Investigation of the Phase Stabilities in AlNiCoCrFe High Entropy Alloys

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Keywords: high-entropy, CALPHAD

Abstract

High-entropy alloys (HEAs) are a developing class of materials that show great potential for a variety of commercial structural and coating applications, particularly where heat and corrosion resistance are desired. In these types of applications, the relative phase stabilities play a crucial role, since they influence the material design process and expected component lifetimes. However, a satisfactory understanding of the phase stabilities in HEAs and the ability to thermodynamically predict their behaviors is limited. This study methodically couples analytical characterization techniques with predictions based on CALPHAD models to investigate the phase equilibria and phase stabilities of a series of AlNiCoCrFe based HEAs. Heat treatments were conducted at 700°C for 1000 hours and 1050°C for 520 hours, followed by water quenching, to ensure adequate time for metastable equilibrium to be achieved. The accuracy and merit of the thermodynamic simulations in predicting the stable phases and their respective chemistries is discussed relative to the experimental observations.

1. Introduction

Traditional alloy development strategies typically involve the study of a major constituent element with minor alloying additions to form suitable microstructures with specific properties (i.e., Ti alloys, Superalloys, etc) [1,2]. With regard to phase diagrams, these types of alloys

generally reside near the corners, leaving the central phase regions relatively unexplored [3]. However, an alternative alloy development approach examining equiatomic and near equiatomic composition space has emerged, producing a novel class of materials termed high-entropy alloys (HEAs) [2-6]. Due to their complex chemistries, HEAs inherently exhibit high ideal configurational entropies of mixing that have been proposed to aid in the retention of high-symmetry, disordered FCC and/or BCC solid solution phases [3,4,7,8]. However, in many cases, these solid solution phases are often accompanied by the formation of ordered intermetallic phases (i.e. B2 and sigma) [9-13]. HEAs have been reported to exhibit a variety of unique properties including enhanced mechanical strength, at both ambient and elevated temperatures [9-11,14-16] and resistance in oxidizing/corrosive environments [9,17-30]. These attributes, amongst others, make them ideal candidates as materials for use in high temperature environments.

The direct implementation of HEAs is hindered by the lack of a fundamental understanding of their high temperature phase stabilities and effective models to predict their behaviors. Thus, additional high-quality, analytical characterization of heat treated HEAs, coupled with computational modeling is vital for future commercial development. There have been various attempts to validate existing models/databases by correlating experimental results with those derived computationally. These modeling attempts include comparisons with empirically determined rules, termed the HEA phase formation rules [8,12-14,31-40], ab-initio based methods [41-47], and thermodynamic calculations based on the CALPHAD (CALculation of PHase Diagrams) method [36,48-53]. The CALPHAD method has evolved over the past 30 years and has become widely utilized in the scientific community due to its simplicity, computational efficiency, and reasonable agreement with experimental data [36,50,51]. This method correlates a predicted equilibrium state to an overall minimum Gibbs free energy in the system. Calculations

conducted in four to six element space are evaluated using extrapolations of experimentally backed binary, ternary, and in some cases quaternary systems [51]. Thus, the accuracy of the resulting predictions is often highly dependent upon the thermodynamic database used and needs to be experimentally validated.

The aim of this work is to fundamentally investigate the high temperature phases in a series of heat treated AlNiCoCrFe based HEAs and evaluate the accuracy of CALPHAD based predictions using ThermoCalcTM [54]. This particular system is ideal for this fundamental phase study since it is one of the most thoroughly investigated HEA systems [11,15,16,29,38,50,55-61]. However, there is currently a lack of published literature examining the phase equilibria at elevated temperatures and little known about the relative phase stabilities over long periods of time. The equilibrium predictions presented in this work were determined using extrapolations from experimentally assessed binary and ternary systems found in the TCNI8 (ThermoCalcTM, Ni-based superalloys) database [62]. Collectively, these results will provide a systematic assessment of the high temperature phase stabilities of AlNiCoCrFe HEAs. Additionally, this work will help to elucidate the accuracy and usefulness of CALPHAD based models for predicting the phase equilibria of compositionally complex alloys.

2. Experimental Procedures

Four bulk alloys with nominal compositions (at.%) of Al₁₀Ni_{22.5}Cr_{22.5}Co_{22.5}Fe_{22.5}, Al₁₅Ni_{21.25}Cr_{21.25}Co_{21.25}Fe_{21.25}, Al₂₀Ni₂₀Cr₂₀Co₂₀Fe₂₀, and Al₃₀Ni_{17.5}Cr_{17.5}Co_{17.5}Fe_{17.5} (designated: Al₁₀, Al₁₅, Al₂₀, and Al₃₀) were arc-melted into buttons from high purity elemental constituents on a water-cooled copper hearth. This process was done under an ultra-high purity (UHP) argon atmosphere. Each button was flipped and re-melted a total of five times to promote uniformity.

