Structural Evolution In Mechanically Alloyed Fe-based Powder Systems

2005

Umesh Patil
University of Central Florida

Find similar works at: https://stars.library.ucf.edu/etd

University of Central Florida Libraries http://library.ucf.edu

Part of the Materials Science and Engineering Commons

STARS Citation

https://stars.library.ucf.edu/etd/603

This Masters Thesis (Open Access) is brought to you for free and open access by STARS. It has been accepted for inclusion in Electronic Theses and Dissertations by an authorized administrator of STARS. For more information, please contact lee.dotson@ucf.edu.
STRUCTURAL EVOLUTION IN MECHANICALLY ALLOYED Fe-BASED POWDER SYSTEMS

by

UMESH PATIL

B. E., Pune University, Pune, India 2002

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Materials Science and Engineering in the Department of Mechanical, Materials, and Aerospace Engineering in the College of Engineering and Computer Science at the University of Central Florida Orlando, Florida

Fall Term
2005
ABSTRACT

A systematic study of iron-based binary and multi-component alloys was undertaken to study the structural evolution in these powders as a function of milling time during mechanical alloying. Blended elemental powders of Fe\textsubscript{100-x}B\textsubscript{x} (where x = 5, 10, 17, 20, 22, 25, 37.5 and 50 at. %) and a bulk metallic glass (BMG) composition (Fe\textsubscript{60}Co\textsubscript{8}Zr\textsubscript{10}Mo\textsubscript{5}W\textsubscript{2}B\textsubscript{15}) were subjected to mechanical alloying in a SPEX 8000 mixer mill. X-ray diffraction technique was employed to study the phase evolution, crystallite size, lattice strain and also to determine the crystal structure(s) of the phases.

Depending on the milling time, formation of supersaturated solid solutions, intermetallics, and amorphous phases was noted in the binary Fe-B powder mixtures. A maximum of about 22 at. % B was found to dissolve in Fe in the solid state, and formation of FeB and Fe\textsubscript{2}B intermetallics was noted in some of the powder blends. However, an interesting observation that was made, for the first time, related to the formation of a crystalline phase on continued milling of the amorphous powder in the BMG composition. This phenomenon, termed mechanical crystallization, has been explored. Reasons for the mechanical crystallization of the amorphous powder using the X-ray diffraction and electron microscopy methods have been discussed. External heat treatments of the milled powder were also conducted to study the complete crystallization behavior of the amorphous phase.

Preliminary attempts were made to consolidate the milled BMG powder to bulk shape by hot isostatic pressing (HIP) and magnetic compaction techniques. Full densification was not achieved. Nanoindentation and microhardness tests were performed
to characterize the mechanical properties of the glassy alloy. Nanoindentation results
gave an elastic modulus of 59 GPa, lower than the expected value of 184 GPa; due to the
presence of porosity in the consolidated sample. Optimization of the consolidation
parameters is required to achieve a fully dense material.
ACKNOWLEDGEMENTS

I take this opportunity to thank Dr. C. Suryanarayana for his support, motivation and valuable discussions during this entire research work. He is a great mentor professionally and I amazed with his simple ways of dealing with the scientific problems. I am very thankful to Dr. Raj Vaidyanathan for his supervision and professional approach that led me into the right track, and Dr. Linan An for his fruitful discussions and invaluable suggestions that turned out to be a great help and also for serving as the thesis committee member and evaluating this thesis. I am grateful to National Science Foundation (NSF) and Mechanical, Materials and Aerospace Engineering department for providing financial support.

I would like to take this opportunity to express my gratitude to all the fellow students under Dr. Sury’s, Dr. Raj’s and Dr. An’s group especially Dr. Soonjik Hong, Dr. Xuan Wu, Satyajeet Sharma, Balaji Prabhu, Subhashree Sridharan, Sudhir Rajagopalan, Chandrasen Rathod, Swanand Patil, Madhavi Thiyyagura and Yiguang Wang for helpful discussions and friendly advice. Special thanks to Kirk Scammon and Zia Rahman for their supervision in the use of XRD, SEM and TEM equipments. I am also thankful to Waheeda Illasarie, Arlene Ollivierre and Linette Reyes for their office assistance and Mr. Abdul Benwali for his technical support.

I express deep gratitude to my parents and my brothers who motivated me to pursue a Master’s degree here in the United States. This thesis is dedicated to their continual love and support to me in times of blues.
**TABLE OF CONTENTS**

LIST OF FIGURES ........................................................................................................................................ viii
LIST OF TABLES ............................................................................................................................................. xi

CHAPTER 1: INTRODUCTION ................................................................................................................................. 1
  1.1 Motivation ................................................................................................................................................ 1
  1.2 Organization ............................................................................................................................................. 3

CHAPTER 2: LITERATURE REVIEW .................................................................................................................. 4
  2.1 Introduction .............................................................................................................................................. 4
  2.2 Metallic Glasses ....................................................................................................................................... 4
  2.3 Bulk Metallic Glasses ............................................................................................................................. 7
  2.4 Fe-Based Bulk Metallic Glasses ............................................................................................................ 11
  2.5 Mechanical Alloying ............................................................................................................................... 12
  2.6 Amorphization During MA .................................................................................................................... 12
  2.7 Comparison Between MA and RSP ....................................................................................................... 14
  2.8 Properties and Applications of Bulk Metallic Glasses ........................................................................ 15

CHAPTER 3: MECHANICAL ALLOYING .............................................................................................................. 18
  3.1 Introduction ............................................................................................................................................ 18
  3.2 Process of Mechanical Alloying ........................................................................................................... 20
  3.3 Important Components of Milling .......................................................................................................... 23
    3.3.1 Raw Materials ................................................................................................................................. 23
    3.3.2 Types of Mills .................................................................................................................................. 24
    3.3.3 Process Variables ............................................................................................................................ 26

CHAPTER 4: EXPERIMENTAL PROCEDURES ................................................................................................. 30
  4.1 Raw Materials ........................................................................................................................................ 30
  4.2 Powder Synthesis .................................................................................................................................... 31
  4.3 Structural Analysis ................................................................................................................................. 32
    4.3.1 X-ray Diffraction .............................................................................................................................. 32
    4.3.2 Scanning Electron Microscopy (SEM) ............................................................................................. 35
    4.3.3 Transmission Electron microscopy (TEM) ....................................................................................... 35
  4.4 Consolidation of Alloyed Powders ......................................................................................................... 36
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.4.1 Hot Isostatic Pressing (HIP)</td>
<td>36</td>
</tr>
<tr>
<td>4.4.2 Pulsed Magnetic Compaction (PMC)</td>
<td>38</td>
</tr>
<tr>
<td>4.5 Heat Treatment of Powders</td>
<td>39</td>
</tr>
<tr>
<td>4.6 Mechanical Characterization</td>
<td>40</td>
</tr>
<tr>
<td>CHAPTER 5: RESULTS AND DISCUSSION</td>
<td>43</td>
</tr>
<tr>
<td>5.1 Particle Size and Morphology</td>
<td>43</td>
</tr>
<tr>
<td>5.2 Phase Structure</td>
<td>50</td>
</tr>
<tr>
<td>5.2.1 Solid Solubility Extension</td>
<td>51</td>
</tr>
<tr>
<td>5.2.2 Crystallite Size and Lattice Strain</td>
<td>66</td>
</tr>
<tr>
<td>5.2.3 Synthesis of Intermetallics</td>
<td>68</td>
</tr>
<tr>
<td>5.2.4 Amorphous Phase Formation</td>
<td>72</td>
</tr>
<tr>
<td>5.3 Mechanical Crystallization of Fe-BMG Composition</td>
<td>74</td>
</tr>
<tr>
<td>5.3.1 As-milled powder</td>
<td>74</td>
</tr>
<tr>
<td>5.3.2 Lattice parameters</td>
<td>77</td>
</tr>
<tr>
<td>5.3.3 External Heat Treatment</td>
<td>79</td>
</tr>
<tr>
<td>5.3.4 Possible reasons for the mechanical crystallization of the amorphous phase</td>
<td>81</td>
</tr>
<tr>
<td>5.3.5 Comparison with related observations</td>
<td>86</td>
</tr>
<tr>
<td>5.4 Consolidation of Fe-BMG powder</td>
<td>88</td>
</tr>
<tr>
<td>5.5 Nanoindentation</td>
<td>90</td>
</tr>
<tr>
<td>CHAPTER 6: CONCLUSIONS</td>
<td>92</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>94</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

Figure 2.1: High resolution TEM images of (a) crystalline Zr-based alloy indicating long-range atomic arrangement and (b) showing the absence of long-range atomic arrangement [7]........................................................................................................................................ 5

Figure 2.2: Critical casting thickness for glass formation as a function of the year the corresponding alloy was discovered [27]. .............................................................................................................. 8

Figure 2.3: Sketch of atomistic network/backbone formed by the large atoms (high coordination number) and small atoms (metalloids) [31]................................................................. 11

Figure 2.4: Typical strengths and elastic limits for various materials. Glassy alloys are unique with a high strength and a high elastic limit. .......................................................... 16

Figure 3.1: Hardened steel vial set used for SPEX Certiprep mixer mill. ................................ 21

Figure 3.2: Schematic representation of (a) powder particles trapped between the balls, (b) milling by crushing of particles between the vial surface and balls [59]................... 21

Figure 3.3: SPEX Certiprep 8000D mixer mill. ......................................................................... 25

Figure 4.1: Equilibrium phase diagram of the Fe-B system [62]. ........................................ 31

Figure 4.2: Layout of the hot isostatic press [66] .................................................................... 37

Figure 4.3: Schematic diagram of the pulsed magnetic compaction system [67] : 1,4,10, pistons; 2, inductor; 3, concentrator; 5, vacuum isolator; 6, vacuum camera; 7, powder; 8, press form; 9, load detector; 11, support................................................................. 38

Figure 4.4: Schematic representation of indentation load-displacement data during one complete cycle of loading and unloading [70]................................................................. 41

Figure 5.1: SEM images of (a) as received pure iron powder, (b) as received pure boron powder, and (c) as blended pure iron and boron powder...................................................... 44

Figure 5.2 (A): SEM images of mechanically alloyed Fe_{90}B_{10} powder mixture as a function of milling time (a) 2 min., (b) 10 min., (c) 30 min., (d) 1 h, (e) 2 h, (f) 3h........ 46

Figure 5.3: Variation of particle size of the mechanically alloyed Fe_{90}B_{10} powder as a function of milling time. ................................................................................................. 49

Figure 5.4: X-ray diffraction patterns of the Fe_{95}B_{5} powder mixture milled for different times in the SPEX mill................................................................. 53
Figure 5.5: X-ray diffraction patterns of the Fe\textsubscript{90}B\textsubscript{10} powder mixture milled for different times in the SPEX mill................................................................. 54

Figure 5.6: X-ray diffraction patterns of the Fe\textsubscript{62.5}B\textsubscript{37.5} powder mixture milled for different times in the SPEX mill................................................................. 55

Figure 5.7: X-ray diffraction patterns of the Fe\textsubscript{50}B\textsubscript{50} powder mixture milled for different times in the SPEX mill................................................................. 56

Figure 5.8: X-ray diffraction patterns of the Fe\textsubscript{100-x}B\textsubscript{x} (x = 5, 10, 17, 20, 22 and 25 at. % B) powders milled for 30 h in the SPEX mill indicating formation of \(\alpha\)-Fe solid solutions. ................................................................. 57

Figure 5.9: Variation of the lattice parameter of Fe\textsubscript{90}B\textsubscript{10} powder blend with milling time. ........................................................................................................... 61

Figure 5.10: Change in the lattice parameter of \(\alpha\)-Fe solid solution with increasing boron content........................................................................................................... 63

Figure 5.11: Comparison of lattice parameter of \(\alpha\)-Fe with boron content during rapid solidification (RSP) [76] and mechanical alloying (MA)................................................................. 64

Figure 5.12: Plot of crystallite size vs. milling time. In the early stage of milling, the crystallite size decreased exponentially with time and reached a saturation value. .............. 67

Figure 5.13: Plot of \% lattice strain vs. milling time. In the early stage of milling, the strain increased rapidly and then decreased due to annihilation of dislocations. .............. 67

Figure 5.14: X-ray diffraction patterns of the Fe\textsubscript{90}B\textsubscript{10} powder mixture milled 50h, 70h and 90h in the SPEX mill indicating the formation of Fe-B intermetallics................................. 69

Figure 5.15: X-ray diffraction patterns of the Fe\textsubscript{50}B\textsubscript{50} powder mixture milled for different times in the SPEX mill. A mixture of \(\alpha\)-Fe, Fe\textsubscript{2}B and amorphous phase was observed around 20 h while Fe\textsubscript{2}B intermetallic was obtained for longer milling hours. ................. 70

Figure 5.16: XRD patterns of two different sets of 70 h milled Fe\textsubscript{62.5}B\textsubscript{37.5} composition. Set I was milled giving some time interval between milling and Set II was milled continuously................................................................. 71

Figure 5.17: TEM micrograph and electron diffraction pattern for 20 h milled Fe\textsubscript{50}B\textsubscript{50} composition. TEM micrograph mainly shows agglomerated particles while partial amorphization was confirmed from the SAD pattern......................................................... 73

Figure 5.18: X-ray diffraction patterns of the blended elemental powder mixture of Fe\textsubscript{60}Co\textsubscript{8}Zr\textsubscript{10}Mo\textsubscript{5}W\textsubscript{2}B\textsubscript{15} milled for different times in a SPEX mill................................. 75
Figure 5.19: Comparison of the X-ray diffraction patterns of the $\text{Fe}_{60}\text{Co}_8\text{Zr}_{10}\text{Mo}_5\text{W}_2\text{B}_{15}$ powder mixture milled for 20 h and 50 h. ................................................................. 76

