PREFACE

Alloying has long been used to confer desirable properties to materials. A good understanding of alloy phase stability and phase equilibria under various service conditions is essential in designing and developing new materials. We know that the properties of materials depend significantly on the nature, number, amounts, and morphology of various possible phases present in the microstructure, and this can be further controlled by altering these quantities. High entropy alloys (HEAs), a new class of alloys, are designed by a combination of multiple principal elements in high concentrations compared to the conventional strategy of adding relatively small amounts of secondary elements to one or two principal elements. HEAs are solid solutions of nearly equiatomic alloys of five or more components with high configurational entropy and low mixing enthalpy and, despite the chemical complexity, are characterized by having simple crystal structures (i.e., FCC, BCC, or HCP solid solutions) with often remarkably better mechanical properties than those of the elemental components. It was observed that the effect of configurational entropy plays a significant role in minimizing the number of phases in these multicomponent alloys. Yeh and co-workers have designated the term ‘High Entropy Alloys’ in 2004 for this new class of materials. The multi-dimensional compositional space to understand the phase stability that can be tackled is practically limitless, and only tiny regions of which have been investigated so far.

The processing of this new class of advanced materials is equally necessary for ensuring the enhanced properties for technological applications. The HEAs can be mostly synthesized by conventional casting and solid-state techniques. The non-equilibrium processing route, such as mechanical alloying, produces nanostructured HEAs for

enhancing the physical and mechanical properties. The consolidation of these nanostructured alloys using conventional methods is a challenging task that can be accomplished through non-equilibrium consolidation techniques like spark plasma sintering (SPS). The HEAs can also be synthesized by liquid state techniques, i.e., vacuum arc melting.

The present work deals with the synthesis and processing of the nanostructured CrFeCoNiCu and low-density MgAlMnFeCu high entropy alloys by mechanical alloying. In addition, two refractory high entropy alloys, namely TiVZrMoW and TiVZrYHf alloys have been prepared by solidification casting technique. The study aims at understanding the phase evolution process during mechanical alloying and arc melting along with the thermal stability of these synthesized alloys. Attempts were made to understand the phase stability of the evolution of the equilibrium phases using theoretical methods, namely density functional theory (DFT) and CALPHAD (using Thermo-Calc software) as well as parametric approaches advocated in literature.

The present thesis is divided into six chapters. **Chapter 1** deals with the basic understanding of the new class of advanced materials based on the literature review available in this area. The four core effects of HEAs are discussed to understand their impact on the properties of these advanced materials. The phase equilibria rules in the binary system that helps in developing an understanding of phase stability in the multicomponent systems are also brought into consideration. Parametric approaches are utilized to make a fast and reasonably correct prediction of the phases that may form in the chosen alloy systems. This chapter also explains the various processing techniques that may be adopted for the synthesis of HEAs. Motivation and the objectives of the present work are presented at the end of the chapter.

Chapter 2 describes the experimental and theoretical methods adopted in the present investigation along with the equipment used and the protocols followed for the synthesis and characterization of the alloys studied. The mechanical alloying technique is used to produce nanostructured CrFeCoNiCu and MgAlMnFeCu HEAs, while the other two refractory alloys are prepared using the vacuum arc melting technique. The structural and microstructural features of these nanostructured powders, as-cast, and annealed samples are examined through X-ray diffraction (XRD) and transmission electron microscope (TEM), and scanning electron microscope (SEM) equipped with energy dispersive spectroscope. The phase evolution of the synthesized alloys during the time-temperature domain is investigated through differential scanning calorimetry (DSC), in-situ XRD, and ex-situ XRD (of the annealed sample). An eight atom special quasi-random structure (SQS) is generated to mimic a disordered state in binary subsystems of CrFeCoNiCu and TiVZrMoW HEAs by alloy theoretic automated toolkit (ATAT). Then the energy of the geometrically relaxed SQS is calculated using DFT (Quantum Espresso software). The enthalpy values of binary systems are extrapolated using the regular solution model to predict the enthalpy of mixing for the disordered quinary systems. CALPHAD approach (using Thermo-Calc software) is used to calculate equilibrium diagrams representing the number and amount of phases. Single point equilibrium calculations are also done for examining compositional variation in the phases as a function of temperature.

