in the Figure refers to model based on Palmqvist cracks.
Figure 4.23 shows values of IFT plotted against boron content of the BMG composites. These IFT values are obtained by using equations for Palmqvist type cracks. It is generally accepted that alloys showing Palmqvist type crack morphology have better fracture toughness than those having half-penny cracks. It is due to the fact that the Palmqvist cracks formed would propagate with increasing load and eventually turn into half-penny cracks provided other energy dissipative mechanisms like chipping and secondary cracking do not take over. One reason for the absence of half-penny cracks is the chipping that commenced at a certain value of load. The other reason is better fracture toughness of these intrinsic composites compared to those ceramic materials that form half-penny cracks at the same level of loads at which these intrinsic composites were tested. Figure 4.23 shows an increase in IFT with an increase in the boron content of the BMG alloys. Boron increases both hardness and strength of the alloy [171].

Lesser c/a ratio is a result of higher strength and better toughness of A3 compared to A1 and A2. The maximum IFT that has been obtained is 3.5 MPa√m for A3 using relation 15 given in Table 2.1. The minimum IFT is 1.85 MPa√m obtained for A1 by using relation 14 proposed in Table 2.1.

So change of Palmqvist to half-penny cracks is considered to take place at a c/a ratio of 3 or greater for these alloys. For Palmqvist cracks, the ratio l/a is appropriate instead of c/a and it should range in 0.25 to 2.5. Equation 14 has been obtained by the calibration of extensive data for palmqvist cracks and is considered suitable for obtaining IFT in case of Palmqvist cracks. Table 4.4 shows IFT (K_C) values calculated using equation 14 that is used for Palmqvist cracks. Critical energy release rate (G_C) was calculated using equation 4.7 while surface energy (γ_S) was taken as G_C/2. The value of v was taken as 0.3 according to the procedure given in [175].

Table 4.4 Values of K_C calculated using equation 14 in Table 2.3. Also given are values of energy release rate G_C, surface energy γ_S, and brittleness index (H/K_C).

<table>
<thead>
<tr>
<th>Alloy</th>
<th>H (GPa)</th>
<th>K_C (MPa√m)</th>
<th>G_C (J/m^2)</th>
<th>γ_S (J/m^2)</th>
<th>H/K_C (μm^-1/2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>12.8 ± 0.61</td>
<td>1.85</td>
<td>14</td>
<td>7</td>
<td>6.92</td>
</tr>
<tr>
<td>A2</td>
<td>13.4 ± 0.63</td>
<td>2.1</td>
<td>18</td>
<td>9</td>
<td>6.38</td>
</tr>
<tr>
<td>A3</td>
<td>14.7 ± 0.6</td>
<td>2.9</td>
<td>34</td>
<td>17</td>
<td>5.07</td>
</tr>
</tbody>
</table>
BMG alloys with poisons ratio (ν) less than 0.32 also show brittle behavior. Fe-based alloys exhibit brittle behavior due to higher degree of directionality of the atomic bonds compared to tougher metallic glasses like Zr-based [176]. Mg-based and rare earth based bulk metallic glasses show K\textsubscript{C} values less than Fe based bulk metallic glasses and closer to oxide glasses [118]. Energy release rate is related to formation of two new surfaces with the surface energy \( \gamma_S (G_C/2) \). The critical energy release rate \( G_C \) for A1, A2, and A3, as shown in Table 4.4, is low but better than \( G_C \) for ideal brittle behavior (\( G_C = 1 \text{ J/m}^2 \)) [53, 177]. Oxide glasses possess \( G_C \) values close to 1. Equation 4.7 gives \( G_C \) in terms of E, K\textsubscript{C} and ν [53, 54, 160, 177].

\[
G_C = \frac{K_C^2}{E(1-\nu^2)} \quad (4.7)
\]

Brittleness index which is the competition between plastic deformation and fracture can be evaluated through the ratio between hardness and toughness (H/K\textsubscript{C}) is also given in Table 4.4. The K\textsubscript{C} value is comparable to other Fe-based BMGs in the literature [53, 160]. A brittleness index value of 5.95 MPa-m\textsuperscript{1/2} had been reported in for an Fe based BMG that is close to the values obtained for these alloys [160]. A3 composite has shown the highest IFT among the three intrinsic composites A1, A2 and A3. The corner crack length was lesser and it also exhibited highest hardness. The cracking system found was Palmqvist (same as A1 and A2).

### 4.4 Study and comparison of magnetic behavior of BMGs

FeCo based BMGs possess excellent soft magnetic properties with low losses making them suitable for electrical conversion devices working at high frequency [11, 13, 178]. The crystalline anisotropy is absent in the amorphous alloys. Residual anisotropies may be present such as shape anisotropy and stress-induced anisotropy due to internal stresses. Table 4.6 show the saturation magnetization (M\textsubscript{S}) and magnetic coercivity (H\textsubscript{C}) of the BMG alloys in the three conditions.