Figure 5.20: Lattice parameter of the $\alpha$-Fe phase as a function of milling time for the $\text{Fe}_{60}\text{Co}_8\text{Zr}_{10}\text{Mo}_5\text{W}_2\text{B}_{15}$ powder mixture. ................................................................. 78

Figure 5.21: X-ray diffraction pattern of the $\text{Fe}_{60}\text{Co}_8\text{Zr}_{10}\text{Mo}_5\text{W}_2\text{B}_{15}$ powder mixture milled for 20 h in a SPEX mill and annealed externally for 1 h at 700 °C. ......................... 80

Figure 5.22: Hypothetical free energy vs. composition diagram to explain the observed transformations in the present investigation. ......................................................... 84

Figure 5.23: BMG composition samples consolidated by (a) HIPing and (b) Pulsed magnetic compaction ................................................................. 89

Figure 5.24: SEM micrograph clearly showing the presence of porosity in the (a) HIPed sample and (b) magnetically compacted sample. ................................. 89

Figure 5.25: Combined load-displacement curves from 26 nanoindentations of HIPed Fe-BMG sample. ................................................................. 91
LIST OF TABLES

Table 3.1: Attributes of mechanical alloying................................................................. 19

Table 4.1: Elemental powders used in the present study............................................. 30

Table 5.1: Particle size of mechanically alloyed Fe$_{90}$B$_{10}$ powder as a function of milling time. ................................................................. 48

Table 5.2: Crystal structure data of the different phases in the Fe-B system [72]......... 51

Table 5.3: Lattice parameter calculations for the mechanically alloyed Fe$_{90}$B$_{10}$ powder composition as a function of milling time. ......................................................... 58

Table 5.4: Values of the average lattice parameter ‘a’ for Fe - 5, 10, 17, 20, 22, 25, 37.5 and 50 at. % B powder blends milled for 30 h......................................................... 62
CHAPTER 1: INTRODUCTION

1.1 Motivation

Since the first synthesis of an Fe-based metallic glass by rapid solidification processing (RSP) from the liquid state in the Fe-P-C system by Duwez and Lin in 1967 [1], Fe-based amorphous alloys have continued to attract the attention of researchers. This is due to their good soft magnetic properties, high strength, high hardness and good corrosion resistance and potential important applications in defense, space, automotive and several other industries. However, the synthesis of Fe-based amorphous (or glassy) alloys by traditional RSP methods requires very high solidification rates so that crystallization could be completely avoided. This condition puts a serious limitation on exploring further applications for these Fe-based metallic glasses. Because of the limitations on the sample size and shape, only wires, ribbons or thin films could be produced [2]. These glassy alloys have excellent soft magnetic properties and hence sheets or ribbons produced by the melt spinning technique of RSP are used for power transformer applications. In fact, their use as transformer core materials in distribution transformers is presently a commercial reality and is a multi-million dollar business [3]. These glassy sheets are used by stacking the amorphous ribbons. But the stacking treatment causes a decrease in $M_s$ due to difficulty in eliminating gaps between the amorphous sheets.
Several non-equilibrium processing techniques like mechanical alloying, laser processing, thermal plasma processing, physical (PVD) and chemical vapor deposition (CVD), ion mixing, and spray forming have been developed to synthesize glassy alloys [4]. Even though bulk metallic glasses have been produced mostly by solidification methods, it has not been possible to produce glassy alloys with sufficient thickness in Fe-based alloy systems using this method. A maximum section thickness of only 6 mm was achieved in the Fe-based alloy systems. Therefore, two approaches are possible to produce Fe-based bulk metallic glasses. One way is to find new alloy compositions which can be made amorphous at relatively low cooling rates (< 10² K/s) and the other is to produce the glassy alloys by other non-equilibrium processing techniques and consolidate them into the desired bulk shape.

Mechanical alloying (MA) is a powder metallurgy technique that involves repeated welding, fracturing, and rewelding of powder particles in a high-energy ball mill [5]. MA can produce a variety of non-equilibrium phases such as supersaturated solid solutions, quasicrystalline and crystalline intermediate phases, nanocrystalline alloys, and glassy alloys [6]. Thus, MA is somewhat similar to RSP. Furthermore, the technique of MA is simple, involves minimal capital equipment, the mechanically alloyed powders can be easily consolidated to bulk shapes, and it is a commercially viable process. Hence, it is desirable to find new alloy compositions that could be formed in the amorphous state by MA and conduct a detailed structural, microstructural, and mechanical characterization on such alloys. However, in order to gain a better understanding of the conditions under which such alloys could be produced, we have first undertaken a detailed study of the mechanical alloying behavior of binary Fe-B powders. This is
followed by a detailed structural study of the mechanically alloyed Fe-based multicomponent alloy that has already been shown to be amorphous by the solidification method, albeit at low solidification rates.

1.2 Organization

In terms of organization of the Thesis, Chapter 2 surveys the existing literature in the field of bulk metallic glasses, and gives an overview of the processing techniques and properties of the glassy systems processed by solidification and mechanical alloying methods. Chapter 3 presents the background of mechanical alloying technique, equipment used and the influence of processing parameters on the final product. Chapter 4 describes the experimental procedures, synthesis of the desired metastable crystalline and amorphous powders, consolidation and the different characterization techniques employed. Chapter 5 presents the results and discussion, and Chapter 6 summarizes the conclusions and future directions for further work, followed by a list of the references.
CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

Bulk metallic glasses are those non-crystalline materials that are traditionally produced at relatively low cooling rates (< $10^2$ K/s) from the liquid state. These alloys exhibit a large difference in the glass transition temperature ($T_g$) and the crystallization temperature ($T_x$), with the difference (supercooled liquid region) $\Delta T_x = T_x - T_g$ ranging from 20 to 135 K in some cases. This large temperature interval $\Delta T_x$ is of technological interest because the high processability in the supercooled liquid state opens a temperature window for easy deformation and shaping of complex glassy components.

2.2 Metallic Glasses

Most metals and alloys are crystalline, i.e., their atoms are arranged in a regular, ordered pattern that extends over large distances (hundreds or thousands of atoms). These regions of ordered atomic arrangement are called as crystals. The regular arrangement of atoms in a crystalline material can be directly viewed using a high resolution transmission electron microscope (TEM). For example, Fig. 2.1 (a) shows the structure of a zirconium-based alloy. Many of the important properties of engineering alloys can be explained in terms of the crystalline order, or, in many cases, in terms of defects in the crystal structure.
Figure 2.1: High resolution TEM images of (a) crystalline Zr-based alloy indicating long-range atomic arrangement and (b) showing the absence of long-range atomic arrangement [7].

An amorphous metal is a metallic material (usually an alloy rather than a pure metal) with a disordered atomic-scale structure, i.e., there is no long-range atomic order. Fig. 2.1 (b) shows the high resolution TEM image of a Zr-based glassy alloy. In this micrograph the spots are more or less randomly arranged and long rows of atoms are absent, as compared to the micrograph of the crystalline Zr-based alloy, Fig. 2.1 (a) [7]. Materials in which such a disordered structure is produced directly from the liquid state during cooling are called “glasses”, and so amorphous metals are commonly referred to as “metallic glasses” or “glassy metals”.

Normally when an alloy is cooled from the liquid state, it may solidify in two alternative ways. If the rate of cooling is below some critical rate, the liquid may freeze to form a crystalline solid. On the other hand, if the rate of cooling is faster than a critical value, it may pass through the freezing range without crystallizing so that it becomes a supercooled liquid that later transforms into a glass below the glass transition temperature.
(T_g). For metallic alloys, the formation of a glassy structure is relatively difficult and requires cooling rates normally in excess of 10^5 K/s.

In 1960, Pol Duwez and co-workers discovered the first metallic glass by rapidly quenching Au_{80}Si_{20} (eutectic composition) alloy at very high solidification rates of about 10^6 K/s [8]. A few years later, Chen and Turnbull synthesized amorphous spheres of ternary Pd-Si-M (where M = Ag, Cu or Au) [9]. They showed that Pd_{77.5}Cu_{6}Si_{16.5} alloy could be made glassy with a diameter of 0.5 mm and the existence of glass transition was demonstrated. Also in some ternary Pd-Cu-Si and Pd-Ag-Si alloys, the supercooled liquid range was extended up to 40 K and these results provided a platform for researchers to perform detailed studies of crystallization in metallic glasses. Chen made a systematic investigation of glass forming ability of Pd-T-P alloys (where, T= Ni, Co, Fe) and obtained a critical thickness of the order of 1 mm in these alloys [10]. A slightly higher critical casting thickness was obtained for Au_{55}Pb_{22.5}Sb_{22.5} in 1982 [11]. In the early 1980s, the Turnbull group was able to synthesize glassy ingots of Pd_{40}Ni_{40}P_{20} with a diameter of 5 mm by subjecting the specimens to surface etching followed by succession of heating and cooling cycles. For the same composition, fluxing the melt with boron oxide further increased the section thickness by minimizing the formation of crystalline nuclei to suppress heterogeneous nucleation. And since these earlier investigations, metallic glasses have attracted increasing attention for their synthesis, characterization and stability mainly because they exhibit a unique combination of properties such as high strength, high hardness, good corrosion resistance, soft magnetic properties and superconductivity in the amorphous state [12-16].
It is difficult to make a distinction between truly amorphous solids and crystalline solids in which the size of the crystals is very small (less than 2 nm). Even amorphous materials possess short-range order (over length scales of about 1 nm). Furthermore, in very small crystals a large fraction of the atoms are located at or near the surface of the crystal; relaxation of the surface and interfacial effects distort the atomic positions, decreasing the structural order. Even the most advanced structural characterization techniques, such as X-ray diffraction and transmission electron microscopy, have difficulty in distinguishing between amorphous and crystalline structures on these length scales. Hence, glassy alloys were used as precursors to produce nanocrystalline alloys [17, 18]. By controlling the devitrification parameters, it has been possible to obtain either a completely nanocrystalline material or a dispersion of nanocrystalline precipitates in a glassy matrix. In both the cases, the alloys exhibit improved physical and mechanical properties [19 - 21].

Most of the metallic glasses have been synthesized via the rapid solidification route. However, there are several other ways in which amorphous metals can be produced, including physical vapor deposition, solid-state reaction, ion irradiation, and mechanical alloying. Amorphous metals produced by these techniques are, strictly speaking, not glasses, but researchers commonly consider amorphous alloys to be a single class of materials, regardless of how they are prepared.

2.3 Bulk Metallic Glasses

During the late 1980s, the Inoue group synthesized glassy rare-earth based materials with exceptional glass forming ability [22]. They used Cu-mold casting method
to produce La_{55}Al_{25}Ni_{20} glassy alloys in cylindrical shapes with a maximum diameter of 5 mm. They obtained the highest glass forming ability in Mg_{65}Cu_{25}Y_{10} [23]. Similarly, they also produced Zr-Al-TM (TM= Co, Ni and Cu) alloys having high glass forming ability and thermal stability [24]. Peker and Johnson developed the alloy Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5} alloy (commonly referred as Vitreloy-1), with a critical casting thickness of several centimeters and very good mechanical properties [25]. Inoue and co-workers re-visited the Pd_{40}Ni_{40}P_{20} alloy and replaced 30 % Ni by Cu and developed an alloy with a critical section thickness of 72 mm, the highest glass forming ability known to date [26]. The critical casting thickness obtained as a function of the year in which it was developed is shown in the Fig. 2.2. It shows that the casting thickness has increased from a few micrometers to a few centimeters [27].

![Figure 2.2: Critical casting thickness for glass formation as a function of the year the corresponding alloy was discovered [27.](image)](image)
Bulk metallic glasses have all the attributes of conventional metallic glasses obtained from the liquid state at high cooling rates (10⁵ – 10⁶ K/s) and are also superior in properties and performance compared to the corresponding crystalline alloys. But they have additional features which include:

1. The critical cooling rate (R_c) for the formation of metallic glasses is very low and reached from about 10³ K/s down to about 0.1 K/s.

2. The sample thickness (t_max) is increased to several millimeters. The lowest cooling rate and the sample thickness are almost comparable to those of the ordinary oxide glasses and fluoride glasses.

3. The bulk metallic glasses have a high reduced glass transition temperature (T_r = T_g/T_m, where T_g and T_m represent the glass transition and melting temperature, respectively), generally above 0.6 and the highest reported value is 0.73.

4. The multi-component bulk metallic glasses have a much wider supercooled liquid region (∆T_x = T_x − T_g), reaching a maximum value of 135 K.

From the strong correlation amongst R_c, t_max, T_r and ∆T_x, it may be concluded that bulk metallic glasses are obtained when the alloy system has high T_r and exhibits large ∆T_x. Based on the extensive investigations that were conducted so far, three empirical rules have been formulated to achieve high glass forming ability [28-30]. These are:

1. The alloy system should contain at least three elements; the larger the number of components the easier it is to form the glassy phase at low cooling rates and consequently with larger section thickness.
2. A significant difference in atomic sizes (>12%) should exist among the main constituent elements.

3. The constituent elements should exhibit negative heats of mixing amongst them.

On quenching multi-component alloy systems, the constituent atoms in the alloy find it “confusing” to go to the right lattice site and form the appropriate crystalline phase. Thermodynamically, high glass forming ability is obtained when the free energy $\Delta G(T)$ for the transformation of liquid to crystalline phase is small. Now the Gibbs free energy is given by

$$\Delta G(T) = \Delta H_f - T \Delta S_f$$  \hfill (2.1)

where $\Delta H_f$ and $\Delta S_f$ are the enthalpy and entropy of fusion, respectively. A low free energy will be obtained for low $\Delta H_f$ and high $\Delta S_f$ values. A large $\Delta S_f$ is expected to be obtained in the multicomponent system as $\Delta S_f$ is proportional to the number of microscopic states.