The experimental bulk compositions, as measured via energy-dispersive x-ray spectroscopy (EDS) in a transmission electron microscope, are shown in Table 1.

Prior to annealing, specimens were sectioned from the as-cast buttons and encapsulated in quartz tubes that were partially backfilled with UHP argon. Two separate annealing treatments were performed, one at 700°C for 1000 hours and another at 1050°C for 520 hours, followed by water quenching. The quartz tubes were broken during quenching to achieve faster cooling rates in the actual specimens. A full microstructural analysis was conducted on each annealed specimen using a combination of x-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and EDS. Backscattered electron (BSE) images were captured on a JEOL 7000F SEM. XRD data was collected on a Philips X'pert MPD XRD with Cu-K α radiation at 45kV and 40mA. Scans were conducted at a rate of 0.1 degrees per minute. All TEM specimens were prepared using a variation of the focused-ion-beam (FIB) in-situ lift-out technique in an FEI Quanta 200 3D Dual Beam FIB-SEM [63]. High angle annular dark field images (HAADF) and selected area diffraction patterns (SADPs) were captured on a 200-KeV FEI Tecnai G² F-20 Supertwin scanning-transmission electron microscope (S)TEM. TEM-EDS data was evaluated using FEI ES Vision software with an applied thickness correction [64]. In this paper, the high temperature phase equilibria were modeled by means of the CALPHAD method using ThermoCalcTM and the TCNI8 database [54,62]. For comparative purposes, the phase equilibria were also modeled using the TCFE8 and TCHEA1 databases [65,66]. As has been noted by Zhang and Kattner [67], the design of alloys consisting of multiple principal elements requires thermodynamic database that include accurate and full thermodynamic descriptions of all of the constituent systems. The TCHEA1 database, which is actually a subset of the TCNI8 database, yielded results that were identical to those obtained using the TCNI8 database. The TCFE8

database, which was designed for alloys containing a minimum of 50 wt% Fe, was found to yield inaccurate results. In this paper, all calculations were based on the experimentally determined alloy compositions.

3. Results and Discussion

3.1. Microstructures and Modeling of $Al_{10}Ni_{22.5}Cr_{22.5}Co_{22.5}Fe_{22.5}$

Figs. 1(a) and (b) show representative backscattered electron (BSE) images of the annealed Al_{10} HEA. After annealing at 700°C for 1000 hours, the microstructure consisted of low atomic number (Z) contrast regions, labeled ID, that were dispersed in a high-Z contrast matrix, labeled D (Fig. 1(a)). Based upon our previous analysis of as-cast alloys [24,68,69], these ID regions are believed to be remnants of the original solidification microstructure. The high-Z matrix phase was found to contain a high distribution of low-Z precipitates with plate-like morphologies (see the inset image in Fig. 1(a)). Similarly, the ID regions consisted of a continuous low-Z matrix with high-Z precipitates of varying sizes and morphologies. Annealing at 1050°C for 520 hours resulted in a coarser microstructure where the low-Z precipitates in region D coarsened into several variants. The ID regions also coarsened but were found to be precipitate free, as is evident from the inset BSE image in Fig. 1(b).

The crystal structures and chemistries of the observed phases were investigated using a combination of XRD and TEM. The XRD spectra for both annealing treatments are shown in Fig. 1(c). At 700°C, the spectrum only contained peaks associated with BCC and/or B2 phases ($a_{BCC} \approx a_{B2} \approx 2.88 \text{ \AA}$). In contrast, the 1050°C spectrum contained peaks associated with BCC and/or B2 ($a_{BCC} \approx a_{B2} \approx 2.88 \text{ \AA}$), and FCC ($a_{FCC} \approx 3.58 \text{ \AA}$) phases. Fig. 2 shows STEM-HAADF images and SADPs from the 700°C and 1050°C annealed Al_{10} HEAs. In addition to the BCC and/or B2 phases derived from XRD experiments, the Al_{10} HEA annealed at 700°C was found to contain

FCC and sigma phases, Fig. 2 (a)-(e). The ID regions consisted of a Ni+Al-rich B2 matrix with high-Z contrast FCC precipitates that were rich in Co and Cr (Fig. 2 (b) and Table 2). In between the ID and D regions, a homogeneous, Cr-rich sigma phase was observed, Fig. 2 (c). The dominant matrix phase exhibited an FCC structure and contained a high density of Ni+Al-rich B2 precipitates, Fig. 2 (e). The Al₁₀ HEA annealed at 1050°C was found to consist of a homogeneous, high-Z, FCC matrix, along with coarse but homogeneous low-Z regions with B2 crystal structures, Fig. 2 (f)-(i). The FCC matrix was rich in Co, Cr, and Fe, while the B2 regions contained high amounts of Ni and Al, as shown in Table 2.

