Synthesis and Phase Stability Study of Some Equiatomic High Entropy Alloys

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by

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Chapter 6

SUMMARY AND SUGGESTIONS FOR FUTURE WORK

This chapter deals with the summary of major findings from the present work. A detailed study of phase stability based on theoretical models was carried out for all the chosen high entropy alloys. A thorough investigation on the sequential phase evolution, microstructural evolution, and thermal stability of the as-milled and as-cast samples were carried out.

6.1 Summary

Two alloy systems, namely, CrFeCoNiCu and MgAlMnFeCu low-density high entropy alloy were synthesized successfully by mechanical alloying. Nanostructured powders were formed after mechanical alloying. The remaining two refractory alloys were synthesized by vacuum arc melting and solidification.

6.1.1 CrFeCoNiCu high entropy alloys

The semi-empirical parameters (Miedema method) were calculated for the prediction of phases, such as enthalpy of mixing (3.2 $kJmol^{-1}$). The weighted average of the atomic size mismatch (1.03%) was calculated. These values are suggested to be within the solid solution-forming range (-10 kJ/mol < ΔH_{mix}< 5 kJ/mol) and $\delta \leq 6.6$). Enthalpy of mixing of binary subsystems of the CrFeCoNiCu HEA was calculated using DFT for FCC, BCC, and HCP phases. An eight atom SQS of binary subsystems was generated using alloy theoretic automated tool (ATAT). The binary enthalpy values were obtained and extrapolated using a regular solution model to predict enthalpy of mixing for FCC phase to be around 11.175 $kJ.mol^{-1}$, which is lower than that of BCC and HCP structures at room temperature leading to the possible formation of multiple structures. As per the prediction of the CALPHAD approach, two ordered FCC and two ordered BCC

phases were evaluated to be stable below 450 °C, whereas two ordered FCC phases were stable above ~ 900 °C. It is to be noted that the nanostructured CrFeCoNiCu equiatomic alloy prepared by MA exhibited two phases, one with BCC crystal structure (a = 2.87 ± 0.02 Å) and the other one with a small amount FCC phase (a= 3.62 ± 0.02 Å). The compositional analysis of the as-milled powder using STEM-EDS has showed seperately Fe-rich and Cu-rich regions. The thermal stability was examined using in-situ XRD showing the prepared powder was stable up to ~623 K, beyond which σ phase precipitated. A simple FCC phase (a = 0.362 ± 0.02 Å) is obtained along with the FCC2 phase (a = 3.61 ± 0.02 Å) after annealing 65 h milled powder at 800 °C for 2 h. The VEC value of 8.8 determined from the present alloy suggest possibility of formation of σ phase. However σ phase formation was observed on annealing above 400 °C (673 K).

6.1.2 Low-density MgAlMnFeCu high entropy alloy

The parametric approach was used to predict phase formation in the MgAlMnFeCu low-density alloy, namely enthalpy of mixing (2.82 $kJ.mol^{-1}$) and the ratio of $-T\Delta S/\Delta H$ (6.2), which lie in the range of solid solution forming HEAs, as reported in literature. The VEC value of 6.2 for this alloy indicates the formation of a single BCC phase. However, atomic size mismatch, δ (9.2%) being dominant factor can destabilize the solid solution and indicates the possible formation of multiple phases. As per the prediction of the CALPHAD approach, BCC_B2 was the major phase along with cubic_A13 type and $CuMg_2$ and $MgCu_2$ type Laves phase at a lower temperature. Mechanically alloyed MgAlMnFeCu powders after 60 h of milling has been found to form a mixture of two solid solution phases, namely, BCC phase having lattice parameter close to that of α-Fe structure ($a = 2.87 \pm 0.02$ Å) and γ-brass type phase having lattice parameter close to that of α-Mn ($a = 8.92 \pm 0.03$ Å) type structure which can also be considered as solid solution of α-Mn. The thermal stability of the synthesized alloy was

studied using differential scanning calorimetry(DSC), indicating that the present alloy was stable up to ~350 °C. Annealing at 400 °C resulted in the precipitation of B2 (AlFe type) and $MgCu_2$ type ((a = 7.02 ± 0.02 Å) cubic Laves phase) ordered phases from the BCC phase (obtained in as-milled powder). While on annealing the as-milled powder at 600 °C, all the phases were observed to be present at 400 °C except the changes in the relative amount. The as-milled powder was compacted using spark plasma sintering (SPS) at 900 °C for 15 min under 50 MPa pressure. The SPsed sample showed a significant reduction in the intensity of the $MgCu_2$ and the increase in the phase fraction of the γ-brass type phase. Consolidated and spark plasma sintered pellet of this HEA showed high hardness (5.06 GPa) and high compressive yield strength (1612 MPa) at relatively low density (4.94 g cc^{-1}), suggesting the potential technological applications.