The combination of significant difference in atomic sizes of the constituent elements and the negative heats of mixing are expected to cause an increase in the random packing density of the supercooled liquid which enables the achievement of high liquid/solid interfacial energy. Furthermore, due to the atomic size differences, short range order is obtained by the formation of atomic pairs between large atoms (with high co-ordination number) and small atoms (which occupy the interstitial sites), which forms the strong reinforced backbone for the amorphous structure as shown in Fig. 2.3 [31]. This backbone structure creates difficulties in atomic re-arrangements leading to a decrease in atomic diffusivity which enhances the stability of the undercooled melt and further suppresses crystallization.
2.4 Fe-Based Bulk Metallic Glasses

Amongst all the bulk metallic glasses investigated so far, Fe-based alloys are of considerable interest for their magnetic and mechanical properties. This class of BMGs possesses tensile strength (1000-2000 MPa) and hardness (Vickers hardness, 900-1200) approaching that of high carbon high alloy steels and 25 % Cr maraging steels [29, 32]. Thus, Fe-based amorphous alloy systems are promising engineering materials and are potential candidates for tool steel applications with superior properties. Additionally they possess high glass forming ability, high corrosion resistance and improved soft magnetic properties. A number of ferrous-based alloys were synthesized using solidification techniques in the bulk form. These systems have the general formula Fe-(Al,Ga)-(P,C,B,Si), (Fe-Co,Ni)-(Zr,Nb,Ta)-B and Fe-Co-(Zr,Nb)-(Mo,W)-B [33-35]. Similarly, bulk Fe-B-Si based alloys (known as Metglas) have been used by stacking glassy ribbons for the low core loss distribution and power transformers [36]. Ponnambalam and co-
workers produced nonferromagnetic amorphous steel alloys by injection casting method which has superior mechanical strengths as compared to super austenitic steels [37]. Even though fully glassy rods could be synthesized up to 72 mm in diameter in a Pd-Cu-Ni-P alloy, the maximum section thickness that could be achieved in Fe-based alloys was only about 6 mm in the (Fe,Co)-Zr-(Mo,W)-B system [35], limiting large scale high-volume applications for these materials [38]. Thus, alternative methods have been sought to produce Fe-based glassy alloys in bulk quantities. Mechanical Alloying is one such potential method.

2.5 Mechanical Alloying

Mechanical Alloying (MA) is a solid state, powder metallurgy technique that involves repeated cold welding, fracturing and rewelding of powder particles in a high energy ball mill [5]. This technique has been shown to be capable of producing a variety of non-equilibrium (metastable) phases that include supersaturated solid solutions, quasicrystalline and crystalline intermediate phases, nanocrystalline alloys and amorphous phases [6]. In this respect, the capabilities of MA are somewhat similar to those of RSP.

2.6 Amorphization During MA

The mechanism(s) for formation of amorphous phases during MA are not clearly understood. Earlier, it was assumed that instantaneous melting of the powder particles due to the high rate of plastic deformation and a large amount of mechanical energy transfer during colliding events of balls takes place. These melted powder particles are
quenched rapidly by heat conduction to the less deformed, cooler interior powder particles and results in the formation of amorphous phase (as in RSP) [6]. However, energy input calculations and temperature estimation during milling suggest that the temperature rise is not large enough for the powder particles to melt. Thus, it is unlikely to produce an amorphous phase by this mechanism. Further, if this mechanism is correct, it fails to explain the wider glass forming ranges obtained during MA in comparison to RSP.

It is now believed that amorphization during MA is not purely a mechanical process and that the amorphous phase forms by reactions within the solid state. That is, during the solid state reaction, the materials are treated at a reaction temperature below the crystallization temperature. This solid state amorphization reaction occurs by interdiffusion [39-43] and without diffusion [44]. And as there is no quenching process involved, glass forming range for MA is expected to be larger than RSP. However, destabilization of the crystalline phase is thought to occur during MA by increase in free energy through accumulation of structural defects such as vacancies, dislocations, grain boundaries and antiphase boundaries. The continuous decrease in the grain size (consequent formation of nanocrystalline structure and therefore increase in the grain boundary area) and lattice expansion would also contribute to increasing the free energy of the system. These lattice defects introduced into the material during MA raise the free energy of the intermetallic system to a level higher than that of the amorphous phase; consequently, it becomes feasible for the amorphous phase to form [6].

Amorphization by solid state-state reaction was first found for the formation of amorphous Zr-Rh-H alloy by reaction of hydrogen with crystalline Zr$_3$Rh [39]. Koch et
reported the formation of an amorphous phase for the first time in Ni$_{60}$Nb$_{40}$ by mechanical alloying [43]. Similarly, Schwarz and co-workers showed that amorphization produced in the Ni-Ti alloy by mechanical alloying was based on the solid state process [45]. The amorphization process by MA has been followed in detail for Ni-Ti [45], Fe-Zr [46], Ni-Zr [47] and Ni-Nb systems [48]. Amorphous phase formation by MA was reported for multi-component Zr-, Mg- and Al-based alloy systems [6].

Schultz observed formation of amorphous phases in Fe-based system (Fe-Zr-B) by mechanical alloying [49]. Schlorke and co-workers reported significant supercooled liquid region (50 K) for multi-component Fe-Al-P-B-C alloys by mechanical alloying [50]. Similarly amorphization by mechanical alloying has been reported in Fe-Co-Ni-Zr-B [51], Fe-Cu-Nb-Si-B [52], Fe-Ni-P-Si [53], Fe-Ni-P-B-Si [54] and Fe-Co-Zr-Mo-W-B [55] among others.

**2.7 Comparison Between MA and RSP**

In comparison to RSP or casting techniques used to produce bulk metallic glasses, MA is an inexpensive and simpler technique to process the material into an amorphous state. Amorphous phases are easily produced by RSP in the vicinity of deep eutectics because the reduced glass transition temperature ($T_r$) is the highest at the eutectic point. But for mechanically alloyed materials the amorphous phase is mostly obtained around the equiatomic composition. Further, it is easier to produce the amorphous phase in a wider composition range as phase diagram restrictions do not directly apply to the phases produced by MA. This is because the whole processing is carried out in the solid state.
But the number of process parameters that could be varied is large and hence optimization of the process is tricky.

It was very difficult to obtain amorphous phases by RSP at compositions corresponding to melting point maxima, alloys with a cascade of peritectic reactions, shallow eutectics and in alloys with positive heats of mixing. However, MA was able to produce amorphous phases in a number of these cases. An important difference observed in amorphous phases formed by MA and RSP is the degree of thermal relaxation. Since MA is conducted at or near room temperature, the amorphous phase produced in an alloy is in a very unrelaxed state [6]. Similarly, the transformation kinetics for some alloys are totally different for both techniques. For example, the amorphous phase produced in Zr$_{76}$Fe$_{24}$ by MA directly transforms to equilibrium Zr$_3$Fe phase. But the crystallization products of the rapidly solidified alloy are metastable Zr$_2$Fe, ω-Zr and α-Zr, which were not observed for mechanically alloyed powders [56].

2.8 Properties and Applications of Bulk Metallic Glasses

Bulk metallic glasses exhibit an excellent combination of properties. They are typically much stronger than their crystalline metal counterparts (by a factor of 2 or 3), are quite tough (much more than ceramics), and have very high strain limits for Hookean elasticity. Further, they also exhibit high elastic energy, good ductility, high impact fracture energy, high bending fatigue strength, high corrosion resistance, good and soft magnetic properties, good workability and castability and high consolidation tendency into bulk form [57, 33-35]. Fig. 2.4 compares the strength and elastic limits of various materials with bulk metallic glasses. Based on these properties several potential
Figure 2.4: Typical strengths and elastic limits for various materials. Glassy alloys are unique with a high strength and a high elastic limit.

applications have been suggested. Amongst these, Zr-based bulk metallic glasses have been used for golf clubs and sporting equipments. This application is based on the increased maximum stored elastic energy, which is roughly four times that of crystalline materials due to doubling of the elastic limit achieved by forming the composite of an amorphous matrix containing a nanocrystalline phase. Another application of the bulk metallic glasses has been in developing “self-sharpening” kinetic energy penetrators. Similarly, a number of other applications like high temperature coatings, defense applications like aircraft fasters, missile components, armor composites, electronic casings, fine jewelry, medical devices and electronic hinges are commercial reality. Fe-based alloys show excellent soft magnetic properties and have been used in the transformer cores to reduce the core losses.
Thus, BMGs, a new class of engineering materials offer an opportunity to revolutionize the field of structural materials with combinations of strength, ductility, toughness, and processability outside the envelope achievable using current technology.
CHAPTER 3: MECHANICAL ALLOYING

3.1 Introduction

Mechanical Alloying (MA) is a non-equilibrium solid-state powder processing technique by which homogeneous materials can be produced starting from blended elemental powder mixtures. It is the ball milling process where a powder mixture placed in the ball mill is subjected to high energy collisions from the grinding balls. The two most important events involved in mechanical alloying are cold welding and fracturing of powder particles and these get repeated until a homogeneous powder is produced [5]. The alloying process is considered completed when the rate of welding balances that of fracturing and the average particle size of the powder remains relatively constant [58]. Milling is continued till every powder particle has the same composition as the proportion of the elements in the starting powder blend.

The technique of MA was developed by Benjamin and coworkers at the International Nickel Company’s (INCO™) Paul D. Merica Research Laboratory around 1966. The initial attempt was to develop a material by combining oxide dispersion strengthening with γ’ precipitation hardening in a nickel-based superalloy for gas turbine applications, heat-resistant alloys for high-temperature applications and aluminum alloys [6]. By using the appropriate processing parameters, this dry powder processing technique allows production of homogeneous equilibrium and non-equilibrium materials.
such as alloys, composites, ceramics, supersaturated solid solutions, crystalline and quasicrystalline intermediate phases and amorphous alloys from blended elemental or pre-alloyed powders [6]. The attributes of mechanical alloying are listed in Table 3.1.

Table 3.1: Attributes of mechanical alloying

1. Production of fine dispersion of second phase (usually oxide) particles
2. Extension of solid solubility limits
3. Synthesis of nanomaterials
4. Development of amorphous (glassy) phases
5. Synthesis of novel crystalline and quasicrystalline phases
6. Disordering of ordered intermetallics
7. Possibility of alloying of difficult to alloy elements
8. Inducement of chemical (displacement) reactions at low temperature

Two different terms are commonly used to denote the processing of powder particles in high energy ball mills [6]. MA describes the process of formation of homogeneous alloys by a material transport mechanism when mixtures of elemental powders (of different metals or alloys/compounds) are milled together. On the other hand, Mechanical Milling describes the process of milling of stoichiometric composition powders where material transfer is not required for homogenization. Earlier, this process of mechanical alloying/milling was confined to dry processing of materials; however,
there have also been some examples of wet processing. These terms, however, would be best suited if the process was restricted to metallic alloy production. Nanocrystalline materials have also been produced, using the MA technique, from single or a mixture of elemental powders that are structurally and chemically similar. Metallic alloy phases can be synthesized using MA of oxide and halide powders along with reducing agents.

Amorphous alloys can be prepared by MA using mixtures of crystalline elemental powders. These amorphous powders can be consolidated into large shapes called bulk amorphous metallic alloys or bulk metallic glasses (BMGs).

### 3.2 Process of Mechanical Alloying

Desired proportions of the powders are mixed and loaded into the milling container called a “Vial” (Figure 3.1) along with the grinding medium (usually steel or tungsten carbide balls). The initial basic event of the milling process is the trapping of elemental powder particles between colliding balls, and between the balls and the inner surface of the vial (Figure 3.2). The force of the impact plastically deforms the powder particles leading to work hardening and fracture. The new surfaces created enable the particles to cold weld together and this leads to an increase in particle size. These particles have characteristic layered structure consisting of various combinations of the starting constituents. Due to the initially low hardness of the powders, the lamellar spacing is fast reduced in the early stages of alloying. Later, due to continued deformation, the particles get work hardened and fracture by fatigue failure mechanism and/or by the fragmentation of fragile flakes [6]. At this stage, the tendency to fracture predominates over cold welding, thus resulting in a particle size reduction. Due to the
Figure 3.1: Hardened steel vial set used for SPEX Certiprep mixer mill.

Figure 3.2: Schematic representation of (a) powder particles trapped between the balls, (b) milling by crushing of particles between the vial surface and balls [59].
continued impact of grinding balls, the structure of the particles is steadily refined, but
the particle size continues to be the same. Consequently, the interlamellar spacing
decreases and the number of layers in the particles increases. Thus the total milling
process consists of repeated cold welding, deformation and fracturing of powder
particles.

After milling for a certain length of time, steady state equilibrium is attained when
a balance is achieved between the rate of welding, which tends to increase the average
particle size, and the rate of fracturing, which tend to decrease the average composite
particle size. Smaller particles are able to withstand deformation without fracturing and
tend to be welded into larger pieces with an overall tendency to drive both very fine and
very large particles towards an intermediate size. At this stage, each particle contains
substantially all of the starting ingredients, in the proportion they were mixed together
and the particles reach saturation hardness due to accumulation of the strain energy [6].

Heavy deformation of particles introduces a variety of crystal defects such as
dislocations, vacancies, stacking faults and increased number of grain boundaries. True
alloying takes place by defect-assisted interdiffusion amongst the constituent elements at
the clean surfaces, if a thermodynamic driving force (negative heat of mixing) exists for
the diffusion couple. Additionally, a slight rise in the temperature during milling aids the
diffusion process.