Chapter 3 presents the study of CrFeCoNiCu HEA. The Miedema model, DFT and CALPHAD approaches are used for the prediction of stable phases. This HEA prepared by MA, forms two phases, i.e., BCC phase ($a = 2.87 \pm 0.02$ Å) and a small amount of FCC phase ($a = 3.62 \pm 0.02$ Å) after 65 h of milling. From the scanning electron micrographs, the flaky nature of milled powders and a wide range of particle

sizes (5 to 10 μm) can be seen. The nanostructure of the crystallites evolved in the 65 h milled powder is analysed using XRD and by selected area electron diffraction techniques, as well as through in-situ high-temperature X-ray diffraction (HT-XRD) over a range of temperatures. The as-milled powder showing two phases is thermally stable up to 400 °C, and then the precipitation of the tetragonal (Cr-Co/Fe) based sigma (σ) phase (a = 8.45 ± 0.02 Å, c = 4.54 ± 0.02 Å) occurs. On annealing at 400 °C, precipitation of the σ phase was observed, while on annealing at 800 °C, the BCC phase disappears along with a decrease in the amount of σ phase. Eventually, the FCC1 (a = 3.62 ± 0.02 Å) appears to be the major phase along with a small amount of σ and FCC2 (3.61 ± 0.02 Å) phase.

Chapter 4 deals with the synthesis and characterization of low-density MgAlMnFeCu HEA. The low-density MgAlMnFeCu HEA has been synthesized successfully by mechanical alloying (MA). Phase evolution of MgAlMnFeCu HEA has been studied using X-ray diffraction (XRD), transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS/XEDS). Milling up to 60 h leads to the formation of a mixture of two phases consisting of a BCC phase (a = 2.87 ± 0.02 Å) and γ-brass type phase (a = 8.92 ± 0.03 Å), with ~2 μm powder particle size. The as-milled alloy after spark plasma sintering (SPS) at 900 ˚C exhibits an experimental density of 4.946 ± 0.13 g cc^{-1}, which is 99.80% of the theoretical density. SPS leads to the formation of C15 Laves phase ($MgCu_2$ type; a = 7.034 ± 0.02 Å) and B2 (AlFe type; (a = 2.89 ± 0.02 Å)) intermetallic along with the γ-brass type phase. The SPSed sample has exceptional hardness value (~5.06 GPa), high compressive strength (~1612 MPa) and appreciable failure strain (~6.4%) coupled with relatively low density. Various thermodynamic parameters have been considered for understanding the phase evolution and their stability during MA.

Chapter 5 presents the investigation of phase stability of two TiVZr based, i.e., refractory HEAs TiVZrMoW and TiVZrYHf. The first section (5.1) and the second section (5.2) deal with the results and discussion of TiVZrMoW and TiVZrYHf refractory HEAs, respectively. The prediction of phases that may form on the synthesis of TiVZrMoW is attempted by following (i) Semi-empirical Miedema model, (ii) an 8 atom SQS generated using ATAT software, and the enthalpy of mixing value for the structure (FCC, BCC and HCP) calculated using DFT and (iii) CALPHAD approach. The as-cast alloy shows the presence of major BCC1 (a = 3.17 ± 0.02 Å) being Mo and W rich and minor BCC2 (a = 3.65 ± 0.02 Å) being Ti, Zr rich along with C15 type ternary $Zr(Mo, W)_2$ Laves phase (a = 7.58 ± 0.02Å). The DSC analysis of the as-cast sample exhibits two endothermic peaks of solid-solid transformation up to 620 °C. However, the alloy does not show any transformation in the temperature range of 620 - 1000 °C. The annealed sample (at 900 °C) reveals that two BCC phases present in the as-cast sample are transformed into the ordered B2 structure. The DFT approach in the study of phase stability of second refractory alloy, i.e., TiVZrYHf is a variation of cluster expansion method with fixed composition and cell size. Enthalpy of mixing of BCC and HCP structures are calculated for the distinct configuration of atoms on the lattice sites using a ten atom cell. The annealed alloy has been examined by XRD, SEM, and SEM-EDS. The annealed sample confirms the presence of two disordered HCP1 (a = 3.18 ± 0.02 Å, c/a = 1.58) and HCP2 (a = 3.67 ± 0.02 Å, c/a = 1.55), along with BCC (a = 3.16 ± 0.02 Å) and the ordered $(Hf, Zr)V_2$ (C15 type Laves phase, a = 7.41 ± 0.02 Å) phase which is in accordance to the theoretically predicted phases. The SEM-EDS mapping of the annealed sample establishes that the major HCP1 phase contains Hf and Zr predominantly along with some Ti.

Chapter 6 describes a summary of the work indicating major findings from the present work along with the suggestions for future work.

References section lists all the references cited in Chapters 1-6 of the thesis.