Vibrating sample magnetometer (VSM) results of as-cast BMG alloys are shown in Figure 4.24. A saturation magnetization (M\textsubscript{S}) value of ~ 90 emu/g was obtained for A1 while A2 and A3 have values between 80 A-m\textsuperscript{2}/kg and 90 A-m\textsuperscript{2}/kg. The value of M\textsubscript{S} obtained depends upon the ferromagnetic (Fe and Co) content in the BMG alloys, the higher this content, higher the M\textsubscript{S} [179].
Table 4.5 Saturation magnetization and magnetic coercivity of the alloys A1, A2, and A3 in the as-cast, annealed and partially crystalline conditions.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Property</th>
<th>As-cast</th>
<th>Annealed</th>
<th>Partially Crystalline</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>M_s (A-m^2/kg)</td>
<td>90.6</td>
<td>92.1</td>
<td>90.6</td>
</tr>
<tr>
<td></td>
<td>H_c (A/m)</td>
<td>3700</td>
<td>2100</td>
<td>2098</td>
</tr>
<tr>
<td>A2</td>
<td>M_s (A-m^2/kg)</td>
<td>88.35</td>
<td>91.2</td>
<td>90.3</td>
</tr>
<tr>
<td></td>
<td>H_c (A/m)</td>
<td>5700</td>
<td>2200</td>
<td>764</td>
</tr>
<tr>
<td>A3</td>
<td>M_s (A-m^2/kg)</td>
<td>78.35</td>
<td>82.65</td>
<td>9.6</td>
</tr>
<tr>
<td></td>
<td>H_c (A/m)</td>
<td>9800</td>
<td>2500</td>
<td>3075</td>
</tr>
</tbody>
</table>

A1 has the highest M_s and Fe and Co content among the three alloys. Stresses present in the alloys due to rapid solidification might deteriorate magnetic properties. Annealing below T_g resulted in relaxation of stresses in the BMG alloys and as a result produced a little higher value of M_s [180, 181] as shown in Figure 4.25.

![Magnetization Loop](image)

Fig. 4.24 Magnetization loop for as-cast BMG alloys A1, A2, and A3 obtained at room temperature.
Figure 4.25 shows magnetization loops of the BMG alloys in the annealed condition. $M_S$ of the annealed BMG alloys has shown an increase due to relaxation of the structure [182]. High saturation magnetization and low magnetic coercivity make these BMG suitable for electromagnetic conversion devices and electromagnetic shielding material [13]. Magnetic coupling of amorphous and crystalline phases in the alloys may lead to enhancement in the saturation magnetization. Magnetization loops of partially crystalline alloys are shown in Figure 4.26. Saturation magnetization for partially crystalline alloys A1 and A2 does not show any increase that is attributed to absence of any enhancement of coupling between the crystalline and amorphous phase. There is a decrease in the saturation magnetization of the partially crystalline alloy A3 that may be due to a decrease in coupling of the crystalline and amorphous phases.

![Magnetization loop for annealed BMG alloys A1, A2, and A3 obtained at room temperature.](image)

Fig. 4.25 Magnetization loop for annealed BMG alloys A1, A2, and A3 obtained at room temperature.

Bulk metallic glasses show soft magnetic properties as evidenced by the magnetic coercivity values shown in Table 4.5 and Figure 4.27.
As-cast BMGs have relatively higher magnetic coercivity due to the presence of residual stresses and higher free volume. Sub-$T_g$ annealing results in reduction in the level of stresses and free volume thus leading to a decrease in coercivity of the BMGs. Partial crystallization forms small crystalline domains that may cause hindrance in the movement of the magnetic domains and as a consequence result in an increase in the magnetic coercivity.

Fig. 4.26 Magnetization loop for partially crystalline BMG alloys A1, A2, and A3 obtained at room temperature.

Fig. 4.27 Magnetic coercivity for as-cast, annealed and partially crystalline BMG alloys A1, A2, and A3 obtained at room temperature.
In A1, A2 and A3, saturation magnetization ($M_S$) has shown a decrease while magnetic coercivity ($H_C$) has increased with an increase in boron content. The maximum value of $M_S$ (92 emu/g) was obtained for annealed A1 that is having the highest iron-cobalt content.
Chapter 5  Conclusions and Future Work

FeCo based bulk metallic glasses (BMG) in the composition range \((\text{Fe}_{0.5}\text{Co}_{0.5})_{69-x}\text{Nb}_x\text{B}_{25+x}\) \((x = 0, 2, 4)\) were cast through arc melting and suction casting technique in a Ti-gettered Ar atmosphere. BMG alloy strips of size 15 mm x 5 mm x 1 mm were produced. For each of the three compositions the samples were prepared in as-cast, annealed and partially crystalline conditions.