The entire process including blending of the powder mixture prior to ball milling
and the ball milling process itself is conducted in a protective environment to prevent
oxidation and contamination and the ball milling process itself. Post milling processes
after mechanical alloying include canning, degassing and consolidation into bulk shape
and finally heat treatment or plastic deformation by extrusion or rolling to obtain the desired microstructure and properties. Studies have shown that the structural transformations and the end product of the milling process depend on the chemical properties of the material being milled, the type of milling device and on specific milling parameters like milling speed, milling time, grinding medium used, ball-to-powder weight ratio, milling temperature, milling atmosphere and process control agents, to name a few [6]. The effect of some of these process variables is briefly discussed in the next section. Apart from the above physical parameters, a few other factors that are equally important from the analytical point of view are the collision velocity and the impact energies that determine the rate of mechanical energy transfer to the powder.

3.3 Important Components of Milling

The important components of MA process are the raw materials, milling equipment and the process variables [6]:

3.3.1 Raw Materials

Blending of powder mixture generally uses commercially pure powders with particle sizes ranging from 1 to 200 µm. The particle size is not crucial because it decreases exponentially during milling with time and reaches values of a few microns only after a short milling time. In most of the cases, the powder mixture consists of at least 15% ductile metal powder, the reason for this being the metal phase acts as a host or a binder. However, recent studies have shown that mixtures of fully brittle materials can be milled effectively without the use of any binding agent for alloy formation [60].
Occasionally, metal powders are milled with liquid medium to obtain fine-ground products. Additionally, it is reported that the rate of amorphization is faster during wet milling than during dry milling [61]. But, dry milling is preferred over wet milling to avoid contamination of the powder.

### 3.3.2 Types of Mills

Different types of milling equipment are available for the mechanical alloying of powders. Two different types of mills generally used for mechanical alloying are discussed here. They differ in their capacity and efficiency of milling.

#### 3.3.2.1 SPEX Shaker Mills

Shaker mills as shown in Figure 3.3 are most commonly used for laboratory investigations and for alloy screening purposes with a capacity of about 10-20 g of powder per run. Two different types of shaker mills used in this investigation are SPEX 8000M and 8000D. The main difference between the two mills is in the number of milling containers or the vials that can be clamped. The M series uses one vial and the D series offers two vials to increase the throughput.

The vial is clamped and swung energetically back and forth several thousand times a minute, along with lateral movement, thus agitating the charge and balls in three mutually perpendicular directions. The rotational speeds are high and can reach up to 1200 rpm and the shaking amplitude can reach up to 5 cm; this is the reason why SPEX mills are considered as high energy mills. Since a major fraction of the energy input is converted into heat, forced cooling is used to minimize the temperature rise.
3.3.2.2 Planetary Mills

A planetary mill is used for bulk powder preparation and around a few hundred grams of powder is obtained at a time. The planetary mill used in this case, as shown in Figure 3.4, is manufactured by Fritsch GmbH, Germany. The planet-like movement of vials around their own axes is achieved by rotating the base plate by a special drive mechanism. Centrifugal force produced by vials rotations around their own axes causes the required grinding action. Since the vials and the supporting disk rotate in opposite directions, the centrifugal forces alternately act in like and opposite directions. The mill has four milling stations and each can accommodate up to 250 g of powder mixture. In this type of mills the linear velocity of balls is much greater than that of SPEX mills but the frequency of impact is lower than that of SPEX and hence it is considered a lower energy mill.
3.3.3 Process Variables

Different parameters greatly influence the process of mechanical alloying; optimization of the variables is thus a very important part of the entire process to produce the desired microstructure and properties. The most important variables are listed below:

3.3.3.1 Milling Container

Due to the constant impact of the grinding balls on the vial surface, there are chances that material will be dislodged from the container and get mixed with the powder. If the container material is different from that of the powder, then the powder

Figure 3.4: FRITSCH GmbH, planetary mill.
may be contaminated and if it is similar then the chemistry of the powder may be altered. In the present work, hardened stainless steel, round-ended vials are used.

3.3.3.2 Milling Speed and Time

Milling speed has a crucial role to play in the process of MA. Very low rotational speeds lead to very long periods of milling and a large inhomogeneity in the alloy because of inadequate kinetic energy input. Hence prolonged milling time is required to achieve homogenization. For speeds greater than the optimum, the milling time gets reduced for the same number of revolutions and thus the effectiveness of alloying again decreases in the time available for interdiffusion of solute and solvents. Very high speeds could lead to excessive heating and high wear of balls causing contamination from the grinding medium and lower yields. Besides, at high speeds balls tend to stick to the vial walls and effective grinding action of powder is not achieved. Further, the temperature increase accelerates the transformation process and results in the decomposition of supersaturated solid solutions or crystallization of amorphous phases. Thus the maximum speed selected should be lower than this critical value. Milling time is the time required to achieve a steady state condition of milling, i.e., balance between rates of fracturing and cold welding of the powder particles. The milling time is different for each powder system; however, the level of contamination increases with unwarranted excessive milling.
3.3.3.3 **Milling Medium**

Hardened steel, tool steel, stainless steel, tempered steel, chromium steel and WC-Co are the most common types of materials used for the milling medium. In most of the cases the milling container and the grinding balls used are made of the same material to avoid any cross contamination of the powder. The density of the milling medium has to be high enough to create enough impact force on the powder. The size of the balls also influences alloying kinetics; larger the size of the balls higher will be the energy transfer. Smaller balls are reported to favor metastable phase formation. If combination of different sizes of balls is used, it minimizes the amount of cold welding of the powder on the surface the balls and the internal surface of the vial. The main reason for this is attributed to high shear forces developed between the balls of different sizes that tend to detach the powder coatings from the surface of the balls.

3.3.3.4 **Ball-to-Powder Weight Ratio**

It is the ratio of the weight of the balls to the powder (BPR), also referred to as charge ratio (CR). Generally BPR depends upon the alloy system under study and as low as 1:1 to as high as 220:1 ratios have been used. For small capacity mills, a BPR of 10:1 is the most common. The effect of BPR on milling time is significant; higher the BPR shorter is the milling time to achieve a particular constitution of the powder. High ball-to-powder ratios (BPR) imply higher weight proportion of balls and in turn higher number collisions per unit time and consequently, more energy is transferred to the powder particles and alloying takes place faster. As alloying takes place due to impact forces of balls, it is necessary that there should be enough space for the balls and powder particles
to move freely in the vial. Generally, the extent of filling the vial is about 50% of its volume, i.e., half of the vial space is left empty for optimum results.

### 3.3.3.5 Process Control Agent

The main purpose of the process control agent (PCA) is to act as a surface active agent to avoid excessive cold welding of the powder particles onto the internal surfaces of the vial and to the surface of the grinding medium. The PCA is also referred to as lubricant or surfactant. Around 1-2 wt. % of stearic acid (CH$_3$(CH$_2$)$_{16}$COOH) is used as PCA in the present study. The PCA gets adsorbed onto the surface of the powder particles and minimizes the effect of cold welding and thus inhibits agglomeration. The powder particle size tends to increase if the weight proportion of PCA to powder is below a critical value, while it decreases above this value. Also it is reported that a homogeneous distribution of particle size could be easily obtained if the PCA is in the liquid state than when it is in the solid state.
CHAPTER 4: EXPERIMENTAL PROCEDURES

4.1 Raw Materials

Table 4.1 gives detailed information on the purity, mesh size and source of the elemental powders used in the present study. Appropriate amounts of Fe and B powders were mixed together to obtain Fe_{100-x}B_x (where x = 5, 10, 17, 20, 22, 25, 37.5 and 50 at. %) compositions. (All the compositions in this study will be reported in atomic percent, unless otherwise stated). These compositions were selected so as to investigate the extension of solid solubility limits and also to study the glass-forming ability in the neighborhood of the eutectic regions in the Fe-B phase diagram (Fig. 4.1). For the BMG composition, nominally pure elemental powders of Fe, Co, Zr, Mo, W, and B were mixed together to obtain the desired composition of Fe_{60}Co_{5}Zr_{10}Mo_{5}W_{2}B_{15}.

Table 4.1: Elemental powders used in the present study.

<table>
<thead>
<tr>
<th>Element</th>
<th>Powder Purity</th>
<th>Powder Size</th>
<th>Company</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron (Fe)</td>
<td>98.00 %</td>
<td>-325 mesh (45μm)</td>
<td>Alfa-Aesar</td>
</tr>
<tr>
<td>Boron (B)</td>
<td>99.00 %</td>
<td>-325 mesh (45μm)</td>
<td>Cerac</td>
</tr>
<tr>
<td>Zirconium (Zr)</td>
<td>99.90 %</td>
<td>-140 mesh (106μm)</td>
<td>Cerac</td>
</tr>
<tr>
<td>Molybdenum (Mo)</td>
<td>99.99%</td>
<td>-325 mesh (45μm)</td>
<td>Alfa-Aesar</td>
</tr>
<tr>
<td>Cobalt (Co)</td>
<td>99.80 %</td>
<td>-100 mesh (130μm)</td>
<td>Alfa-Aesar</td>
</tr>
<tr>
<td>Tungsten (W)</td>
<td>99.90 %</td>
<td>-200 mesh (70μm)</td>
<td>Rhenium Alloys Inc.</td>
</tr>
</tbody>
</table>
4.2 **Powder Synthesis**

MA was conducted in a high energy SPEX 8000 mixer mill using hardened steel vial and stainless steel balls. About 50% of the vial space was left empty to provide enough space for the balls and powder particles to move around freely in the milling container. For each experiment, 10 g of the blended elemental powder mix and 100 g of stainless steel balls were loaded into the milling container, thus maintaining a ball-to-powder weight ratio of 10:1 during milling. Two different sizes (6.35 and 4.76 mm) of
balls were used in the present study. Stearic acid \( \text{CH}_3(\text{CH}_2)_{16}\text{COOH} \), amounting to about 1 wt. % of the powder charge was used as a process control agent during milling to reduce excessive cold welding of the powder particles amongst themselves and to the grinding tools.

To ensure minimum powder contamination, weighing, loading and unloading of the powders into the vial was always conducted in a glove box, which was maintained under a protective argon atmosphere. Milling was done for different times depending upon the system under investigation. The longest milling time employed was 90 h in the Fe-B system. After each run of 5 h, the vial was opened inside the glove box and a small quantity of the powder was collected for structural investigations. It was found that the powder tends to stick to the walls of the vial, especially in the early stages of milling. This could hamper the alloying kinetics of the powders. Therefore, to minimize this effect, the vial was opened at regular intervals, inside the glove box, and the powder was scraped off the walls of the vial and milling was resumed.

### 4.3 Structural Analysis

Structural analysis of the mechanically alloyed powders was carried out by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) methods.

#### 4.3.1 X-ray Diffraction

X-ray diffraction was employed to study the phase evolution, crystallite size, lattice strain and also to determine the crystal structure(s) of the phase(s). XRD patterns
at different stages of milling were recorded using a Rigaku-DXR 3000 X-ray
diffactometer using CuKα radiation (λ = 0.154056 nm) at 30 kV and 30 mA settings.
Since the three major peaks in the X-ray diffraction patterns of iron (110, 200 and 211)
would be in the 2θ range of 30° to 90°, all the X-ray diffraction patterns were recorded for
the above 2θ range with a step size of 0.05°, and a scanning rate of 1.2 degrees/minute.
The phases present in the pattern were identified using the standard procedures by
comparing the observed interplanar spacings and intensities with those expected for the
different possible phases. Furthermore, the crystallite size and lattice strain introduced
during MA were calculated from the peak width of the XRD patterns and by using
Scherrer’s equation [63, 64]. The lattice parameter(s) were calculated from the XRD
patterns by using equations 4.1 and 4.2. The diffraction condition is described by
Bragg’s law that relates the wavelength of the X-ray beam to the spacing of the atomic
planes.
The actual equation is of the form:

\[ \lambda = 2dsin \theta \]  \hspace{1cm} (4.1)

where \( \lambda \) = wavelength of the incident radiation

\( d \) = interplanar spacing, and

\( \theta \) = diffraction angle

Thus, by measuring the \( \theta \) values and knowing the \( \lambda \) value, it was possible to calculate the
interplanar spacing (d) for all the \( \theta \) values.

Further, for a cubic structure,

\[ \frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} \]  \hspace{1cm} (4.2)
where, \( h, k, l \) are the Miller indices of the diffracting plane and \( a \) is the lattice parameter of the cubic material.

Peak broadening was evaluated to calculate the crystallite size and it was done by measuring the width \( B \), in radians, at an intensity equal to half the maximum value, called the full width at half maximum (FWHM). The peak width, \( B_{\text{crystallite}} \), is related to the crystallite size, \( L \), through:

\[
L = \frac{k \lambda}{B_{\text{crystallite}} \cos \theta}
\]  

(4.3)

where

\( k = \text{Constant (usually taken as 0.9)} \)

\( L = \text{Crystallite size} \)

\( B_{\text{crystallite}} = \text{Broadening of the XRD peaks due to small crystallite size} \)

The lattice strain induced during mechanical alloying also causes broadening of the diffraction peaks, which is given by

\[
B_{\text{strain}} = \eta \tan \theta
\]  

(4.4)

where \( \eta \) is the strain in the material.

Thus, the total width (\( B_r \)) after subtracting the instrumental broadening will be,

\[
B_r = B_{\text{crystallite}} + B_{\text{strain}}
\]  

(4.5)

\[ i.e., B_r = \frac{k \lambda}{L \cos \theta} + \eta \tan \theta \]  

(4.6)

By multiplying both sides of the above equation by \( \cos \theta \), we get,

\[
B_r \cos \theta = \frac{k \lambda}{L} + \eta \sin \theta
\]  

(4.7)
Thus, when \((B, \cos \theta)\) is plotted against \((\sin \theta)\), a straight line with a slope \(\eta\) and an intercept \(\frac{k\lambda}{L}\) is obtained. From the intercept, the crystallite size, \(L\) can be calculated. The larger the intercept is the smaller will be the size of the crystallites and for very large crystallites; the straight line will pass through the origin.

