PREFACE

Discovering new materials and metallic alloys have always been an exciting to the materials science & engineering community. Traditionally, alloys have been developed based on one or rarely two principal elements along with addition of minor elements in order to enhance the desirable properties. In sharp contrast, a new concept of alloy design involving multiple elements in equiatomic or non-equiatomic compositions to form single phase alloys was advocated in 2004 independently by two eminent materials scientists, i.e. J.W Yeh (Taiwan) and Brian Cantor (UK). These multicomponent alloys are designated as ‘High Entropy Alloys’ (HEAs). In general, HEAs are defined to have five or more principal elements in equiatomic or non-equiatomic concentration. The concentrations of these principal elements are varying in the range of 5-35 at%. Apart from this composition based definition, HEAs are also understood on the basis of configurational entropy, which should be more than 1.61R (R = universal gas constant). The interesting fact about HEAs is that they crystallize into the simple solid solution phases, i.e. BCC, FCC or HCP structure. On account of their unique compositional design concept and simple solid solution forming ability, HEAs are anticipated to possess good properties, i.e. high hardness, high strength, excellent thermal stability, magnetic properties as well as good resistance to wear, oxidation and corrosion. High-entropy alloys (HEAs) are developed by various processing routes, i.e., vacuum arc melting, vacuum induction melting, melt spinning, rapid solidification, vapour deposition technique and solid-state technique. In literature, most of the HEAs are prepared by melting/casting routes. The common problem of the melting route is the non-homogeneous microstructure in the solidified products. Therefore, it is essential to provide the annealing treatment at higher temperature followed by quenching to obtain the homogeneous microstructure. From the literature, it has been estimated that the solid-state technique, i.e. mechanical alloying

(MA) of producing HEAs have been utilized to produce nanostructured materials, involving milling of elemental powders to obtain alloying at the atomic scale. However, the systematic study on alloying behaviour and phase evolution in course of milling for formation of HEAs are still lacking. The major concern of consolidation of the nanostructured material has been addressed to some extent by using advanced sintering techniques, i.e. hot isostatic pressing (HIP), vacuum hot pressing (VHP) and spark plasma sintering (SPS). Retaining the nanostructured phases in bulk form will help in tuning the desired property of the materials.

The present work deals with the synthesis of the nanocrystalline equiatomic AlCoCrFeNi, AlCoCrFeNiMn and AlCoCrFeNiTi HEAs. The study aims at understanding the phase evolution, thermal stability and microstructural evolution in all these alloys. Attempts have been made to consolidate the milled powder through microwave heating. In another study, a non-equiatomic composition of $Fe_{40}Cr_{25}Ni_{15}Al_{15}Co_5$ HEA has been under taken to analyze the effect of configurational entropy on phase formation and subsequent precipitation leading to strengthening. The phase, microstructure, thermal stability and mechanical properties of induction melted HEAs have been investigated in details. The thermodynamic phase prediction parameters, i.e. configurational entropy (ΔS_{conf}), mixing enthalpy (ΔH_{mix}), atomic mismatch (δ%), valence electron concentration (VEC), and omega (Ω) parameter have been determined in order to evaluate the solid solution phase forming ability of these alloys. The comparison of these alloys with bulk metallic glasses has been made to have the insight for multicomponent alloy formation.

The thesis is organized into seven chapters. **Chapter 1** provides a brief introduction and an overview of the current understanding on the subject of study. This chapter describes how the alloy design principles of high- entropy alloys (HEAs) are different from the conventional alloys and what are the major core effects of HEAs, which make these alloys to form simple solid solution phases. It also provides information regarding different processing routes along with the major ones for synthesizing HEAs. The objectives of the present work are mentioned at the end of this chapter.

Chapter 2 deals with the details of the materials and experimental procedures used for the present work. It briefly introduces the equipment used for processing, characterization and testing of the materials. Mechanical alloying (MA) and induction melting (IM) techniques are used to prepare the HEAs. The phase identification at different milling hour has been done by X-ray diffraction (XRD) technique. The microstructures have been characterized using optical microscopy (OM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) equipped with energy dispersive spectroscopy (EDX). The thermal stability of the alloys are investigated by differential scanning calorimetry (DSC), in-situ x-ray diffraction and suitable annealing treatments. The compression test was performed for the as-cast alloy. Vickers microhardness tester was used to measure the hardness of the samples.