The experimental phase observations derived from SEM, XRD, and TEM analyses were compared with those predicted via CALPHAD based thermodynamic modeling. Fig. 1 (d) shows the calculated phase fractions as a function of temperature for the Al₁₀ HEA with the 700°C and 1050°C isotherms identified with vertical markers. At 1050°C, a combination of ~80 % FCC and ~20 % B2 phases are predicted, which is consistent with the experimental results, Fig. 2 (f)-(i). At 700°C, the model predicts a combination of ~45 % B2, ~35 % FCC, and ~20 % sigma phases. This also correlates well to the experimental findings, Fig. 2 (a)-(e). CALPHAD based models were also used to predict the relative chemistries of the phases predicted at 700°C and 1050°C, as shown in Table 2. With the exception of the B2 phases, the predicted chemistries for each phase were comparable to the TEM-EDS results. To quantify the differences between the predicted chemistries and the experimental results, the average atomic percent difference between each element in a given phase, neglecting reported errors, are also reported in Table 2. On average, the predicted chemistries are at most ~8.3 at. % different and most fall below 2 at. % different than experimental values.

3.2. Microstructures and Modeling of Al₁₅Ni_{21.25}Cr_{21.25}Co_{21.25}Fe_{21.25}

Representative BSE images for the annealed Al₁₅ HEA are shown in Figs. 3(a) and (b). Annealing at 700°C for 1000 hours promoted the formation of a modulating net-like structure, consisting of interpenetrating high-Z and low-Z phases, Fig. 3(a). The microstructure was coarse in some regions, although the phase distribution and morphologies remained similar to the finer regions. Additionally, a nano-scale high-Z phase was detected in the low-Z regions, as labeled with an arrow in the inset high magnification image in Fig. 3(a). Comparable to the Al₁₀ HEA, annealing of the Al₁₅ HEA at 1050°C for 520 hours produced a heavily coarsened microstructure, consisting of a high-Z phase encompassing a low-Z regions, Fig. 3(b). The high-Z phase was homogeneous, while the low-Z regions contained fine-scale, high-Z precipitates in a low-Z matrix (see the inset high magnification BSE image in Fig. 3(b)).

Fig. 3(c) shows XRD spectra from the annealed alloys. At 700°C, the spectrum exhibits peaks associated with FCC ($a_{\text{FCC}} \approx 3.59 \text{ \AA}$), BCC/B2 ($a \approx 2.88 \text{ \AA}$), and sigma phases ($a_{\sigma} \approx 8.8 \text{ \AA}$, $c_{\sigma} \approx 4.54 \text{ \AA}$). Interestingly, at 1050°C, the sigma phase is suppressed and the spectrum only contains peaks correlating to FCC ($a_{\text{FCC}} \approx 3.59 \text{ \AA}$), and BCC/B2 ($a \approx 2.88 \text{ \AA}$) phases. The phases were then examined using TEM, as shown by the STEM-HAADF images and SADPs in Fig. 4. As was shown in the XRD results, the 700°C Al₁₅ HEA consisted of a low-Z, B2 matrix phase, along with FCC and sigma phases, Fig. 4 (a)-(d). Similar to the Al₁₀ HEA, the B2 regions were enriched in Ni and Al, while the FCC regions contained high concentrations of Co, Cr, and Fe, Table 3. As expected, the sigma phase displayed a high concentration of Cr and was nearly depleted of Al. In agreement with the XRD results, the Al₁₅ HEA annealed at 1050°C did not contain the sigma phase and consisted of high-Z, FCC regions enriched in Co, Cr, and Fe, along with low-Z B2 regions enriched in Ni and Al, Fig. 4 (e)-(h). Contrast variations indicative of nano-scale precipitation were observed within the B2 regions. We were unable to quantitatively identify

these precipitates chemically or structurally due to their small size and morphology. However, a comparison of these results to those of Wang et al. [11,56,61] on similar alloys, suggests that these precipitates likely exhibit BCC structures. This is also supported experimentally by the observation of the primary B2 zone axes (i.e. $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$), which reveals a strong epitaxial relationship between the matrix and precipitate, with perfect overlapping in the electron diffraction spots.