4.3.2 Scanning Electron Microscopy (SEM)

SEM images of the mechanically alloyed powders were recorded using a JEOL-JSM 6400 F scanning electron microscope. The equipment uses a cold cathode field emission source, has a resolution of 1.5 nm and a maximum magnification of 500,000X. The maximum size of the specimen that can be accommodated is a cylinder of about 32 mm diameter and 20 mm in height. All the SEM images were captured in the secondary electron mode and GENESIS EDAX software gives the flexibility of image control. The main aim of the SEM analysis was to obtain information on the particle morphologies as a function of milling time. The particle size was calculated using the linear intercept method. This procedure was repeated for a number of particles to estimate the approximate average particle size.

4.3.3 Transmission Electron microscopy (TEM)

Transmission electron microscopy of the mechanically alloyed powders was carried out using an FEI Tecnai F30 TEM which can function as a conventional transmission electron microscope (maximum 1,000,000X magnification) or a scanning transmission electron microscope (maximum 10,000,000X magnification). The
equipment uses a very fine tungsten tip, field emission gun and an excitation voltage of 300 kV was used. Electrons from the tungsten tip are accelerated by positively charged anode and apertures and lens system channels these electrons to interact with the specimen.

The main purpose of the TEM analysis was to confirm the presence of the amorphous phase and to get microstructural details of the mechanically alloyed Fe-based systems. If a crystalline phase is present in the system, electrons are diffracted by the crystal planes of the sample satisfying the Bragg’s condition giving well defined spot or ring patterns whereas due to the absence of crystalline planes in the amorphous phase, only broad diffuse halos or rings will occur.

4.4 Consolidation of Alloyed Powders

Preliminary attempts were made to consolidate the mechanically alloyed BMG composition by hot isostatic pressing (HIP) and pulsed magnetic compaction (PMC) techniques. Brief details of the two-processes are mentioned in the following paragraphs.

4.4.1 Hot Isostatic Pressing (HIP)

Hot Isostatic Pressing (HIP) is a process for densification of castings and consolidation of powder metallurgy products by removal of pores. Pores in powder metallurgical components originate from gas evolution, shrinkage and agglomeration of vacancies by interdiffusion during bonding of dissimilar materials. HIP involves the simultaneous application of a high gas pressure (usually inert gas like argon) and elevated temperature (greater that 0.7 \( T_m \), where \( T_m \) is the solidus temperature) in a specially
constructed vessel. The driving force for densification is achieved by reduction of surface area (and hence the surface energy) of pores. During the application of high gas pressure each gas atom acts as an individual “hot forge”. On average the number of gas atoms moving through unit area and their velocities are the same in all directions. It is assumed that because of the isostatic nature of pressure application proportional shrinkage of shapes of pores will occur [65].

Figure 4.2: Layout of the hot isostatic press [66]

A HIP system is basically a pressure vessel [66] as shown in Figure 4.2. The heating is done by means of an electric heating element with the walls insulated from the outer shell. The pressure can only be transmitted to the interior of the component if the surface is sealed using metal cans. In the present work the HIPing equipment used is manufactured by American Isostatic Press – AIP10-30H.
The HIPing parameters used were:

Pressure: 30,000 psi

Temperature: 600 °C

Hold time: 3 h

4.4.2 Pulsed Magnetic Compaction (PMC):

A typical pulsed magnetic compaction system is shown in Fig. 4.3.

![Schematic diagram of the pulsed magnetic compaction system](image)

**Figure 4.3**: Schematic diagram of the pulsed magnetic compaction system [67]: 1, pistons; 2, inductor; 3, concentrator; 5, vacuum isolator; 6, vacuum camera; 7, powder; 8, press form; 9, load detector; 11, support.
The PMC method is based on the principle of throwing the conductor out of the pulsed magnetic field zone. The throwing force results from the interaction of current in the conductor and the magnetic field. The energy of the magnetic pulse and hence the pressure applied to the powder is controlled by pulsed generators. In the present case, 13.8 kV was applied which generated a pressure of 1GPa for 120-180 µs. The pulse of the pushing magnetic force on the side of the inductor 2 is received by the hard current-conducting concentrator 3. The concentrator transmits the mechanical pulse to the piston 1 made of a hard alloy which compresses the powder inside the mould. Ring shaped compact of outer diameter: 30mm, inner diameter: 20mm and height: 5 mm was obtained. The main advantage of the pulsed magnetic compaction (PMC) is the ability to reach higher relative density of compacts of nano powders owing to sufficiently high pressure in a very short duration of a few µs [68].

4.5 Heat Treatment of Powders

The amorphous phase formed in the BMG composition was heat treated in an inert atmosphere to study the complete crystallization behavior. Annealing of the sample was carried out at 700°C for 1 hr in an inert atmosphere to avoid oxidation of the sample. After heat treatment, the samples were taken out for X-ray diffraction to determine the phases formed after crystallization of the amorphous alloy.
4.6 **Mechanical Characterization**

Mechanical characterization of the consolidated amorphous alloy was carried out by instrumented indentation testing (IIT), also called depth sensing indentation or nanoindentation. Depending upon the system under study, loads as small as 1 nN can be applied and a displacement of 0.1 nm can be measured in nanoindentation. Mechanical properties are derived from the analysis of the load-displacement (P-h) curve following the Oliver and Pharr method [69]. Fig. 4.4 shows the typical (P-h) curve for one complete cycle of loading and unloading where load is applied from zero to a maximum value followed by a steady withdrawal from maximum to zero load. The loading curve represents the material’s resistance against the indenter penetration whereas the initial part of the unloading curve describes the elastic recovery of the indent. Due to plastic deformation, the material fails to regain its original shape, after the load is completely removed.
Figure 4.4: Schematic representation of indentation load-displacement data during one complete cycle of loading and unloading [70].

In the above figure

$P_{\text{max}}$ = Maximum load applied at the indenter tip

$h_{\text{max}}$ = Maximum displacement of the indenter into the material

$S$ = Slope of initial portion of the unloading curve (used to determine the unloading stiffness)

$h_p$ = Plastic displacement

$h_r$ = Residual displacement after load removal

The mean contact pressure [70] is taken as the indentation hardness (H) of the material and is calculated by dividing the load applied at the indenter by the projected area of the contact. For the case of a spherical indenter the elastic contact between the indenter and the material surface (considered to be of infinite radius of curvature) is taken
into account and it has been shown that the relation between the load \( (P) \) and depth of indentation \( (h) \) is given as [71]:

\[
P = C h^{3/2}\tag{4.8}
\]

\[
C = \frac{2^{3/2} E^* D^{1/2}}{3}\tag{4.9}
\]

Here, \( D \) is the diameter of the indenter and \( E^* \) is the reduced modulus and is given by:

\[
E^* = \left( \frac{1-v_i^2}{E_i} + \frac{1-v_m^2}{E_m} \right)^{-1}\tag{4.10}
\]

Where \( E_i \) and \( v_i \) are the elastic modulus and Poisson’s ratio of the indenter, respectively and \( E_m \) and \( v_m \) represent the elastic modulus and Poisson’s ratio of the indented material, respectively. The constant \( C \) in equation (4.9) can be calculated by fitting the 3/2 power fit to the initial elastic portion of the P-h curve (loading) and the elastic modulus from equation (4.10). Hence the elastic portion should have the slope of 3/2 on a log P vs. log h plot and any deviation from this slope indicates onset of large scale inelastic deformation.
CHAPTER 5: RESULTS AND DISCUSSION

5.1 Particle Size and Morphology

SEM images of as received pure iron and pure boron powders and blended iron-boron powder mixture are shown in Fig. 5.1. It can be seen from the SEM images (Fig. 5.1 (a)) that pure iron particles are roughly spheroidal in shape and that the average particle size is around 45 µm whereas boron particles have thin plate-like structure of average 35 µm size (Fig. 5.1(b)). In the blended condition, the distribution of boron particles in the iron matrix can be observed from Fig. 5.1 (c).

SEM images of mechanically alloyed Fe₉₀B₁₀ powder as a function of milling time are shown in the Fig. 5.2. From the figures it is clear that the mechanically alloyed powder particles have very irregular morphology with different size ranges. Furthermore, in the early stages of milling, formation of large particles due to agglomeration of small particles was noticed. During MA, whenever two grinding balls collide, a small amount of the powder is trapped in between them and subjected to plastic deformation by the colliding force of balls. In the initial stages, ductile iron was flattened to platelet/pancake shaped cold welds by micro-forging process. The more brittle boron particles were occluded into these cold welds and formed the iron-boron composite and an increase in the particle size was observed. The competing events of cold welding and fracturing continue repeatedly throughout the milling process. With increasing milling time, the
Figure 5.1: SEM images of (a) as received pure iron powder, (b) as received pure boron powder, and (c) as blended pure iron and boron powder.
composite powder particles get work hardened and the hardness and brittleness consequently increased, leading to the fragmentation of composite particles. At this stage, the rate of fracture becomes more than the rate of welding and this was evident from a continuous decrease in the particle size with milling time (Fig. 5.2).

After milling for certain time (around 30 h), steady state equilibrium between the rate of welding and fracturing was attained when the rate of welding (which tends to increase the average particle size) was balanced by rate of fracturing (which tends to decrease the average particle size). Beyond this condition prolonged milling did not have any significant effect on the particle size and a narrow particle size distribution was obtained because particles larger than the average were reduced in size at the same rate that fragments smaller than the average grow through agglomeration of smaller particles.

Table 5.1 gives the average particle size for Fe$_{90}$B$_{10}$ powder as a function of milling time. Fig. 5.3 shows the variation in average particle size vs. milling time in case of Fe$_{90}$B$_{10}$ powder particles. From this plot it is clear that particles were continuously refined up to the steady state condition and after that the particle size was relatively constant. Similar observations of increase in particle size in the initial stages of milling, continuous refinement up to the steady state and constant particle size after the steady state, were obtained for all the mechanically alloyed Fe$_{100-X}$B$_X$ (x = 5, 10, 17, 20, 22, 25, 37.5 and 50 at. %) powder compositions.
Figure 5.2 (A): SEM images of mechanically alloyed Fe$_{90}$B$_{10}$ powder mixture as a function of milling time (a) 2 min., (b) 10 min., (c) 30 min., (d) 1 h, (e) 2 h, (f) 3h.
Figure 5.2 (B): SEM images of mechanically alloyed Fe₉₀B₁₀ powder mixture as a function of milling time (g) 5 h, (h) 10 h, (i) 20 h, (j) 30 h, (k) 50 h.
Table 5.1: Particle size of mechanically alloyed Fe$_{90}$B$_{10}$ powder as a function of milling time.

<table>
<thead>
<tr>
<th>Milling Time</th>
<th>Particle Size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 min.</td>
<td>324</td>
</tr>
<tr>
<td>10 min.</td>
<td>272</td>
</tr>
<tr>
<td>30 min.</td>
<td>89</td>
</tr>
<tr>
<td>1 h</td>
<td>74</td>
</tr>
<tr>
<td>2 h</td>
<td>67</td>
</tr>
<tr>
<td>3 h</td>
<td>48</td>
</tr>
<tr>
<td>5 h</td>
<td>30</td>
</tr>
<tr>
<td>10 h</td>
<td>25</td>
</tr>
<tr>
<td>20 h</td>
<td>23</td>
</tr>
<tr>
<td>30 h</td>
<td>20</td>
</tr>
<tr>
<td>50 h</td>
<td>15</td>
</tr>
</tbody>
</table>
Figure 5.3: Variation of particle size of the mechanically alloyed Fe$_{90}$B$_{10}$ powder as a function of milling time.
5.2 Phase Structure

X-ray diffraction was employed to study the phase evolution, crystallite size, lattice strain and also to determine the crystal structure(s) of the phase(s) for the mechanically alloyed Fe-B powders. These results are systematically discussed in the following sections.

Some of the general features of the Fe-B equilibrium phase diagram are mentioned here. The equilibrium Fe-B phase diagram was shown in Fig. 4.1 [62]. The crystal structure data of the equilibrium phases in the Fe-B system are listed in Table 5.2 [72]. The features of this phase diagram are:

- The body centered cubic (Fe) solid solution. The maximum solid solubility of B in α-Fe and γ-Fe is about 0.01 and 0.025 at. %, respectively. Considering the experimental difficulties and very low absolute solubilities, results of solubility data are in fair agreement within the researchers. The solid solubility of B in γ-Fe increases with decrease in temperature.

- B forms a substitutional solid solution with α-Fe and an interstitial solid solution with γ-Fe.

- The intermediate phases are line compounds Fe₂B and FeB. Fe₂B is formed peritectically at 1389 °C while FeB melts congruently at 1650 °C.
Table 5.2: Crystal structure data of the different phases in the Fe-B system [72]

<table>
<thead>
<tr>
<th>Phase</th>
<th>Crystal Structure</th>
<th>Space Group</th>
<th>Lattice Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>a (nm)</td>
</tr>
<tr>
<td>Fe</td>
<td>BCC (A2 type)</td>
<td>Im 3m</td>
<td>0.2861</td>
</tr>
<tr>
<td>B</td>
<td>Rhombohedral (R12 type)</td>
<td>R 3m</td>
<td>1.0932</td>
</tr>
<tr>
<td>FeB</td>
<td>Orthorhombic (B27 type)</td>
<td>Pnma</td>
<td>0.5495</td>
</tr>
<tr>
<td>Fe2B</td>
<td>BC Tetragonal (C16 type)</td>
<td>14 2m</td>
<td>0.5099</td>
</tr>
<tr>
<td>Fe3B*</td>
<td>BC Tetragonal (C16 type)</td>
<td>I 4</td>
<td>0.8689</td>
</tr>
</tbody>
</table>

* Fe3B is not an equilibrium phase in the Fe-B system.

