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THESIS SUBMITTED FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN

METALLURGICAL ENGINEERING

BY

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It is certified that the work contained in the thesis entitled **"Effect of processing routes on microstructure,phase evolution and indentation characteristics of $Fe_{56.24}Cr_4Mo_{14}C_{15}Si_{3.8}B_6$, $Fe_{43.47}Cr_{15}Mo_{14}C_{15.12}Si_{3.78}B_6Y_2$, $Fe_{40.2}Cr_{20}Mo_{10}W_2C_{15}Si_{4.2}B_6Y_2$ and $Fe_{40.2}Cr_{15}Mo_{14}Co_3C_{15}Si_{4.2}B_6Y_2$ alloys"** by **"Sarika Kumari"** during this period she worked as a Ph.D. research scholar in this Department. The results and data presented in this thesis are genuine and original.

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CANDIDATE'S DECLARATION

I, **Sarika Kumari,** certify that the work embodied in this Ph.D. thesis is my own bonafide work carried out by me under the supervision of **Prof. Rajiv Kumar Mandal** for a period of **July 2017 to June 2024** in the department of **Metallurgical Engineering IIT (BHU), Varanasi**. The matter embdied in this Ph.D. thesis has not been submitted for the award of any other degree/diploma.

I declare that I have devotedly acknowledged, given credit and refered to the research workers wherever their works have been cited in the text and the body of thesis. I further certify that I have not willfully copied some other's work, paragraph, text, data, as well as any results etc.,reported in journals, books, magazines, reports dissertations, thesis, etc., or available at websites and have not included them in this thesis and have not cited as my own work.

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She may be allowed to submit the Ph.D. thesis entitled "Effect of Processing Routes on Microstructure, Phase evolution and Indentation Characteristics of $Fe_{56.24}Cr_4Mo_{14}C_{15}Si_{3.8}B_6$,$Fe_{43.47}Cr_{15}Mo_{14}C_{15.12}Si_{3.78}B_6Y_2$,$Fe_{40.2}Cr_{20}Mo_{10}W_2C_{15}Si_{4.2}B_6Y_2$ and $Fe_{40.2}Cr_{15}Mo_{14}Co_3C_{15}Si_{4.2}B_6Y_2$ alloys".

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(Sarika Kumari)

Table of Contents

LIST OF ABBREVIATIONS

MGs	Metallic glasses
BMGs	Bulk metallic glasses
ETMs	Early transition metals
TTT	Time-tempereature-transformation
GFA	Glass forming ability
DRP	Dense random packing
ECP	Efficient cluster packing
RSP	Rapid solidification process
PBZ	Pseudo Brillouin zone
MA	Mechanical alloying
MM	Mechanical milling
SPS	Spark plasma sintering
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
RE	Rare earth element
DSC	Differential scanning calorimeter
DTA	Differential thermal analyser
STZ	Shear transformation zone
SLM	Selective lesser melting
SAED	Selected area electron diffraction
HRTEM	High resulation transmission electron microscopy
SRO	Short-range order
MRO	Medium-range order
OM	Optical microscopy
XRD	X-ray diffraction
SE	Secondary electrons
EDAX	Energy Dispersive X-ray Spectroscopy
CI	Cast iron
PCA	Processing control reagent
WC	Tungsten carbide
BMP	Ball milled powder
PIPS	Precison ion polishing system
VHN	Vicker's hardness number
MS	Melt spinning
BF	Brigth field
ISE	Indentation size effect
PM	Powder metallurgy
RISE	Reverse indentation size effect

LIST OF FIGURES

LIST OF SYMBOLS

T_g	glass transition temperature
T_m	melting temperature
R_c	critical cooling rate
T_N	nose temperature
Tl	liquidus temperature
t_N	time required for the nucleation of the first crystallite
Dc	critical thickness
e/a	electron to atom ratio
V_R	volume ratio
R_R	radius ratio/ atomic size ratio
K_F	Fermi wave vector
T_{rg}	reduced glass transition temperature
ΔT	undercooled liquid regime
Tx	crystallization temperature
ΔG_m	activation energy of motion
Ω	atomic volume
υ	Poisson's ratio
γ_0	Shear stain
ε	dilatational strain
Hv	Vicker's hardness
G	radius of pseudo-Brillouin zone surface
λ	wave length
t	crystallite size
β	total broadening
θ	Bragg angle
ρ	bulk density
P	load
d	indentation diagonal length
K_{IC}	indentation fracture toughness
E	Young's modulus
σo	offset yield strength
n	Meyer's exponent
K	material constant
We	plastic work
Wp	elastic work
R	elastic recovery
hf	final depth of the indentation
h_{max}	maximum penetration depth
Rw	plastic criterion

LIST OF TABLES

PREFACE

Kelton (2023) has recently commented, "Metallic glasses have the potential to become transformative materials, but this is hindered by the lack of ability to accurately predict which metallic alloys will form good glasses. Current approaches are limited to empirical rules that often rely on parameters that are unknown until the glasses are made, rendering them not predictive". The research work carried out as a part of this doctoral thesis shall revolve around such a hypothesis. The thesis has two distinct parts. One of them relates to evolving parameters of metallic systems for empirically predicting metallic glass compositions. These parameters are: electron to atom ratio (e/a), Volume ratio of total volume per mole of the alloy to largest atom volume (V_R), and radius ratio of the larger atom to smaller atom in alloy (R_R). In addition to these, the concept of Fermi energy (E_F) and Fermi vector (K_F) will also be computed. Further the interaction of Fermi surface with that of Pseudo-Brillouin Zone (PBZ) boundary has also been explored. Based on these considerations four iron based alloy compositions have been chosen for experimental investigations. The thesis has been organised in seven chapters and one appendix.

