CHAPTER 7

SUMMARY AND SUGGESTIONS FOR FUTURE WORK

This chapter summarizes the major findings arising out of the present work. A detailed study on phase evolution, thermal stability and microstructural evolution of equiatomic compositions of mechanically alloyed HEA as well as non-equiatomic composition of induction melted high-entropy alloy (HEA) were carried out. Although the observation made on different aspects are listed at the end of the respective chapters, overall major findings are summarized as follows.

7.1 Summary

Three alloy systems of AlCoCrFeNi, AlCoCrFeNiMn and AlCoCrFeNiTi HEAs were synthesized successfully by mechanical alloying (MA). Nanocrystalline nature of all these alloys were confirmed through transmission electron microscopy. It means that the mechanical alloying is an effective route to develop nanostructure HEAs. In AlCoCrFeNi HEA formation of a single-phase BCC structure (a= 2.88± 0.02 Å) was observed after 30 h of milling. During the systematic study of elemental dissolution and phase evolution in AlCoCrFeNi HEA, it has been observed that the elements other than cubic structure of Fe and Cr goes to the solid solution first followed by lower melting point elements. However this is an empirical observation, dissolution of elements might also depend on the other factors as well. Addition of Mn in equiatomic proportion of AlCoCrFeNi HEA showed the similar observations. AlCoCrFeNiMn is found to give rise to a BCC structure (a= 2.89 ± 0.02 Å). The mechanism of solid solution formation was understood by dividing the hexanary AlCoCrFeNiMn HEA into two ternary alloy systems of AlCoCr and

FeMnNi. These two ternary alloy systems were milled separately for a definite period of 20 h and then mixed together. This mixed powder was milled for another 20 h led to the formation of a single phase BCC structure. It was concluded form this study, that although MA is non-equilibrium process no change in phase structure was observed by following the different milling schedules for this particular alloy. In another work, addition of Ti in equiatomic proportion of AlCoCrFeNiTi HEA was studied. Similar to the previous two alloy systems formation of a single phase BCC structure (a = 2.85±0.01 Å) was primarily observed after 40 h of milling. So from all these studied alloys, it is concluded that the phase selection of HEAs could be driven by maximum number of constituent elements of higher melting point. Addition of elements further increases the entropy of the alloys and helps in formation of simple structures.

Contamination of milling powder for longer milling duration is also inevitable during wet milling. The AlCoCrFeNiTi HEA was observed to contaminate with the tungsten carbide (WC). It is believed that the carbide phase formed due to reaction of toluene (process control agent) with WC vials and balls used for the milling. However, contamination of powder will not affect the phase formation but it may affect the other properties of the alloy. The problem of the contamination of milled powder could be overcome by the proper selection of milling medium and atmosphere. Thermodynamic calculations i.e. mixing entropy (ΔS_{mix}), mixing enthalpy (ΔH_{mix}) , atomic size difference (δ) and omega (Ω) parameters of phase prediction are favorable for the solid solution formations for all these alloys.

Thermal stability of the mechanically alloyed HEAs was investigated through differential scanning calorimetry (DSC), in-situ XRD and suitable heat-treatments. In all these alloys, diffusion assisted phase transformation was observed. The AlCoCrFeNi HEA is not stable above 350 ºC (623K) and it precipitates to $L1_2$, B2 and Cr-Co based σ phases with increase in temperature. Compared to AlCoCrFeNi HEA, AlCoCrFeNiMn HEA is stable upto 500 ºC (773K) and then it undergoes to two diffusional transformations of $L1_2$ type and Mn_3Co_7 intermetallic phases. On the other hand, AlCoCrFeNiTi HEA is found to be stable upto 600 ºC (873K). Formation of all the above mentioned intermetallics is somehow closely related to the binary mixing enthalpy. A new approach of microwave sintering was utilized to consolidate the MAed powder of HEAs. Significant coarsening of grains was observed with presence of porosity in all alloys. This helps in understanding that the fast sintering technique i.e. spark plasma sintering (SPS) is required for retaining the nanocrystalline nature of the HEAs.

A non-equiatomic $Fe_{40}Cr_{25}Ni_{15}Al_{15}Co_5$ HEA was successfully designed and prepared to have precipitation hardened microstructure based on the AlCoCrFeNi HEA. This also helped in understanding the effect of configurational entropy on phase formation by slightly deviating from the equiatomic compositional definition of HEA. The alloy showed the duplex type of structure consisting of Fe-Cr rich disordered BCC matrix with the fine precipitates of Ni-Al rich ordered B2 type phases. These phases were identified through TEM and XRD analysis. The alloy showed the better phase and microstructural stability over 900ºC (1173K). The precipitation hardened alloy had the better combination of high compression yield strength and hardness, i.e. ~1012 MPa & 428±5 HV respectively. This property of the HEA is superior to many conventional alloys and HEAs. This helps in understanding that through reasonable composition design an alloy may be designed and developed which will have wide range of applications in the field of structural and high temperature components.

7.2 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:

1. High entropy effect on sluggish diffusion needs to be understood in more details by specific diffusion controlled experiments.
2. Vast compositional space of HEAs necessitates the development of computation tools for phase structure predictions, i.e., CALPHAD and first principle calculation.
3. Careful optimization of milled powder and sintering condition will help to control the microstructure and leads to enhanced properties.
4. The choice of the alloy composition needs to be made carefully keeping in mind that the most of the alloys showed the change in phase constituents after heat-treatment.
5. Different milling media and process control agent should be tried to avoid the contamination of the milled powder.