5.2.1 **Solid Solubility Extension**

Fig. 5.4 shows the X-ray diffraction patterns for the mechanically alloyed Fe95B5 powder blend as a function of milling time. All the peaks in the XRD patterns could be identified as belonging to the b.c.c. iron structure. Furthermore, shifting of the Fe peaks with increasing milling time indicated alloying of Fe with B, leading to the formation of supersaturated solid solutions. Comparison of these patterns with the XRD pattern of pure iron showed a slight shifting of the peaks to the lower angle side. That means alloying of B with Fe increased the lattice parameter of the α-Fe solid solution. Boron
atoms have a small atomic size (0.1880 nm) as compared to the iron atoms (0.2482 nm). Due to this atomic size difference, it is expected to increase the lattice parameter of the solid solution. And the observed values suggest that the B atoms have dissolved interstitially in the $\alpha$-Fe lattice.

With increasing milling time broadening of the XRD peaks and decrease in peak heights was observed for the mechanically alloyed powders. During MA, the powder particles experience severe plastic deformation which ultimately leads to the particle and crystallite size refinement and increase in the lattice strain with increasing milling time. These two effects cause broadening of the XRD peaks and consequent decrease in peak height. Furthermore, formation of nanocrystalline solid solutions can significantly broaden the XRD peaks.

Figs. 5.5, 5.6 and 5.7 show the XRD patterns for mechanically alloyed Fe$_{90}$B$_{10}$, Fe$_{62.5}$B$_{37.5}$ and Fe$_{50}$B$_{50}$ compositions. Fig. 5.8 shows the X-ray diffraction patterns of the Fe$_{100-x}$B$_{x}$ (x = 5, 10, 17, 20, 22 and 25 at. % B) powder mixture milled for 30 h in the SPEX mill. All these XRD patterns clearly show formation of supersaturated Fe-B solid solutions. But, in the XRD patterns from Fe$_{100-x}$B$_{x}$ powder blends, additional peaks are seen when $x$ = 37.5 and 50.
Figure 5.4: X-ray diffraction patterns of the Fe$_{95}$B$_5$ powder mixture milled for different times in the SPEX mill.
Figure 5.5: X-ray diffraction patterns of the Fe_{90}B_{10} powder mixture milled for different times in the SPEX mill.
Figure 5.6: X-ray diffraction patterns of the Fe$_{62.5}$B$_{37.5}$ powder mixture milled for different times in the SPEX mill.
Figure 5.7: X-ray diffraction patterns of the Fe$_{50}$B$_{50}$ powder mixture milled for different times in the SPEX mill.
Figure 5.8: X-ray diffraction patterns of the Fe$_{100-x}$B$_x$ (x = 5, 10, 17, 20, 22, and 25 at. % B) powders milled for 30 h in the SPEX mill indicating formation of α-Fe solid solutions.
From the XRD patterns of Fe\textsubscript{90}B\textsubscript{10} powder blends (Fig. 5.5), formation of \( \alpha \)-Fe solid solution could be confirmed. The lattice parameter of the Fe-B solid solution was calculated as a function of milling time and the results are shown in the Table 5.3. The average value of ‘a’ was calculated from different peaks and this average value was reported as the lattice parameter for the particular milling time. The lattice parameter of the \( \alpha \)-Fe solid solution, increased from 0.2837 nm in the as-blended condition to 0.2847 nm in Fe\textsubscript{90}B\textsubscript{10} the powder milled for 25 h and thereafter remained constant around 0.2848 nm (Fig. 5.9) indicating that steady state condition has been achieved in about 30 h. From this it is clear that all of the 10 at. % B could be dissolved in Fe-matrix in the solid state by MA. Similarly, for the other compositions Fe\textsubscript{100-x}B\textsubscript{x} (x = 17, 20 and 22 at. % B), the lattice parameter of \( \alpha \)-Fe solid solution increased with milling time as solute B atoms continued to occupy the interstitial positions in the Fe lattice.

For the Fe\textsubscript{75}B\textsubscript{25} composition, comparison of XRD patterns with the XRD pattern of pure iron showed a slight shifting of the peaks to the higher angle side. That means alloying of B with Fe decreased the lattice parameter of the \( \alpha \)-Fe solid solution, suggesting that the B atoms have now occupied the substitutional sites in the \( \alpha \)-Fe lattice. A similar situation is obtained in other Fe-B compositions containing more that 25 at. % B.

The lattice parameter(s) of solid solutions are very sensitive to the solute content in the solid solution and the variation of average lattice parameter for different B contents is presented in Table 5.4. Fig. 5.10 shows the variation of the lattice parameter of the \( \alpha \)-Fe solid solution with boron content. The general trend shows an increase in the lattice parameter for increasing boron content up to 22 % and then it decreases up to 25 % B.
content. Thereafter it remains constant for higher B concentration. The solid solubility limit is expected to increase with milling time as diffusion progresses and reach the supersaturation level, beyond which no further solid solubility occurs and a constant lattice parameter for the given solid solution is obtained. Hence, we can conclude that a maximum of 25 at. % B solid solubility was obtained in the present study. Close observation of Fe_{62.5}B_{37.5} and Fe_{50}B_{50} XRD patterns gives indication of the formation of intermetallics around 30 h of milling. It should be noted that, even if the reflection is present in the diffraction pattern, its broadening makes the location of peak position difficult and consequently, there are chances that there are possible inaccuracies in the calculated lattice parameters.
Table 5.3: Lattice parameter calculations for the mechanically alloyed Fe\textsubscript{90}B\textsubscript{10} powder composition as a function of milling time.

<table>
<thead>
<tr>
<th>Milling Time (h)</th>
<th>$2\theta$ (°)</th>
<th>‘d’ (nm)</th>
<th>(hkl)</th>
<th>‘a’ (nm)</th>
<th>Average ‘a’ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0h</td>
<td>45.414</td>
<td>0.1995</td>
<td>110</td>
<td>0.2822</td>
<td>0.2837</td>
</tr>
<tr>
<td></td>
<td>65.745</td>
<td>0.1419</td>
<td>200</td>
<td>0.2838</td>
<td></td>
</tr>
<tr>
<td></td>
<td>82.904</td>
<td>0.1164</td>
<td>211</td>
<td>0.2850</td>
<td></td>
</tr>
<tr>
<td>10h</td>
<td>45.050</td>
<td>0.2011</td>
<td>110</td>
<td>0.2844</td>
<td>0.2857</td>
</tr>
<tr>
<td></td>
<td>65.153</td>
<td>0.1431</td>
<td>200</td>
<td>0.2861</td>
<td></td>
</tr>
<tr>
<td></td>
<td>82.315</td>
<td>0.1170</td>
<td>211</td>
<td>0.2867</td>
<td></td>
</tr>
<tr>
<td>15h</td>
<td>45.069</td>
<td>0.2010</td>
<td>110</td>
<td>0.2842</td>
<td>0.2854</td>
</tr>
<tr>
<td></td>
<td>65.056</td>
<td>0.1433</td>
<td>200</td>
<td>0.2865</td>
<td></td>
</tr>
<tr>
<td></td>
<td>82.764</td>
<td>0.1165</td>
<td>211</td>
<td>0.2854</td>
<td></td>
</tr>
<tr>
<td>20h</td>
<td>45.090</td>
<td>0.2009</td>
<td>110</td>
<td>0.2841</td>
<td>0.2846</td>
</tr>
<tr>
<td></td>
<td>65.616</td>
<td>0.1422</td>
<td>200</td>
<td>0.2843</td>
<td></td>
</tr>
<tr>
<td></td>
<td>82.797</td>
<td>0.1165</td>
<td>211</td>
<td>0.2853</td>
<td></td>
</tr>
<tr>
<td>25h</td>
<td>45.201</td>
<td>0.2004</td>
<td>110</td>
<td>0.2835</td>
<td>0.2847</td>
</tr>
<tr>
<td></td>
<td>65.496</td>
<td>0.1424</td>
<td>200</td>
<td>0.2848</td>
<td></td>
</tr>
<tr>
<td></td>
<td>82.644</td>
<td>0.1167</td>
<td>211</td>
<td>0.2858</td>
<td></td>
</tr>
<tr>
<td>30h</td>
<td>45.202</td>
<td>0.2004</td>
<td>110</td>
<td>0.2835</td>
<td>0.2848</td>
</tr>
<tr>
<td></td>
<td>65.216</td>
<td>0.1429</td>
<td>200</td>
<td>0.2859</td>
<td></td>
</tr>
<tr>
<td></td>
<td>82.846</td>
<td>0.1164</td>
<td>211</td>
<td>0.2852</td>
<td></td>
</tr>
<tr>
<td>35h</td>
<td>45.146</td>
<td>0.2007</td>
<td>110</td>
<td>0.2838</td>
<td>0.2849</td>
</tr>
<tr>
<td></td>
<td>65.449</td>
<td>0.1425</td>
<td>200</td>
<td>0.2850</td>
<td></td>
</tr>
<tr>
<td></td>
<td>82.621</td>
<td>0.1167</td>
<td>211</td>
<td>0.2858</td>
<td></td>
</tr>
<tr>
<td>40h</td>
<td>45.100</td>
<td>0.2009</td>
<td>110</td>
<td>0.2841</td>
<td>0.2847</td>
</tr>
<tr>
<td></td>
<td>65.572</td>
<td>0.1422</td>
<td>200</td>
<td>0.2845</td>
<td></td>
</tr>
<tr>
<td></td>
<td>82.740</td>
<td>0.1165</td>
<td>211</td>
<td>0.2855</td>
<td></td>
</tr>
<tr>
<td>50h</td>
<td>45.051</td>
<td>0.2011</td>
<td>110</td>
<td>0.2844</td>
<td>0.2848</td>
</tr>
<tr>
<td></td>
<td>65.526</td>
<td>0.1423</td>
<td>200</td>
<td>0.2847</td>
<td></td>
</tr>
<tr>
<td></td>
<td>82.734</td>
<td>0.1166</td>
<td>211</td>
<td>0.2855</td>
<td></td>
</tr>
<tr>
<td>60h</td>
<td>45.094</td>
<td>0.2009</td>
<td>110</td>
<td>0.2841</td>
<td>0.2849</td>
</tr>
<tr>
<td></td>
<td>65.433</td>
<td>0.1425</td>
<td>200</td>
<td>0.2850</td>
<td></td>
</tr>
<tr>
<td></td>
<td>82.670</td>
<td>0.1166</td>
<td>211</td>
<td>0.2857</td>
<td></td>
</tr>
<tr>
<td>70h</td>
<td>45.150</td>
<td>0.2007</td>
<td>110</td>
<td>0.2838</td>
<td>0.2847</td>
</tr>
<tr>
<td></td>
<td>65.412</td>
<td>0.1426</td>
<td>200</td>
<td>0.2851</td>
<td></td>
</tr>
<tr>
<td></td>
<td>82.781</td>
<td>0.1165</td>
<td>211</td>
<td>0.2854</td>
<td></td>
</tr>
</tbody>
</table>

Where, $\theta$ = Bragg angle, d = interplanar spacing and h,k,l = Miller indices of the plane.
Figure 5.9: Variation of the lattice parameter of Fe$_{90}$B$_{10}$ powder blend with milling time.
Table 5.4: Values of the average lattice parameter ‘a’ for Fe-B powder blends milled for 30 h.

<table>
<thead>
<tr>
<th>Powder Composition</th>
<th>Average Lattice Parameter, ‘a’ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Iron§</td>
<td>0.2837</td>
</tr>
<tr>
<td>Fe$<em>{95}$B$</em>{05}$</td>
<td>0.2857</td>
</tr>
<tr>
<td>Fe$<em>{90}$B$</em>{10}$</td>
<td>0.2848</td>
</tr>
<tr>
<td>Fe$<em>{83}$B$</em>{17}$</td>
<td>0.2855</td>
</tr>
<tr>
<td>Fe$<em>{80}$B$</em>{20}$</td>
<td>0.2857</td>
</tr>
<tr>
<td>Fe$<em>{78}$B$</em>{22}$</td>
<td>0.2858</td>
</tr>
<tr>
<td>Fe$<em>{75}$B$</em>{25}$</td>
<td>0.2846</td>
</tr>
<tr>
<td>Fe$<em>{62.5}$B$</em>{37.5}$</td>
<td>0.2851</td>
</tr>
<tr>
<td>Fe$<em>{50}$B$</em>{50}$</td>
<td>0.2850</td>
</tr>
</tbody>
</table>

§ Indicates the value of unmilled iron
This solid solubility limit obtained in the present investigation is much higher than that reported in earlier investigations by MA or RSP. Perez et al. [73] reported a solubility of 4 at. % B in Fe by MA whereas less than 1.5 at. % B solubility was reported by Portnoi and Romashov [74]. The maximum solubility observed by RSP was 4.3 at. % B [75] whereas Ray and Hasegawa reported a maximum of 12 at. % B solubility by a chill casting/solidification technique [76].

The solubility extension observed by MA was higher than the maximum extension observed using RSP in many alloy systems [75]. Large extension of solid solubility limits is possible by quenching the liquid alloy to a temperature below $T_o$, the temperature at which the solid and liquid phases have the same free energy for a given
composition [77]. It is expected that the solid solubility extension by MA will be higher because MA is a near room temperature process and phase diagram restrictions do not apply to the phases produced by MA as compared to RSP.