Chapter 1 gives brief introduction of various reports by researchers on metallic glasses (MGs) and bulk metallic glasses (BMGs). The historical background of MGs shall begin with first report by Pol Duwez (1960) followed by seminal contributions made by T.R. Ananthraman from this department. Majority of MGs compositions investigated since their inception refer to exploring the properties related to transformer core application as soft magnetic material. Such MGs was having iron as the main alloying element. It has recently been shown that Fe-based MGs compositions can also be useful for structural application. Several researchers compared hardness to density ratio (H/ρ) of Fe-based BMGs with that of maraging steel. They have concluded such a ratio for BMGs is around four times more than maraging steel. This investigation has kept in mind this aspect while choosing four compositions based on the empirical criteria studied for around 1000 alloys. A series of Venn diagrams were constructed for each of the categories of metallic alloys for MGs/BMGs. The thesis will present the detail computational steps for all of them. The data utilised for this purpose will be given as an Annexure-I. Essential steps pertaining to these will be explained in **(chapter 2)**. The four compositions chosen as a part of this investigation along with relevant empirical parameters will be given at the end of this chapter as a part of conclusion. This chapter will emphasize only details of MGs/BMGs compositions with iron as a main alloying element for the reasons

explained above. The alloy compositions selected as a part of this investigation has been synthesized by Cu-mould casting. Such a synthesized alloy will be designated as Cu-mould cast alloy in the thesis.

Chapter 3 deals with experimental part along with details of raw materials utilized for alloy making. These four alloys were subjected to further processing. The processing methods relate to (i) melt-spinning and (ii) high energy ball-milling followed by compaction through spark plasma sintering (SPS). The characterization tools employed for Cu-mould cast, melt-spun ribbons, ball-milled powders as well as their compact will be briefly discussed in this chapter. They refer to optical and electron microscopy. Extensive uses of X-ray diffraction (Rigakuu Miniflex 600, EMPYREAN PANALYTICAL HR-XRD) have been done. Melt-spun ribbons were examined under transmission electron microscope in diffraction and imaging modes for conformation of glassy nature. The hardness of samples of as-cast alloy as well as after processing was measured through instrumented hardness tester (make: Anton Paar MHT^3). The stability of the alloys under processing different processing conditions was studied with the help of DTA (make: NETZSCH DSC 404F3).

Chapter 4 begins with discussion on the evolution of structures/microstructures of Cu-mould cast alloys. The phases evolved in these alloys were having structure hP20, oP40, mC28, cF112, cI58, cF116, and oP16 type. Most of the phases are common in them. Alloy-A has shown dendritic features in their microstructure. Alloy-D exhibits minimum density (7.23g/cc) and maximum melting temperature (1418K) among all. This chapter also deals with relation of hardness with alloying additions. Alloy-D (3 at% addition of Co) exhibits maximum microhardness (~13 GPa) and Young's modulus value (~240GPa) at 100g indentation load. The hardness to density ratio for all as-cast alloys are higher than maraging steel.

Chapter 5 deals with synthesis, characterization, thermal stability and indentation behaviour of melt-spun ribbons. Alloy compositions A and D in ribbon form exhibits X-ray amorphous structures. Transmission electron microscopy (TEM) observations confirm that ribbon MS-A and MS-D are indeed amorphous. In contrast MS-B and MS-C consist of very fine nanocrystalline phases are distributed in the amorphous matrix. These nanocrystals are one of the two phases or both (α-Fe and $Fe_{11}Mo_6C_5$ phases). Melt-spun ribbon MS-D also exhibits maximum melting temperature (1433K). Melt-spun ribbons MS-A and MS-C have clear glass transition temperature at T_g 923K and 882K respectively. The reduced glass transition temperatures Trg of these ribbons are found to be 0.55 and 0.53 respectively.

The next synthesis method, I have used high energy ball milling technique. This is discussed in **chapter 6.** As-cast alloys when processed through high energy ball milling retain only two phases at the end of 100h of milling. They are α-Fe and $Fe_{11}Mo_6C_5$ phase. These phases are present under all processing conditions. The average crystallite size and average strain were calculated. Further, 100h ball-milled powders were consolidated through SPS technique. Spark plasma sintered samples (SPSed) give rise to additional crystalline phases $Fe_{23}C_6$ (cF116) and $FeMoB_2$ (tP10). Phase transformation takes place during the process of SPS in addition to consolidation. The densities of sintered powder samples are same as those of as-cast sample except SPSed-A and SPSed-D. The hardness to density ratio of SPSed alloys are also better than maraging steel.

Chapter 7 summarizes the outcome of entire work. It also has a section on the scope of future work.