Fig. 3 (d) shows the calculated phase fractions as a function of temperature for the Al₁₅ HEA. At 1050°C, the model accurately predicts a combination of FCC and B2 phases. At 700°C, the model predicts the B2 and sigma phases, but does not accurately predict the experimentally observed FCC phase. The predicted phase chemistries are also shown in Table 3, along with those determined by TEM-EDS. On average, the predicted chemistries were fairly consistent and differed at most by ~ 4.7 at. %. However, the model did not accurately predict the stability, and therefore the chemistry of the FCC phase.

3.3. Microstructures and Modeling of Al₂₀Ni₂₀Cr₂₀Co₂₀Fe₂₀

Figs. 5(a) and (b) show representative BSE images of the annealed Al₂₀ HEA. Annealing at 700°C for 1000 hours resulted in a complex distribution of phases, Fig. 5(a). The microstructure exhibited highly transformed, low-Z regions enriched in Ni and Al (labeled Ni+Al rich), along with coarser, high-Z surrounding regions enriched in Co, Cr, and Fe. The high-Z regions displayed a combination of high-Z precipitates in a low-Z matrix. Similarly, the highly transformed regions contained a fine-scale distribution of high-Z cuboidal precipitates in a low-Z matrix, as evident from the inset high magnification BSE image in Fig. 5(a). A plate-like, high-Z phase was observed near the boundaries of the highly transformed region, as indicated by arrows in the inset image in Fig. 5(a). Annealing at 1050°C for 520 hours promoted a coarse distribution of high-Z phases in

a Ni+Al-rich, low-Z matrix, Fig. 5(b). A semi-continuous, high-Z phase was observed along grain boundaries and within individual grains. Some of the high-Z phase within the individual grains contained low-Z precipitates, as indicated by the arrow in the inset BSE image in Fig. 5(b). The Ni+Al-rich matrix was also observed to have a uniform distribution of high-Z, nanoscale precipitates.

At 700°C, the XRD spectrum contained peaks associated with FCC ($a_{\text{FCC}} \approx 3.60 \text{ \AA}$), BCC/B2 ($a \approx 2.89 \text{ \AA}$), and sigma phases ($a_{\sigma} \approx 8.80 \text{ \AA}$, $c_{\sigma} \approx 4.54 \text{ \AA}$), Fig. 5(c). However, at 1050°C the XRD spectrum only exhibited peaks associated with FCC ($a_{\text{FCC}} \approx 3.60 \text{ \AA}$), BCC and/or B2 ($a_{\text{BCC}} \approx a_{\text{B2}} \approx 2.89 \text{ \AA}$) phases. These observations are similar to those of Tang et al. [15] on a HIPed and homogenized, equimolar AlCoCrFeNi HEA. The phases were further investigated using TEM, as shown by the STEM-HAADF images and SADPs in Fig. 6. The 700°C Al₂₀ HEA contained a combination of FCC, B2, BCC, and sigma phases, Fig. 6 (a)-(e). The highly transformed region (labeled B2 + BCC) exhibited a Ni+Al-rich B2 matrix with coherent, Cr-rich BCC precipitates, Table 4. The coarser regions consisted of a B2 matrix with a discontinuous, Co, Cr, and Fe rich FCC phase. As observed via SEM, Fig. 5 (b), plate-like, sigma phase precipitates were found near the boundaries of the highly transformed B2 + BCC regions, Fig. 6 (a) and (e). This sigma phase was extensively rich in Cr and Fe, as shown in Table 4. In contrast, the sigma phase was not observed in the 1050°C Al₂₀ HEA and the microstructure consisted of FCC, B2, and BCC phases, Fig. 6 (f)-(i). The grain boundaries were found to be populated by a continuous, Co, Cr, and Fe rich FCC phase, Fig. 6 (i). The FCC phase was found to be bordered by a Ni+Al-rich B2 matrix, containing nano-scale precipitates. Similar to the Al₁₅ HEA, these precipitates are likely to be BCC since they share a strong epitaxy with the B2 matrix and perfectly overlap in the SADPs. Additionally, medium-Z contrast regions (labeled BCC + B2) were observed and

exhibited BCC crystal structures, Fig. 6 (g). These BCC regions also contained Ni+Al-rich B2 precipitates. Differentiation of the BCC matrix and B2 precipitate structures were determined by observing the $\langle 001 \rangle_{\text{B2}} // \langle 001 \rangle_{\text{BCC}}$ and $\langle 011 \rangle_{\text{B2}} // \langle 011 \rangle_{\text{BCC}}$ SADPs. Diffraction patterns taken near precipitates displayed distinct superlattice reflections consistent with a B2 structure, Fig. 6 (h). Likewise, patterns captured in precipitate free regions contained no superlattice reflections, Fig. 6 (g). Therefore, the matrix phase is inherently BCC while the precipitates exhibit B2 structures.

