

PREFACE

The engineering materials used for various applications generally consist of one or two major elements along with other minor alloying elements for improving the mechanical and functional properties. Over the years, the paradigm shifts in alloy design and development strategies has led to the discovery of various new classes of advanced materials for engineering applications such as composites, quasicrystals, bulk metallic glasses and more recently the multi-component high entropy alloys, among other materials.

The new categories of alloys emerging on the concept of alloys with multiple principal elements are referred to as High Entropy Alloys (HEAs). The early conceptualizations of equimolar alloys date back to late 1700s in a book written in French by Karl Franz Achard. He described the idea of equimolar alloys having five to seven elements. However, in the modern days the first report on multi-component HEAs was published independently by Brian Cantor and J.W. Yeh in the year of 2004. The term ‘High Entropy Alloys’ was first coined by J.W. Yeh and he described HEAs as multi-principal alloys containing five or more elements with equiatomic or near-equiatomic atomic fraction in the range of 5-35 at%. In the recent years, D. B. Miracle & co-workers classified these HEAs into three broad categories, i.e. (i) transition metal based HEAs, (ii) refractory metal based HEAs and (iii) low-density metal based HEAs. The transition metal-based HEAs are made up of mostly transition metals. The elements like Ti, V, Cr, Nb, Mo, Hf, Ta, and W are used as major elements to develop refractory HEAs. For developing low density high entropy alloys (LDHEAs) normally lighter elements like Li, Be, Mg, Al, Si, Sc etc. are selected as the major components.

The present work is focused on the phase evolution, microstructural features, thermal stability and mechanical properties of three LDHEAs such as MgAlSiCrFe, MgAlSiCrFeNi and MgAlSiCrFeCuZn, which were processed by mechanical alloying (MA) and spark plasma sintering (SPS) techniques. The present thesis is organized into of six chapters.

Chapter 1: The first chapter gives a brief introduction of the HEAs and basic principles of their stability. This chapter discusses the phase prediction rules for the design and development of HEAs and the core effects. Additionally, this chapter provides the literature survey of the processing methods for HEAs. Various kinds of possible phases that can form in HEAs and its influence on the properties of these HEAs are elaborated. A brief discussion about the low-density HEAs (LDHEA) is also included. The motivation and objectives of the present studies has been highlighted at the end of this chapter.

Chapter 2: The second chapter of this thesis deals with the materials and experimental techniques that were employed in the preparation of the LDHEAs. The synthesis of LDHEAs by mechanical alloying (MA) and its consolidation using spark plasma sintering (SPS) with details on the parameters and operational protocol have been described. Various characterization techniques such as X-ray diffraction (XRD), transmission electron microscopy (TEM) and scanning electron microscopy (SEM) adopted for characterizing microstructure and structures of the phases are mentioned. The nominal chemical composition of the LDHEA powder and of consolidated samples were investigated using SEM equipped with EDS (energy dispersive x-rays spectroscopy) detector. The chemical composition and elemental distribution of the nanostructured powders were further analysed by STEM-EDS techniques. The thermal stability of the milled powders were evaluated through differential scanning calorimetry (DSC) and ex-situ XRD of the annealed milled powders. The experimental determination of density and hardness of the sintered samples (using conventional and instrumented indentation techniques) were described briefly.

Chapter 3: The third chapter of this thesis examines an equiatomic MgAlSiCrFe HEA prepared by using mechanical alloying. This chapter discusses the alloying behavior, phase evolution, phase composition, and thermal stability of as-milled nanostructured HEA powders. The milling of elemental powders of MgAlSiCrFe for 60 h led to the formation of HEA having

