Phase Evolution, Thermal Stability and Mechanical Properties of Some Low-Density High Entropy Alloys

Thesis submitted in partial fulfilment for the

Award of Degree

Doctor of Philosophy

By

NANDINI SINGH

DEPARTMENT OF METALLURGICAL ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY

(BANARAS HINDU UNIVERSITY)

VARANASI – 221005

INDIA

Roll No.: 13141501 **2021**

CHAPTER – 6

Summary
and
Suggestions for Future Work

CHAPTER 6

SUMMARY AND SUGGESTIONS FOR FUTURE WORK

This chapter summarizes the significant findings of the present work. A detailed study on phase evolution, thermal stability, microstructural evolution and mechanical properties were studied in the mechanically alloyed equiatomic compositions of low-density high entropy alloys. Although, the major observations are listed at the end of the respective chapters, the summary of the overall findings and the suggestions for the future work are presented here.

6.1 Summary

Nanocrystalline equiatomic composition of MgAlSiCrFe, MgAlSiCrFeNi, and MgAlSiCrFeCuZn low density high entropy alloys have been successfully synthesized by mechanical alloying (MA) and spark plasma sintering.

- The formation of the major BCC solid solution phase was observed in all three compositions. The mechanically alloyed powder of MgAlSiCrFe (BCC, a=0.2887 ± 0.005 nm) and MgAlSiCrFeNi (BCC, a= 0.2876 ± 0.003 nm) LDHEAs, showed the formation of major BCC phase along with the minor amount of undissolved Si (~3 %). However, the MgAlSiCrFeCuZn alloy exhibited a major solid solution phase of BCC structure (a= 0.2895 ± 0.003 nm) along with the minor fraction of γ-brass type phase (a= 0.878± 0.002 nm) and undissolved Si (~5 %). The dissolution of alloying element and phase evolution during milling was observed to depend on its melting point and bond strength. Generally, higher bond strength element can act as a host lattice of other alloying elements in multicomponent alloys. Moreover in present work it is found that the self-diffusion coefficient of the element also played an important role. The undissolved Si after mechanical alloying is mainly

due to its low self-diffusion coefficient and non-metallic character. However, this aspect of alloying behavior of Si requires further investigations.

- Mixing enthalpy of the MgAlSiCrFe alloy (ΔH_{mix} ~ -15.84 kJ/mol) and atomic size mismatch factor (12 %) were found to lie outside the solid solution formation range ($-15 \leq \Delta H_{mix} \leq 5$ kJmol^{-1}K^{-1}, $\delta \leq 6.6\%$). Similarly, the mixing enthalpy of the MgAlSiCrFeNi alloy (ΔH_{mix} ~ -19.84 kJ/mol) and atomic size mismatch factor (11 %) was also found to be outside the solid solution formation range. These values further support the possibility of evolution of multiphase structure. In fact, the samples in the annealed and SPSed state showed multiphase structures not following the criteria for the formation of a single solid solution phase.

  The CALPHAD predicted five ordered phases i.e., Al and Fe rich B2 phase and Mg_2Si phase in major proportion along with the Cr_5Si_3, Cr_3Si, and Al_2Fe phases in minor amounts. The experimental results confirm the similar phases along with the two FCC phases. The formation of the minor intermetallic phases at higher temperature is attributed to the sluggish diffusion effect. The SPSed MgAlSiCrFe LDHEA contained a major B2 and BCC phases along with a minor amount of $Al_{13}Fe_4$, β-Al_3Mg_2 intermetallic and Cr_5Si_3 silicide phases.

- The SPSed MgAlSiCrFe HEA had shown a low-density of ~4.38 g.cm^{-3} with a relative density of ~99.98%. The formation of the B2-type AlFe phase and the BCC phase and minor amounts of intermetallics and silicide may be responsible for the high hardness ~7.11±0.31 GPa of these SPSed MgAlSiCrFe LDHEA without any signature of indentation cracks.

  The SPSed MgAlSiCrFeNi LDHEA also exhibited a similar phase as observed for the annealed sample at 800 °C (1073 K) with the density of 5.06 g.cm^{-}

^{3}. The high value of hardness and modulus of elasticity of ~9.98 and 229 GPa were observed due to co-existence of B2, $Al_{13}Fe_4$ phase, silicides along with parent BCC phase. The SPSed MgAlSiCrFeCuZn LDHEA exhibited a significant BCC phase and B2 along with a minor amount of other phases i.e., $Al_{13}Fe_4$ and γ-brass phases. The alloy showed very high value of hardness, modulus of elasticity and density of ~8.38, 211 GPa and 5.37 $g.cm^{-3}$ respectively due to the co-existence of B2-type, $Al_{13}Fe_4$ phase, along with parent BCC phase in the SPSed LDHEA. It has been observed in all the studied alloys that the formation of intermetallics have led to the higher values of hardness.

Among these three alloys, MgAlSiCrFeNi seems to exhibit highest hardness (9.98 GPa) and Young's modulus (229 GPa). Hence, it will be worth pursuing this particular alloy for further investigation.

6.2 Suggestions for Future Work

The following suggestions are made for future investigations based on the present results and analysis with regards to the phase evolution, thermal stability and microstructural study:

- The mechanical alloying of MgAlSiCrFe and MgAlSiCrFeNi LDHEAs can be prepared with a ball to powder ratio of 20:1 or higher for observing the dissolution of minor fraction of retained Si in the BCC phase or formation of any metastable or glassy phases.
- The interface structure and stability need to be investigated in the systematically through in-situ TEM and nano-indentation studies.
- Theoretical modelling of mechanical properties of SPSed LDHEAs for establishing its correlation with experimental findings should be carried out.

- The phase evolution and phase stability data should be co-related with the results to be obtained from ThermoCalc and DFT calculations.
- The wear and corrosion behavior of SPSed LDHEAs can be studied for understanding its tribological properties and resistance to corrosion respectively.