6.1.3 Refractory high entropy alloys

Two refractory high entropy alloys, namely TiVZrMoW and TiVZrYHf, were synthesized using vacuum arc melting. Phase stability study of both the alloys was carried out by theoretical and experimental methods. The TiVZrMoW refractory HEA was analyzed by parametric approaches to predict the stability of the phases that may form. The enthalpy of mixing (-4.98 $kJ.mol^{-1}$) for the refractory alloy favours the formation of a single phase solid solution, whereas the atomic size mismatch factor (7.17 %) is higher then the critical value (<6.6%), might be held responsible for de-stabilizing the lattice to form a multiphase structure. Enthalpy of mixing of the alloy for BCC phase was calculated using extrapolation of the enthalpy value of the disordered 8 atom SQS of binary subsystems and found to be 4.25 $kJ.mol^{-1}$, which is lower than that of the FCC and HCP structures. Thus the BCC can be assumed to be more stable than other structures, but having a possibility of miscibility gap at a lower temperature leading to multiple structures. As per the prediction of the CALPHAD approach, three ordered BCC phases

along with two Laves phases were stable at ~500 °C, whereas only two BCC phases are stable above ~ 600 °C. However, the three BCC phases, as predicted, were not found in this experimental observation, which requires further investigation. The as-cast alloy showed the presence of two BCC phases, i.e., major BCC1 (a = 3.17 ± 0.02 Å) being Mo and W rich, and minor BCC2 (a = 3.65 ± 0.02 Å) being Ti and Zr rich along with C15 type ternary $Zr(Mo, W)_2$ Laves phase (a = 7.58 ± 0.02 Å). The DSC analysis of the as-cast sample showed two endothermic peaks of solid-solid transformation up to 620 °C. However, the alloy did not show any transformation in the temperature range of 620 – 1000 °C. The sample annealed at 900 °C showed that two BCC phases present in the as-cast sample were transformed into the ordered B2 structures. There was also an increase in the amount of Laves phases, indicating the equilibrium distribution of the elements.

The TiVZrYHf refractory HEA was also first examined by the parametric approach. The parametric approach indicated the phase separation tendency due to positive enthalpy of mixing (ΔH_{mix} = 7kJ.mol^{-1}) and higher range of atomic size mismatch factor (10.37 %) supporting multiphase structure. The enthalpy of mixing calculated using DFT (ΔH_{mix}^{DFT} =23.845 kJ.mol^{-1}) with the minimum value for the HCP phase also indicated the miscibility gap in the chosen alloy resulting in multiphase microstructure at room temperature. The variation of amount of phase and its compositional variation was studied using Thermo-Calc. As per the prediction of the CALPHAD approach, three disordered HCP and one Laves phase (ZrV_2) were observed to be stable at room temperature, whereas the BCC_B2 phase was found to be stable at above 1000 °C. The as-cast sample was annealed in order to evolve the equilibrium phases. The annealed sample shows 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 a BCC (a= 3.16 ± 0.02 Å) and the ordered $(Hf, Zr)V_2$, i.e., (C15 type Laves phase, (a = 7.41 ± 0.02 Å). This observation

was also supported by SEM-EDS results. The SEM-EDS mapping of the annealed sample showed that the primary major HCP1 phase contains predominantly Hf and Zr along with some amount of Ti.

6.2 Suggestions for future work

The present work deals with the phase evolution and thermal stability of the four high entropy alloys by theoretical and experimental methods. In view of the analysis performed and investigation carried out, the following suggestions can be proposed for future investigations:

1. High entropy effect on sluggish diffusion needs to be understood in more details by specific diffusion-controlled experiments and commercial software (such as DICTRA).
2. The mechanical and electronic properties of alloys can be estimated by using DFT and later to be verified by experiments to checks their applicability in the industry.
3. Careful optimization of milled powder and sintering condition should be studied in order to control the microstructure that leads to enhanced properties.
4. Alloy selection, to obtain a single solid solution should be made, which have the maximum number of binary subsystems with isomorphous phase diagrams.
5. Phase field modeling should be applied, as it may help in controlling the microstructure to obtain desirable properties in the alloys.
6. The mechanical properties of all the powder materials after suitable consolidation by advanced sintering techniques, e.g., SPS should be carried out by indentation, tensile and compression testings.
7. The low density high entropy alloy should be developed further for enhanced tensile properties required for technological applications.

8. Attempts can be made to develop single phase HCP HEAs close to Ti-based system, but having better properties and performance compared to commercial Ti-based alloys.
9. The in-situ TEM studies at higher temperature can be persued to understand the nature of phase transformation and the exact elemental distribution. This will help to realise the phase separation of the metastable HEAs. The interface studies should be worth pursuing.
10. Atom Probe Tomography (APT) should be carried out to rationalise the various phase formation and their chemical distribution. The size, shape, distribution as well as volume fraction should be quantitatively estimated and correlated with the stability and mechanical properties of the HEAs.