The calculated phase fractions as a function of temperature for the Al₂₀ HEA is shown in Fig. 5 (d). The model predicts a combination of BCC and B2 phases at 1050°C. This is only semi-consistent with the experimental results, since an additional FCC phase was observed along the grain boundaries. At 700°C, only B2 and sigma phases are predicted by the model. This is vastly different than the experimental observations, where additional FCC and BCC phases were found. However, the calculated chemistries of the phases that the model did predict were found to correlate with experimental TEM-EDS. Quantitatively, the average atomic percent difference between elements in each phase was found to be no more than ~ 5.2 at. %.

3.4. Microstructures and Modeling of Al₃₀Ni_{17.5}Cr_{17.5}Co_{17.5}Fe_{17.5}

Figs. 7(a) and (b) show representative BSE images of the annealed Al₃₀ HEAs. Annealing at 700°C for 1000 hours did not appear to coarsen the microstructure, which consisted of a low-Z matrix with a nano-scale distribution of high-Z precipitates, Fig. 7(a). This high-Z phase was also found to populate along the grain boundaries, as indicated with arrow in the inset image of Fig. 7 (a). Annealing at 1050°C for 520 hours significantly coarsened the microstructure, Fig. 7(b). Similar to the 700°C treatment, the microstructure consisted of a low-Z matrix with coarse high-Z precipitates. The high-Z phase along the grain boundaries appeared to dissolve at the expense of

the growth of surrounding high-Z precipitates. Higher magnification imaging revealed that the low-Z matrix contained fine-scale high-Z precipitates, and the high-Z phase contained low-Z precipitates, as evident from the inset BSE image in Fig. 7(b).

In order to determine the phase structures and chemistries, XRD and TEM techniques were also conducted on the annealed Al₃₀ HEAs. At 700°C, the XRD spectrum displayed peaks associated with BCC ($a_{\text{BCC}} \approx 2.88 \text{ \AA}$) and/or B2 ($a_{\text{B2}} \approx 2.88 \text{ \AA}$) phases, Fig. 7(c). This was the same for 1050°C; however, some indistinguishable peak broadening around $43^\circ 2\theta$ was observed. The annealed alloys were then investigated using TEM, as shown by the STEM-HAADF images and SAPDs in Fig. 8. Similar to the B2 + BCC regions in the Al₂₀ HEA, Fig. 6 (a), the 700°C Al₃₀ HEA consisted entirely of a Ni+Al-rich B2 matrix, with Cr-rich BCC precipitates, Fig. 8 (a)-(d) and Table 5. The structures of the matrix and precipitate were inferred from the same methodology used for the phase determinations in the Al₁₅ HEA. This precipitate / matrix relationship is also consistent with those determined in the work of Wang et al. on similar HEAs [11,56,61]. The 1050°C Al₃₀ HEA contained a mixture of Ni+Al-rich B2 regions with BCC precipitates and Cr-rich, BCC regions exhibiting B2 precipitates, Fig. 8 (e)-(i).

The thermodynamically calculated phase diagram for the Al₃₀ HEA is depicted in Fig. 7 (d). Unlike all of the other simulations, no sigma phase was predicted to be stable for this alloy between 200°C to 1500°C. At both 1050°C and 700°C, the model predicts a combination of B2 and BCC phases, with a slightly higher fraction of B2 phase at the higher temperature. These predictions are in agreement with the experimentally determined phases, Fig. 8. The calculated phase chemistries were also found to correlate with those determined via TEM-EDS, Table 5. The average atomic percent difference for any one element in a given phase was no more than $\sim 8.1 \text{ at. \%}$ and as low as $2.0 \text{ at. \%}$.