Conclusions

The following conclusions were drawn from the study carried out on the FeCo based BMG alloys.

1. \((\text{Fe}_{0.5}\text{Co}_{0.5})_{69-x}\text{Nb}_x\text{B}_{25+x}\) \((x = 0, 2, 4)\) BMGs possess high hardness and compressive strength with values in excess of 1100 H\(_V\) and 4000 MPa. The maximum hardness obtained was 1408 H\(_V\) in partially crystalline condition for alloy A3 while the highest compressive strength calculated was 4776 MPa for sub-\(T_g\) annealed alloy A1.

2. Plastically deformed zone produced in the as-cast and annealed BMG alloys underneath the indent consisted of semicircular shear bands with some radial shear bands also present. The number of radial shear bands present in as-cast alloys is lower as compared to sub-\(T_g\) annealed alloys. For partially crystalline alloys, cracking and fragmentation was observed instead of shear bands.

3. The measured values of the size of the plastically deformed zone produced by the Vickers indenter in bonded interface technique were smaller as compared to those calculated from various models. The size of deformed zone estimated by model suggested by Zhang et. al., was on much higher side while the values calculated by using the model of Giannokopolous et. al., predicted values closer to the measured ones.

4. Partial crystallization treatment led to embrittlement of these BMG alloys. Indentation of the partially crystalline alloys produced corner cracks above a certain critical load. Palmqvist crack morphology was observed at all the indentation loads above the critical loads of 1.96 N, 2.94 N, and 3.84 N for partially crystalline alloys A1, A2 and A3 respectively.
5. The indentation fracture toughness values of the partially crystalline alloys calculated using corner crack lengths were lower than as-cast and sub-\( T_g \) annealed samples with values of 1.85 MPa√m, 2.1 MPa√m, and 2.9 MPa√m for alloys A1, A2 and A3 respectively.

6. High fracture toughness was estimated in as-cast and sub-\( T_g \) annealed samples with values in excess of 80 MPa√m. The fracture toughness estimated was 91 MPa√m, 85 MPa√m, and 82 MPa√m for as-cast A1, A2 and A3 respectively. For sub-\( T_g \) annealed A1, A2 and A3, the estimated values were 93 MPa√m, 87 MPa√m and 85 MPa√m respectively.

7. \((\text{Fe}_{0.5}\text{Co}_{0.5})_{69-x}\text{Nb}_6\text{B}_{35+x} (x = 0, 2, 4)\) BMGs possess good thermal stability with the glass transition temperatures in excess of 800 K. The glass transition temperatures are 815 K, 820 K and 840 K for the alloys A1, A2, and A3 respectively.

8. The supercooled liquid region (SLR) of these bulk metallic glass alloys increases when boron content is increased. The size of SLR, that defines the plastic working range, is 38 K, 43 K and 65 K for the alloys A1, A2 and A3 respectively.

9. No peaks were observed in the X-ray diffraction scans of the as-cast and sub-\( T_g \) annealed BMG alloys while crystalline peak was observed in the BMG alloys annealed for 1 minute at their respective 1\(^{st}\) crystallization temperature.

10. Soft ferromagnetic behavior was shown by these BMG alloys. The saturation magnetization of these BMGs increased with the sub-Tg annealing treatment showing a maximum of 92.1 A-m\(^2\)/kg for A1.
Future Work

Some physical and mechanical properties has been studied of the (Fe_{0.5}Co_{0.5})_{69-x}Nb_{x}B_{25+x} (x = 0, 2, 4) bulk metallic glasses. In future, the research on FeCo based alloys may be carried out in the following directions.

1. The properties of the BMG alloys are affected by a change in the boron concentration of the alloy. The study of the effect of boron content higher than 29 at% on the physical, mechanical and magnetic properties will extend the existing understanding of the behavior of these BMG alloys.

2. BMGs posses excellent properties and are considered better than their crystalline counterparts. A comparison of properties of crystalline and amorphous (Fe_{0.5}Co_{0.5})_{69-x}Nb_{x}B_{25+x} (x = 0, 2, 4) alloys will allow to quantify the change in the values.

3. Nickel is a ductile and magnetic element. It has negative heat of mixing with the elements present in the studied BMG alloys. Ni addition to (Fe_{0.5}Co_{0.5})_{69-x}Nb_{x}B_{25+x} (x = 0, 2, 4) BMG alloys may be useful to enhance the plasticity of these amorphous alloys.

4. Addition of Ag, Au or Cu to a few atomic percent in these alloys may enhance the toughness through nanocrystallization. The properties of the BMG alloys with and without these elements can be compared to observe the change in properties.

5. Presence of rare earth elements in the composition of BMG alloys improves the glass forming ability and may also result in the improvement of other properties of the BMG as well. Effect of the addition of rare earth elements e.g., Tb, Sm and Gd etc. on the physical, mechanical and magnetic properties may be investigated.
References

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