Chapter 3 presents a detailed study of the synthesis and characterization of AlCoCrFeNi HEA by mechanical alloying (MA). A systematic study of the dissolution of elements and evolution of phases in course of milling through x-ray diffraction analysis has been presented. After 30h of milling, the formation of a single-phase BCC structure (a=2.89±0.02Å) was observed. The study also aimed at predicting the phase formation criteria for the present alloy. The alloy is found to fit well within the range of the solid solution formation criteria. The nanostructured nature of milled powder was confirmed through transmission electron microscopy (TEM). Thermal stability of the milled powder was analyzed through differential scanning calorimetry (DSC), in-situ x-ray diffraction and suitable annealing treatments. The alloy powder is not stable above as 350 ºC (623K).

It leads to precipitation of intermetallic phases of B2, $L1_2$ and σ with an increase in temperature. The precipitation of these phases and strong baseline shift in DSC confirms the diffusive nature of the phase transformation. This chapter also aimed at consolidating the milled powder through microwave sintering. Formation of the similar phases was observed after sintering. It is now obvious that the evolution of the high entropy phases in milled condition leads to a combination of high-entropy and medium-entropy phases after annealing treatment.

Chapter 4 presents the phase evolution and thermal stability of the mechanically alloyed hexanary AlCoCrFeNiMn HEA. The alloy showed the formation of a single-phase BCC structure after 40 h of milling. A similar type of BCC solid solution phase was also obtained after processing through two different milling schedules. These two milling schedules contained three elements, i.e. AlCoCr and FeMnNi separately. Thermal stability of the milled powder was monitored through DSC, in-situ x-ray diffraction and suitable annealing treatments. The alloy is stable upto 500ºC (873K) and further leads to the formation of an FCC phase closely related to Ni_3Al type and Mn_3Co_7 type phases. The study also aimed at calculating the activation energy required for the phase transformation of this alloy. Microwave sintered samples showed behaviour similar to that in heat-treated powder having BCC phase coexisting with Ni_3Al type $L1_2$ ordered phase. In order to elucidate its classification as HEA, thermo-physical properties were studied. In the last section of the chapter, the essential differences of these alloys with multicomponent bulk metallic glasses are discussed.

Chapter 5 describes the alloying behaviour, phase evolution and thermal stability of equiatomic AlCoCrFeNiTi HEA. The 40h milled powder confirms the formation of a nanostructured single phase BCC along with a minor amount of tungsten carbide (WC) phase arising from contamination during milling, which is observed after certain milling duration. The main source of the carbide formation is the wet atmosphere of milling, where toluene is used as a process control agent. It is argued that the toluene may react with tungsten vials and balls and may lead to the formation of the carbide phase. It has also been emphasized that the formation of the carbide phase will not affect the composition of hexanary HEA. Alloy is thermally stable upto 600ºC (873K). Microwave sintered samples at 1000ºC (123K) showed the transformation of the BCC phase into the B2 phase co-existing with the minor hexagonal WC phase.

Chapter 6 presents the non-equiatomic$Fe_{40}Cr_{25}Ni_{15}Al_{15}Co_5$high-entropy alloy (HEA) processed through induction melting (IM). The alloy exhibits two-phase microstructure of BCC and ordered B2 type phase in the as-cast condition. These phases were confirmed through X-ray diffraction (XRD) and transmission electron microscopy (TEM). The Ni-Al enriched ordered B2 precipitates of cuboidal shapes are homogeneously distributed in Fe-Cr rich disordered BCC matrix. The formations of columnar dendrites are identified through optical microscopy (OM) and scanning electron microscopy (SEM). The structural and microstructural stability of the alloy was examined through different heat-treatment schedules. Heat-treated samples at different temperatures exhibit a similar morphology of columnar dendrites. Moreover, the alloy showed the two-phase microstructure in all heat-treated conditions, which infers the good thermal stability. The alloy had shown a good combination of high compressive yield strength and hardness, i.e. ~1012 MPa & 428±5 HV respectively at room temperature. The structure-property correlation was further discussed.

Chapter 7 presents an overall summary of the work from the present investigation along with suggestions for future work.

In the reference section, all the relevant references, which are cited in the thesis, are sequentially compiled.