The lattice parameters corresponding to 30 h milled Fe-B compositions are plotted and compared with those obtained by RSP (Fig. 5.11). It was observed that the variation in lattice parameter during MA follows the Vegard’s law, according to which the variation of lattice parameter with solute content is linear.

![Graph showing lattice parameter vs. boron content during RSP and MA](image)

**Figure 5.11:** Comparison of lattice parameter of $\alpha$-Fe with boron content during rapid solidification (RSP) [76] and mechanical alloying (MA).
The higher energy SPEX mill used in the present study is probably responsible for this higher amount of solid solubility observed in the Fe-B system as compared to the earlier reported results. Repeated welding and fracturing of powder particles during MA introduces heavy deformation of particles. This is manifested by the presence of a variety of crystal defects such as dislocations, vacancies, stacking faults, and increased number of grain boundaries [6, 75]. The presence of these defects enhances the diffusivity of boron atoms in the iron matrix. Due to continued milling, grain size refinement takes place and diffusion distances get reduced. Additionally, a slight increase in temperature during milling aids the diffusion mechanism. Thus, due to the defect-assisted diffusion, reduced diffusion distances, and small temperature rise, true alloying between boron and iron could occur and the lattice parameter of the solvent iron matrix changed due to boron dissolution. The boron content in the solid solution is expected to increase with milling time as diffusion progresses. On continued milling, steady state condition was reached beyond which no further extension of solid solubility is possible and this was clear from the constant values of lattice parameter obtained.

Crystallite size reduction and increase in lattice strain occurring during MA causes broadening of XRD peaks and consequent decrease in the peak height. This makes it difficult to find the exact location of the peaks and calculation of lattice parameters. In some cases, the second component may become amorphous on milling which will be present in the XRD pattern as a broad peak of very low intensity and may not be detected. Similarly, the presence of small amounts of second phase cannot be easily detected by XRD techniques. Impurities due the grinding medium further affect the contraction or dilation of the lattice and have a direct effect on the final results obtained [75].
5.2.2 Crystallite Size and Lattice Strain

As the XRD methods to determine the crystallite size or grain size and lattice strain are very simple as compared to TEM analysis, these methods were employed to estimate the grain size and strain in the mechanically alloyed powders. The grain size as obtained by the XRD methods is an average length of columns of the unit cells normal to the reflecting planes also called as the column length. The grain size and lattice strain calculation by measuring the width of the XRD peaks and using standard procedures was discussed in the previous chapter (section 4.3.1).

Fig. 5.12 shows the plot of crystallite size vs. milling time for the Fe$_{95}$B$_5$ and Fe$_{90}$B$_{10}$ powder blends. In the early stages of milling, the crystallite size of both the compositions (Fe$_{95}$B$_5$ and Fe$_{90}$B$_{10}$) decreased exponentially with time and then reached the saturation value of around 10 nm. The saturation grain size also corresponds to the steady state condition of milling and will not change even if the powder is milled for a longer time. Simultaneously, lattice strain increased due to the generation of dislocations and other crystal defects (Fig. 5.13). However, beyond the time when the particle size reached a saturation value, continued milling will not produce more dislocation density due to the difficulty of generating new dislocations at very small crystallite sizes. Further the existing dislocations may be rearranged or annihilated. This effect was evident from the decreased strain values obtained corresponding to the saturation grain size.
Figure 5.12: Plot of crystallite size vs. milling time. In the early stage of milling, the crystallite size decreased exponentially with time and reached a saturation value.

Figure 5.13: Plot of % lattice strain vs. milling time. In the early stage of milling, the strain increased rapidly and then decreased due to annihilation of dislocations.
5.2.3 Synthesis of Intermetallics

The technique of MA has been extensively used to synthesize intermetallic phases in many alloy systems. Intermetallics have crystal structures different from those of the starting elements with atoms of one type preferentially surrounded by unlike atoms, giving them an ordered structure [4]. But in most of the cases, a subsequent heat treatment was necessary for the synthesis of intermetallics to balance the disordering introduced from MA by thermally activated reordering.

The XRD pattern of the Fe$_{90}$B$_{10}$ powder milled for 50 h showed early signs of the formation of Fe$_2$B and Fe$_3$B intermetallics with body centered tetragonal structures (Fig. 5.14). From the equilibrium Fe-B phase diagram it is clear that equilibrium phase constitution corresponding to the 10 at. % B composition will be $\alpha$-Fe and Fe$_2$B. But formation of the additional metastable Fe$_3$B phase was also observed. This metastable phase formation at longer milling times might be attributed to decomposition of the $\alpha$-Fe supersaturated solid solution due to temperature rise caused by the severe plastic deformation during MA.

For the Fe$_{50}$B$_{50}$ composition we observed partial amorphous phase formation around 20 h and continued milling led to the formation of Fe$_2$B intermetallics (Fig. 5.15). This observation was in contrast to formation of intermetallics reported by Miguel and co-workers [78]. They reported the formation of $\alpha$-Fe, FeB and Fe$_2$B after 842 h of milling in a planetary ball mill and using a ball-to-powder weight ratio of 14:1. This difference might be attributed to their use of a lower-energy planetary mill for the study which alters the alloying kinetics.
Similarly different phases like, FeB, Fe$_2$B and Fe$_3$B by MA in the Fe-B system were reported in the literature [79, 80]. Furthermore, we observed one interesting result in two sets of Fe$_{62.5}$B$_{37.5}$ powder composition milled in different modes for up to 70 h (Fig. 5.16). The Set I was milled, giving some time interval during milling while the Set II was milled continuously. For the first set, $\alpha$-Fe, FeB, Fe$_2$B and Fe$_3$B intermetallics were observed after 70 h of milling while a mostly supersaturated $\alpha$-Fe-solid solution...
Figure 5.15: X-ray diffraction patterns of the Fe$_{50}$B$_{50}$ powder mixture milled for different times in the SPEX mill. A mixture of α-Fe, Fe$_2$B and amorphous phase was observed around 20 h while Fe$_2$B intermetallic was obtained for longer milling hours.
Figure 5.16: XRD patterns of two different sets of 70 h milled Fe$\text{_{62.5}B_{37.5}}$ composition. Set I was milled giving some time interval between milling and Set II was milled continuously.

with one unidentified peak (indicated by an arrow) was obtained for the second set. As MA is a complex process, milling parameters greatly influence the final product and it is very difficult to get the same type of materials for the given composition under different processing conditions [6]. It is possible that for the first set, interrupted milling led to
recovery of the strain and formation of near equilibrium phases. Accordingly, the equilibrium \( \text{Fe}_2\text{B} \) and \( \text{FeB} \) phases have been detected. On the other hand, on continuous milling, the powder continued to be in a metastable state and therefore a supersaturated solid solution was obtained.

5.2.4 Amorphous Phase Formation

From Fig. 5.15, it is clear that an amorphous phase has formed after milling the \( \text{Fe}_{50}\text{B}_{50} \) composition for 15 to 20 h. To confirm this “X-ray amorphous” phase, electron microscopy investigations were carried out. Fig. 5.17 shows the transmission electron micrograph and selected area electron diffraction pattern of the \( \text{Fe}_{50}\text{B}_{50} \) composition milled for 20 h. The mechanically alloyed powder was sonicated in alcohol for about 15 minutes to break the agglomerated particles. Then a drop of this dispersion was placed on a carbon-coated TEM grid. However, from the TEM micrograph it is clear that the particles are still in an agglomerated condition. Selected area diffraction (SAD) pattern showed that some Bragg reflection spots were superimposed on the two diffuse halo rings. This reveals that nanocrystalline \( \text{Fe}_2\text{B} \) crystals are dispersed in an amorphous matrix, i.e., mechanical alloying produced partial amorphization in the \( \text{Fe}_{50}\text{B}_{50} \) composition after 20h. Amorphization was not observed in other binary Fe-B compositions. It is reported that a fully amorphous phase by ball milling was formed between 50 and 60 at. % B [81].
Figure 5.17: TEM micrograph and electron diffraction pattern for 20 h milled Fe$_{50}$B$_{50}$ composition. TEM micrograph mainly shows agglomerated particles while partial amorphization was confirmed from the SAD pattern.

During MA, destabilization of the crystalline structure occurs by the accumulation of structural defects. The continuous decrease in grain size and lattice expansion also contributes to the increase in free energy of the system. The free energy of the intermetallic is raised to a level higher than that of the amorphous phase and consequently, it becomes possible for the amorphous phase to be relatively stable [6].
5.3 Mechanical Crystallization of Fe-BMG Composition

5.3.1 As-milled powder

Fig. 5.18 shows the XRD patterns of the Fe\textsubscript{60}Co\textsubscript{8}Zr\textsubscript{10}Mo\textsubscript{8}W\textsubscript{2}B\textsubscript{15} powder blend as a function of milling time, up to 50 h. The initial powder blend shows all the expected major diffraction peaks from all the metal powders. Since the crystal structure is the same and the lattice parameters are very close to each other for both W and Mo, their peak positions could not be distinguished from each other. Consequently, these peaks have been labeled as W/Mo.

With increasing milling time, the intensity of the diffraction peaks decreased and their width increased, due to particle refinement (reduction of crystallite size) and increase of lattice strain. This trend continued to beyond about 15 h of milling time. The diffraction pattern of the powder milled for 20 h shows mostly a broad halo, suggesting formation of an amorphous phase. However, a relatively low intensity peak may be noticed at $2\theta \cong 40.5^\circ$, which by comparison with standard XRD patterns, has been identified to be either Mo or W. Thus, the amorphous phase formed at 20 h of milling time is lean in W and/or Mo. On continued milling, however, this W/Mo peak intensity decreased and was almost completely absent in the powder milled for 30 h. But, at longer milling times, a few sharp diffraction peaks started appearing and this trend continued till 50 h, the maximum milling time employed in the present investigation.
Figure 5.18: X-ray diffraction patterns of the blended elemental powder mixture of Fe$_{60}$Co$_{8}$Zr$_{10}$Mo$_{5}$W$_{2}$B$_{15}$ milled for different times in a SPEX mill.
Fig. 5.19 compares the XRD patterns of the powder milled for 20 h and 50 h in the SPEX mill. One can easily notice a very sharp $\alpha$-Fe peak around $2\theta = 45^0$ and another relatively low intensity peak around $2\theta = 64.7^0$ in the powder milled for 50 h, whereas only a broad halo is present in the powder milled for 20 h. These additional
diffraction peaks in the powder milled for 50 h were identified as arising from the $\alpha$-Fe phase. This observation suggests that the amorphous phase has started to crystallize on long-term milling.

### 5.3.2 Lattice parameters

A close observation of the diffraction patterns from the powders milled for different times (Fig. 5.18) indicates that the $\alpha$-Fe peaks have shifted to lower $2\theta$ angles with increasing milling time, suggesting an increase of the lattice parameter. Even though measurement of the lattice parameter is not very accurate, due to peak broadening, the trend clearly shows that the lattice parameter increases up to about 15-20 h and then starts to decrease (Fig. 5.20). This variation in the lattice parameter of the $\alpha$-Fe solid solution can be related to its composition. In the initial stages of milling, the solute elements seem to be dissolving in the Fe lattice forming a supersaturated solid solution. Since all the solute elements have a larger atomic size (Co: 0.2506 nm, Zr: 0.3186 nm, Mo: 0.2726 nm, and W: 0.2742 nm) than Fe (0.2482 nm), their dissolution is expected to increase the lattice parameter of the $\alpha$-Fe solid solution.

Boron atoms with a size of 0.188 nm will dissolve interstitially in the Fe lattice and this will also dilate the lattice. Thus, it is easy to visualize that the lattice parameter has increased in the early stages of milling. Once the threshold amount of distortion of the lattice is achieved due to the size mismatch between the solvent and solute atoms, the crystalline lattice becomes destabilized and an amorphous phase is expected to form [82, 83]. Further, accumulation of lattice defects may have aided formation of the amorphous phase.
As noted above, milling of the powder beyond the formation of the amorphous phase (20-30 h) resulted in the reappearance of diffraction peaks of the α-Fe phase, suggesting that the amorphous phase has started to crystallize. It is well known, that metallic glasses, whether formed at very high cooling rates as by traditional melt spinning techniques or by relatively slow rates as in bulk metallic glasses, begin to crystallize in the primary mode through formation of the primary-metal-based solid solution [33,84-86]. That is, crystallization of the homogeneous amorphous phase in the Fe-based glasses occurs by the formation of the (α-Fe)′ phase (with a composition different from the α-Fe phase formed prior to the amorphous phase) and the remaining amorphous
phase acquiring a different composition (Amorphous'). This new Amorphous' phase may subsequently crystallize by either the eutectic or polymorphous modes. Thus, the Fe-based amorphous phase synthesized by MA can be expected to transform to the equilibrium phases in two stages:

\[
\text{Amorphous phase} \rightarrow (\alpha\text{-Fe})' + \text{Amorphous'} \quad (5.1)
\]

and

\[
\text{Amorphous'} \rightarrow \text{equilibrium phases} \quad (5.2)
\]

Formation of the \((\alpha\text{-Fe})'\) phase in the present case confirms that primary crystallization has occurred here. It should also be noted that the amount of the \((\alpha\text{-Fe})'\) solid solution formed is small in quantity, as evidenced by the relatively low intensity of the peaks. Thus, the solute elements got repartitioned into the Amorphous' phase (containing a higher solute content) and the \((\alpha\text{-Fe})'\) solid solution (with a lower solute content). Consequently, the lattice parameter of the \(\alpha\text{-Fe}\) solid solution started to decrease, once crystallization has started.