3.5. Merit of Thermodynamic Predictions of Compositionally Complex Alloys

To better evaluate the scientific merit of CALPHAD based models for predicting the phase equilibria of AlNiCoCrFe HEAs, isothermal phase fraction diagrams at 700°C and 1050°C were simulated, Fig. 9. Unlike the predictions used in Figs. 1(d), 3(d), 5(d), and 7(d), these calculated phase fractions illustrate the isothermal phase evolution over the expanded composition range of $\text{Al}_x(\text{NiCoCrFe})_{100-x}$ where $x = 5$ to 40 at. %. As previously discussed, a combination of FCC, B2, and/or BCC phases are predicted at 1050°C depending on the alloy composition, Fig. 9 (a). At low Al concentrations, ~ 5 at. %, a single phase, solid solution FCC microstructure is predicted. This is beyond the composition range of the HEAs in this study, but is likely experimentally accurate when considering the results of this study, as well as the work of Wang et al. [11,56,61] on other AlNiCoCrFe HEAs. As the Al concentration is increased beyond ~ 6 – 7 at. %, the solid solution phase is predicted to separate into FCC and B2 phases, with the phase fraction of B2 increasing at the expense of the FCC phase. This trend was observed in the 1050°C annealed Al_{10} and Al_{15} HEAs, Figs. 1(b) and 2(b). The experimental results at 1050°C appear to be very consistent with the modeling predictions up to the ~ 15 at. % level. As the Al concentration is increased further, two major observations can be made. The first is the stabilization of a BCC phase at ~ 16 at. % Al and the full destabilization of the FCC phase at ~ 20 at. % Al. At exactly 20 at. % Al, a combination of BCC and B2 phases is predicted. However, as reported above, an additional FCC phase was found along the grain boundaries of the 1050°C annealed Al_{20} HEA, Figs. 5(b) and 6(f). This discrepancy is not too surprising since the Al_{20} HEA is the most compositionally complex and lies in the center of the AlNiCoCrFe phase diagram. As the Al concentration is increased further, up to 40 at. %, a nearly constant ratio of B2 and BCC phases is predicted, which is fully consistent with the experimental results for the Al_{30} HEA at 1050°C.

At 700°C, a similar distribution of FCC, B2, and/or BCC phases are predicted over the set composition range. However, an additional topologically close-packed (TCP) sigma phase is predicted over an extended range of alloys (5 to ~ 28.5 at. % Al), Fig. 9 (b). This phase has been reported in a variety of relevant HEAs [70-7570-75] and is generally undesired due to its brittleness. At low Al concentrations (5 to ~ 14.5 at. %) a combination of FCC, B2, and sigma phases are predicted. Similar to the predicted behaviors at 1050°C, increased Al content decreases the predicted phase fraction of FCC phase, while both the B2 and sigma phases tend to increase. The experimental observations of the 700°C Al₁₀ HEA correlate well with the simulated trends, Figs. 1(a) and 2(a). As the Al concentration is increased beyond ~ 14.5 at. %, the FCC phase is predicted to completely destabilize, leaving a mixture of B2 and sigma phases. Once the Al concentration reaches ~22 at. %, a BCC phase is predicted to be stable. However, experimentally the 700°C Al₁₅ HEA was found to contain B2, sigma, and FCC phases. The 700°C Al₂₀ HEA exhibited B2, BCC, FCC, and sigma phases. The presence of the FCC phase in the Al₁₅ HEA and BCC phase in the Al₂₀ HEA does not correlate with the simulations. This infers that the complete destabilization of the FCC phase likely occurs at a higher concentration of Al, while the stabilization of the BCC phase occurs at a lower Al concentration. Once the Al concentration reaches ~ 28.5 at. %, the sigma phase is predicted to be fully destabilized, leaving a combination of B2 and BCC phases. This apparent destabilization of the sigma phase is consistent with the experimental findings of the 700°C Al₃₀ HEA, which contained only B2 and BCC phases.

The CALPHAD based thermodynamic models employed here were reasonably accurate in predicting the high temperature phase stabilities in a range of AlNiCoCrFe based HEAs. Also, the selected annealing times appeared to be sufficient for all of the HEAs to reach a metastable equilibrium state. In particular, the predicted stability range of sigma phase was consistent with

all experimental observations. The only modeling discrepancies observed related to the composition where that the FCC phase is fully destabilized at 700°C and 1050°C, as well as the composition where the BCC phase first becomes stable at 700°C. No order/disorder inconsistencies were found in the high temperature range. Additionally, the predicted chemistries of each phase were also in agreement with those determined experimentally. Thus, it is suggested that the current thermodynamic databases, though reasonably correct, still require some improvement.