BCC phase with a lattice parameter of 0.2887 ± 0.005 nm (close to that of the α -Fe) along with a minor fraction of undissolved Si. The nanostructured HEA powders having crystallite size of ~ 19 nm was observed to form after milling. The STEM–EDS mapping of these milled powders confirmed uniform elemental distribution in the sample milled for 60 h. The DSC thermogram of 60 h milled HEA powder demonstrated its thermal stability up to 400 °C. The exothermic heating events detected in the DSC thermogram corresponded to the phase transformation of MgAlSiCrFe LDHEA powder. Attempts have been made to corroborate these observation with the results obtained in ex-situ XRD analysis of the powders annealed at various temperatures up to 700 °C. The systematic investigation established the presence of parent BCC phase along with other minor phase's i.e. B2 type Al–Fe phase, FCC phases (Al–Mg solid solution), Cr_5Si_3 , Mg_2Si , and $\text{Al}_{13}\text{Fe}_4$. Additionally, this chapter correlates the experimental results with the thermodynamic parameters in order to understand the phase evolution and stability. This chapter also shows the phase evolution, chemical composition, and microstructure of the SPSed sample consolidated at 800 °C (1073 K) through XRD and SEM techniques. The SPSed samples revealed the formation of B2-type AlFe phase ($a=0.2889$ nm) along with the parent disordered BCC phase and a minor fraction of $\text{Al}_{13}\text{Fe}_4$, β - Al_3Mg_2 , and Cr_5Si_3 phases. The instrumented microindentation techniques was used to examine the mechanical properties of these LDHEAs. The hardness, Young's modulus and yield strength were found to be approximately 7.42 ± 0.18 GPa, 212 ± 2 GPa and 2.47 GPa with an appreciable relative density of 99.98% for the SPSed samples. This chapter also describes the phase evolution using Thermo-Calc software, the thermodynamic parameters and property diagrams which were generated through the CALPHAD approach.

Chapter 4: The fourth chapter of this thesis deals with the equiatomic MgAlSiCrFeNi LDHEA prepared by mechanical alloying followed by spark plasma sintering (SPS). In this chapter, the phase evolution, chemical composition, and thermal stability of the alloy were

analyzed. The formation of a BCC phase with lattice parameter of 0.2876 ± 0.03 nm and along with undissolved Si (~ 3 at%) was observed after 60 h of milling. The DSC experiment up to 1200 °C (1473 K) showed five exothermic heating events corresponding to the various phase transformations, which were further correlated with the results obtained from the XRD experiments. This chapter reports various phase transformation events due to annealing at different temperature upto 800 °C (1073 K) resulting in the formation of a major B2 type phase ($a=0.289$ nm) and BCC phase along with small amounts of FCC Al-Mg solid solution phase (FCC 1 ($a=0.4082$ nm) and FCC 2 ($a=0.4215$ nm)), and intermetallic phases such as monoclinic $\text{Al}_{13}\text{Fe}_4$ ($a=1.549$ nm, $b=0.808$ nm, $c=1.248$ nm, $\alpha=\beta=90^\circ$), Mg_2Si ($a=0.6351$ nm), Cr_5Si_3 ($a=b=0.9165$ nm, $c=0.4638$ nm). The SPSed sample also exhibited BCC and B2-type phases coexisting with the minor amount of other phases observed for 800 °C (1073 K) annealed sample. It has been further observed that the co-existence of minor phases along with the parent BCC phase in SPSed alloy (having a relative density of $\sim 99.40\%$) led to high hardness and modulus of elasticity of $\sim 9.98 \pm 0.3$ GPa and 229 ± 0.3 GPa respectively. The present chapter also focuses on calculating thermodynamic parameters in order to correlate the experimental findings of phase evolution and stability of the annealed powder as well as SPSed samples.

Chapter 5: The fifth Chapter of this thesis deals with equiatomic septenary MgAlSiCrFeCuZn LDHEA synthesized by mechanical alloying for 60 h followed by spark plasma sintering. The phase evolution, powder morphology, chemical composition and thermal stability of the 60 h milled HEA powder was ascertained. The mechanical alloying led to the formation of a major BCC phase (lattice parameter of 0.2895 nm) with the minor fraction of retained Si. The thermal stability of the milled powders were discerned through the DSC thermogram upto 1200 °C (1473 K) and the various exothermic heating events were corroborated with the phases observed in the ex-situ XRD of annealed powders. The MgAlSiCrFeCuZn HEA was consolidated at 800 °C using spark plasma sintering. The hardness and yield strength of

conventionally sintered and SPSed samples were determined using instrumented indentation techniques. The hardness and modulus was found to be ~8.38 GPa and 211 GPa. The excellent indentation hardness is understood due to the appreciable density achieved in the SPSed samples. The present chapter also focuses on calculating thermodynamic parameters, in order to correlate with the experimental findings of phase evolution and stability of the annealed powder and SPSed samples.

Chapter 6: The sixth chapter provides a summary of the work, highlighting the important findings and significant results arising from the present thesis. It has also addressed the suggestions for future work in the areas of LDHEAs required for further understanding.

References: This section contains a list of pertinent references more than one hundred and fifty publications that have been refereed while discussing the various aspects of the issues related to the present thesis.