5.3.3 **External Heat Treatment**

Since the amorphous phase contains several metals and one nonmetal component, it is most unlikely that complete crystallization of the amorphous phase will result in the formation of only the \(\alpha\text{-Fe}\) phase. To confirm that the \((\alpha\text{-Fe})'\) phase is the product of only the primary crystallization of the amorphous phase and that it is not the only phase in the final product, the amorphous powder (milled for 20 h) was heat treated externally for 1 h at 700 °C.
While the powder milled for 20 h shows mostly a broad halo (except for a low intensity Mo/W peak), the powder heat treated for 1 h at 700 °C (Fig. 5.21) shows a number of sharp diffraction peaks. Comparison with standard XRD patterns of the possible phases that could be present in an alloy of this composition suggests that the annealed powder now contains several phases such as ($\alpha$-Fe)$'$, Fe$_3$B, Fe$_2$B, MoB$_2$, FeMo$_2$B$_2$, and ZrFe$_2$. A few additional peaks have also been noted indicating that at least another unidentified phase exists. A similar phase constitution was also observed in the bulk metallic glass of the same composition, but processed by the solidification route [87]. Since ($\alpha$-Fe)$'$ is the major phase in the crystallization product, and it is the first
phase to form as a result of crystallization of the amorphous phase, it may be assumed that the presence of the \((\alpha\text{-Fe})'\) phase in the milled powder suggests start of crystallization of the amorphous phase on milling the powder for 50 h; almost complete crystallization has occurred on annealing the powder at 700 °C.

5.3.4 Possible reasons for the mechanical crystallization of the amorphous phase

Four possibilities can be visualized for this unusual transformation of crystallization of the amorphous phase on continued mechanical alloying observed in the present investigation. One is the temperature rise of the powder during MA. It has been clearly shown in several instances [6, 75, 88] that the powder temperature increases during milling. Even though some investigators assume a very large instantaneous local temperature rise, the global temperature rise was never reported to be more than about 200 °C. Since the crystallization temperature of the present Fe-based metallic glass has been reported to be 950 K [87], it is unlikely that formation of the \(\alpha\text{-Fe}\) phase during milling is due to an increase of the powder temperature to a value above that of the crystallization temperature of the amorphous phase.

The second possibility is powder contamination. The MA literature contains several examples of impurity-stabilized crystalline phases, which have formed after the formation of the amorphous phase [75, 89, 90]. Since the amorphous phase in the present alloy powder has crystallized into all the expected intermetallic phases (in addition to the \(\alpha\text{-Fe}\) phase) on external heat treatment, the amorphous phase can be assumed not to contain any substantial amount of impurities. Thus, this possibility can also be discounted.
The third possibility is inverse melting, a phenomenon first observed in Ti-Cr alloys [91, 92]. Subsequently this transformation was also reported to occur in several transition-metal (Ti, Zr, Nb, and Ta) based binary alloys, especially those synthesized by MA [93, 94]. In this inverse melting phenomenon, heating a homogeneous metastable b.c.c. solid solution formed by mechanical alloying to higher temperatures produced an amorphous phase polymorphously. On further heating to still higher temperatures, the amorphous phase crystallized into the b.c.c. phase again, i.e., the phenomenon was reversible. The stabilization of the amorphous phase below the melting temperature was explained on the basis that the amorphous phase has a higher chemical short- and medium-range order than the corresponding crystalline phase. Consequently, destruction of this order (disordering of the amorphous structure), e.g., by heating (or continued milling) enhanced its free energy and favored formation of the equilibrium crystalline phase.

In a process similar to what has been reported for inverse melting in the b.c.c. solid solutions above, it is possible that the crystalline $\rightarrow$ amorphous $\rightarrow$ crystalline phase transformation in the present Fe-based alloy could also be explained on the basis of an inverse melting phenomenon. But, the inverse melting phenomenon in all the systems so far has followed certain requirements. It occurs in (a) binary transition metal alloy systems, (b) starts from a homogeneous crystalline phase, (c) the atomic co-ordinations of the amorphous and the equilibrium crystalline Laves phase are very similar, (d) it is reversible and (e) for the kinetics of the amorphization reaction to be appreciable, the temperature at which amorphization occurs is reasonably high (746 ± 20 °C in Ti-55 at.% Cr and 810 °C in Nb-55 at.% Cr alloys). Further, the electron-to-atom (e/a) ratio of the
alloy exhibiting inverse melting was found to be between 5.0 and 5.5. The (metastable) b.c.c. solid solution is stable at e/a values <5.0 and the amorphous phase is stable at values >5.5. Most of the above criteria are not met in the present case and therefore, it may be concluded that the crystalline → amorphous → crystalline phase transformation in the present Fe-based alloy is not due to the inverse melting phenomenon.

The last possibility is that MA has caused changes in the relative thermodynamic stabilities of the different phases and phase combinations, due to the introduction of mechanical energy into the system. It is well known that mechanical milling introduces a variety of lattice defects such as vacancies, dislocations, and grain boundaries [6, 75] and since the concentration of these defects can be very high [95], the sequence of phase transformations observed in the present investigation can be explained with reference to the relative thermodynamic stabilities of the different phases or phase combinations. Fig. 5.22 represents a schematic free energy vs. composition diagram indicating the relative positions of the amorphous, amorphous’, α-Fe, and (α-Fe)’ phases and the blended elemental powder mixture.

In alloy systems with a large negative heat of mixing (as in the present case), the blended elemental powder mixture has obviously a high free energy (point 1) and therefore on MA, the powder blend is expected to change into a more stable configuration by reducing its free energy. Since a crystalline solid solution has a lower free energy than the blended elemental powder mixture, the first transformation product will be the α-Fe solid solution phase, corresponding to point 2 in the free energy curve.
Figure 5.22: Hypothetical free energy vs. composition diagram to explain the observed transformations in the present investigation.
This $\alpha$-Fe phase is a supersaturated solid solution of Fe with all the solute elements dissolved in it. Continued milling introduces a high density of defects and thus increases the free energy of the crystalline $\alpha$-Fe phase to above that of the amorphous phase. Thus, the $\alpha$-Fe phase becomes destabilized and the amorphous phase begins to be more stable (point 3). The phase mixture of the ($\alpha$-Fe)$'$ solid solution (containing a lower solute content) and the amorphous$'$ phase with a much higher solute content than what was started with (due to the crystallization of the initial amorphous phase) is likely to have a lower free energy than a single amorphous phase (point 4) and that is why continued milling resulted in the primary crystallization of the amorphous phase. Thus, it could be concluded that formation of the ($\alpha$-Fe)$'$ phase after the formation of the amorphous phase is neither just because of the excessive temperature rise of the powder, nor because of powder contamination, nor due to inverse melting. Even though the powder temperature is much lower than the crystallization temperature of the amorphous phase, partial crystallization through the primary mode has occurred and this can be ascribed to the increased diffusion of solute atoms due to the presence of a high density of milling-induced defects. A slight powder temperature rise may also have contributed to this transformation.
5.3.5 *Comparison with related observations*

A cyclic crystalline-amorphous-crystalline transformation has been reported earlier in Co-Ti alloys [96-98]. Starting with the elemental powders, the authors had synthesized a metastable intermetallic phase, which on continued milling became amorphous. This process of crystalline $\rightarrow$ amorphous $\rightarrow$ crystalline transformations was observed repeatedly. Even though an amorphous phase has transformed into a crystalline phase in the present investigation also, important differences may be noted between our results and those on Co-Ti alloys. In the case of the Co-Ti alloys, the amorphous phase has transformed into a metastable crystalline bcc-Co$_3$Ti phase, which has again changed into an amorphous phase. On continued milling, the bcc-Co$_3$Ti phase transformed again into the amorphous phase. A stable crystalline phase had never formed in these alloys on milling; it formed only on externally annealing the amorphous alloy powder. However, in our present investigation, the $\alpha$-Fe phase is an almost equilibrium phase (although the solute content is different) and on subsequent annealing the full equilibrium constitution has been achieved.

Secondly, we have formed a solid solution phase on MA of the powder blend. Even though formation of an amorphous phase on milling a crystalline phase depends on the increase of free energy as a result of accumulation of lattice defects in the crystalline phase, it is not clear whether an amorphous phase can be produced more easily from the solid solution or the intermetallic phase. The literature has examples of both the situations [6, 75]. However, since intermetallic phases are usually ordered and their crystal structures more complex than those of the primary solid solutions, it has been noted that
it is easier to amorphize intermetallics than solid solution phases [99]. This is because it is easy to induce a lot of defects such as grain boundaries, dislocations, antiphase boundaries, and disordering of the lattice, all of which raise the free energy of the crystalline intermetallic above that of the amorphous and consequently, the amorphous phase becomes more stable. Thus, we believe that it is more difficult to form the amorphous phase from a solid solution (as in our Fe-based alloy composition) than from an intermetallic as in the Co-Ti system [96-98].
5.4 Consolidation of Fe-BMG powder

To characterize the mechanical properties of the Fe BMG composition (Fe$_{60}$Co$_8$Zr$_{10}$Mo$_5$W$_2$B$_{15}$) alloy, the mechanically alloyed amorphous powder was attempted to consolidate to the bulk shape by hot isostatic pressing (HIP) and pulsed magnetic compaction techniques. HIPing the of 30 h milled sample was carried out at a pressure of 30,000 psi and 600 °C for 3 h, whereas pulsed magnetic compaction of the same powder was carried out at 13.8 kV magnetic pulse (pulse duration: 120-180 µs). The HIPed sample was cylindrical in shape (10 mm in diameter and 25 mm in height) whereas the magnetically pressed sample was in a ring form (outer diameter: 30 mm, inner diameter: 20 mm and height: 5 mm).

The consolidated samples were not in regular shape and broke into pieces (Fig. 5.23), possibly due to the residual stresses in the powder. These consolidated samples were characterized for their density and microstructure. The density calculated from the Archimedes principle was around 92 %. Fig. 5.24 shows the SEM images of the consolidated samples. From the SEM micrographs it is clear that both the samples contain porosity and this was also confirmed by scattered microhardness values obtained.
Figure 5.23: BMG composition samples consolidated by (a) HIPing and (b) Pulsed magnetic compaction.

Figure 5.24: SEM micrograph clearly showing the presence of porosity in the (a) HIPed sample and (b) magnetically compacted sample.
5.5 Nanoindentation

Nanoindentation tests were carried out on Nanotest-600® manufactured by Micromaterials Limited of Wrexham, UK. Two Fe-BMG samples compacted by hot isostatic pressing were indented using a spherical diamond indenter. The elastic modulus and the yield stress were calculated as described in section 4.6.1 The process parameters are as follows:

- Loading rate: 50 mN/sec
- Maximum load: 750 mN
- Diameter of the indenter (D): 2.800 mm
- Poisson’s ratio of the indenter ($\nu_i$): 0.07
- Poisson’s ratio of the consolidated sample ($\nu_m$): 0.31
- Elastic modulus of the indenter ($E_i$): 1141 GPa

The machine compliance was determined by indenting a standard steel sample of known modulus and by deriving a relationship between machine displacement and applied load. To verify this relationship, a standard fused quartz sample (with a known elastic modulus of $E = 72$ GPa) was indented and the modulus was experimentally determined to be 73 GPa which was well within ± 2 GPa error zone. Fig. 5.25 shows the load vs. indentation depth (P-h) response of the Fe-BMG sample. The loading portion from this curve was plotted on a log scale to determine the onset of large scale plasticity. The elastic modulus was determined by fitting a 3/2 curve to the elastic region in the loading portion of the curve.
The elastic modulus was determined to be $53.05 \pm 15$ GPa. The errors reported represent a standard deviation from 26 comparable indents. In comparison to the value of elastic modulus reported earlier ($E = 184 \pm 12$ GPa), the present nanoindentation test results show much lower numbers. The reason for such low values might be the porosity present in the compacts. These are only the preliminary results for the mechanical properties of the consolidated bulk amorphous samples. The consolidation parameters used for the HIPing and magnetic compaction of BMG powder, are obviously not optimum to achieve 100 % density. Hence, it is necessary to optimize the consolidation process for mechanically alloyed amorphous powders for full density.
CHAPTER 6: CONCLUSIONS

To gain a better understanding of the conditions under which an amorphous phase will be obtained in the Fe-based alloys by mechanical alloying, we have undertaken a detailed mechanical alloying behavior of the binary Fe-B alloy system. A range of Fe-B binary compositions were selected for the present study so as to investigate the extension of solid solubility limits and also to study the glass-forming ability in the neighborhood of the eutectic region in the Fe-B phase diagram. In the present study the maximum solid solubility extension of up to 25 at. % B was observed. Due to the increased defect density, reduced diffusion distances and temperature rise during MA true alloying between B and Fe took place. Furthermore, due to severe plastic deformation during MA, decomposition of the supersaturated Fe-solid solution took place and FeB, Fe2B and Fe3B intermetallics had formed. The solid-state reaction involved in MA and due to increased defect density and small crystallite size, the free energy of the intermetallic system was raised to a level higher than that of the amorphous phase and consequently, formation of amorphous phase was feasible. In the present study, partial amorphous phase was obtained in equiatomic Fe-B composition.

It has been shown that an unusual phase transformation occurred on MA in an Fe-based alloy of bulk metallic glass of composition Fe60Co8Zr10Mo5W2B15. Starting with blended elemental powders, a supersaturated solid solution of solute elements in Fe was obtained in the early stages of milling. On milling to 20 h, an amorphous phase had
formed, which on continued milling to 50 h, crystallized in a primary mode resulting in the formation of the (α-Fe)′ phase and another amorphous′ phase with a higher solute content. Complete crystallization was achieved on heat treating the amorphous powder externally for 1 h at 700 °C. Reasons for such an unusual transformation have been explained and was attributed to the relative thermodynamic stabilities of the different phases and phase combinations, due to the introduction of mechanical energy into the system.
REFERENCES