4. Conclusions

This work investigated the 700°C and 1050°C phase equilibria in $\text{Al}_{10}\text{Ni}_{22.5}\text{Cr}_{22.5}\text{Co}_{22.5}\text{Fe}_{22.5}$, $\text{Al}_{15}\text{Ni}_{21.25}\text{Cr}_{21.25}\text{Co}_{21.25}\text{Fe}_{21.25}$, $\text{Al}_{20}\text{Ni}_{20}\text{Cr}_{20}\text{Co}_{20}\text{Fe}_{20}$, and $\text{Al}_{30}\text{Ni}_{17.5}\text{Cr}_{17.5}\text{Co}_{17.5}\text{Fe}_{17.5}$ (at. %) HEAs. Through the use of analytical characterization techniques, coupled with CALPHAD based thermodynamic modeling, the following can be concluded:

- 1) Annealing the HEAs at 1050°C promoted coarse microstructures consisting of FCC, BCC, and/or B2 phases depending on the relative Al content. Similarly, annealing at 700°C tended to stabilize a mixture of FCC, B2, BCC, and/or sigma phases. The B2 phases were commonly rich in Ni and Al, while the FCC phases were Co, Cr, and Fe rich. When observed, the BCC phases exhibited higher Cr content than the B2 phases and the sigma phases were extensively rich in Cr and Fe.
- 2) The experimentally determined phases were assessed using CALPHAD based thermodynamic modeling. In the majority of cases, the simulations predicted reasonably accurate phase fractions at temperatures of 700°C and 1050°C for a range of compositions. In general, the simulations also tended to capture experimentally observed trends in phase

evolution with varied Al concentration. The predicted phase chemistries were also fairly consistent with those determined via TEM-EDS. The only discrepancies in the modeling were related to the compositions where the FCC phase destabilizes at 700°C and 1050°C, along with when the BCC phase stabilizes at 700°C. No other order/disorder or sigma phase discrepancies were observed.

- 3) The experimental and simulated results of this study demonstrate the usefulness of CALPHAD based models for predicting the phases that form in compositionally complex HEAs. The thermodynamic databases still need improvement, but have demonstrated their usefulness and merit in this study.

Acknowledgement

This work utilized equipment owned by the Central Analytical Facility (CAF), which is housed at the University of Alabama. The authors also acknowledge partial support from the National Science Foundation under grant DMR-1411280.

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Table 1. The overall chemical compositions of the as-cast HEAs in this study (at. %).

Alloy		Al	Ni	Co	Cr	Fe
Al₁₀	Target	10	22.5	22.5	22.5	22.5
	EDS	10.2 ± 0.2	23.6 ± 0.2	21.7 ± 0.1	22.6 ± 0.2	21.8 ± 0.2
Al₁₅	Target	15	21.25	21.25	21.25	21.25
	EDS	15.6 ± 0.1	20.5 ± 0.1	20.8 ± 0.1	21.9 ± 0.1	21.1 ± 0.1
Al₂₀	Target	20	20	20	20	20
	EDS	20.2 ± 0.1	19.3 ± 0.1	19.7 ± 0.1	20.8 ± 0.2	20.1 ± 0.1
Al₃₀	Target	30	17.5	17.5	17.5	17.5
	EDS	29.2 ± 0.2	17.4 ± 0.1	17.6 ± 0.1	18.3 ± 0.1	17.6 ± 0.1

Table 2. Phase compositions of the annealed Al₁₀Ni_{22.5}Cr_{22.5}Co_{22.5}Fe_{22.5} HEA determined via TEM-EDS (at.%). The thermodynamically predicted phase chemistries at 700°C and 1050°C are also shown for comparison. The average difference (at. %) between the experimental and predicted values for all of the elements in a given phase are also shown.

Temp.	Phase	Al	Ni	Co	Cr	Fe	Average Difference (at.%)
700°C	FCC	2.9 ± 1.5	23.6 ± 4.8	24.0 ± 2.4	25.7 ± 1.1	23.8 ± 2.3	1.9
	FCC (<i>Predicted</i>)	1.6	26.2	21.8	24.3	26.2	--
	B2	22.4 ± 1.1	48.7 ± 0.7	14.9 ± 0.2	3.0 ± 0.5	11.0 ± 0.1	8.3
	B2 (<i>Predicted</i>)	21.7	28.7	22.4	7.3	19.9	--
	Sigma	1.1 ± 1.2	4.1 ± 2.1	21.4 ± 0.9	54.5 ± 1.8	19.0 ± 0.5	1.3
	Sigma (<i>Predicted</i>)	0	7.2	20.0	54.7	18.2	--
1050°C	FCC	4.5 ± 0.4	22.2 ± 0.7	25.0 ± 0.6	24.7 ± 0.9	23.5 ± 1.0	1.3
	FCC (<i>Predicted</i>)	5.5	21.7	22.3	26.8	23.8	--
	B2	23.3 ± 0.8	42.0 ± 0.5	17.7 ± 0.7	5.3 ± 0.7	11.7 ± 0.4	4.8
	B2 (<i>Predicted</i>)	26.2	30.0	19.8	8.8	15.2	--

Table 3. Phase compositions of the annealed Al₁₅Ni_{21.25}Cr_{21.25}Co_{21.25}Fe_{21.25} HEA determined via TEM-EDS (at.%). The thermodynamically predicted phase chemistries at 700°C and 1050°C are also shown for comparison. The average difference (at. %) between the experimental and predicted values for all of the elements in a given phase are also shown.

Temp.	Phase	Al	Ni	Co	Cr	Fe	Average Difference (at. %)
700°C	B2	22.1 ± 0.5	37.6 ± 0.4	18.8 ± 1.3	7.5 ± 1.7	13.9 ± 1.2	4.5
	B2 (<i>Predicted</i>)	23.2	27.6	22.4	6.2	20.5	--
	FCC	4.2 ± 0.2	17.6 ± 0.5	25.2 ± 1.7	29.2 ± 0.9	23.8 ± 0.7	N/A
	FCC (<i>Predicted</i>)	--	--	--	--	--	--
	Sigma	0.6 ± 0.2	5.0 ± 1.1	20.1 ± 2.2	53.1 ± 1.6	21.4 ± 0.6	1.3
	Sigma (<i>Predicted</i>)	0	5.6	17.4	54.7	22.3	--
1050°C	FCC	3.5 ± 0.2	19.5 ± 0.4	24.9 ± 0.3	26.9 ± 0.4	25.2 ± 0.2	2.6
	FCC (<i>Predicted</i>)	5.0	16.2	21.7	31.2	25.9	--
	B2	21.1 ± 0.5	38.5 ± 4.3	19.0 ± 0.6	8.7 ± 4.5	12.6 ± 0.6	4.7
	B2 (<i>Predicted</i>)	26.2	26.9	20.7	10.1	16.1	--

Table 4. Phase compositions of the annealed Al₂₀Ni₂₀Cr₂₀Co₂₀Fe₂₀ HEA determined via TEM-EDS (at.%). The thermodynamically predicted phase chemistries at 700°C and 1050°C are also shown for comparison. The average difference (at. %) between the experimental and predicted values for all of the elements in a given phase are also shown.

Temp.	Phase	Al	Ni	Co	Cr	Fe	Average Difference (at. %)
700°C	B2	22.7 ± 3.5	36.0 ± 1.3	23.6 ± 1.0	2.9 ± 0.5	14.7 ± 1.3	4.2
	B2 (<i>Predicted</i>)	29.1	26.7	22.6	4.7	17.0	--
	FCC	1.2 ± 0.4	7.7 ± 3.2	22.3 ± 1.6	44.0 ± 5.9	24.9 ± 1.8	N/A
	FCC (<i>Predicted</i>)	--	--	--	--	--	--
	BCC	8.5 ± 1.7	15.8 ± 3.4	19.2 ± 2.3	33.6 ± 5.4	22.9 ± 1.0	N/A
	BCC (<i>Predicted</i>)	--	--	--	--	--	--
	Sigma	1.7 ± 0.8	3.4 ± 0.6	10.2 ± 3.5	51.4 ± 2.3	33.3 ± 1.6	3.5
	Sigma (<i>Predicted</i>)	0	2.7	13.3	56.9	27.0	--
1050°C	B2	18.7 ± 1.8	32.9 ± 2.1	22.6 ± 1.4	10.2 ± 2.6	15.6 ± 0.9	3.6
	B2 (<i>Predicted</i>)	25.7	24.9	21.5	10.2	17.7	--
	FCC	4.2 ± 0.3	14.0 ± 0.8	24.8 ± 0.6	28.5 ± 0.6	28.4 ± 0.8	N/A
	FCC (<i>Predicted</i>)	--	--	--	--	--	--
	BCC	1.3 ± 0.5	4.1 ± 1.0	19.4 ± 0.8	47.2 ± 1.9	28.0 ± 0.3	5.2
	BCC (<i>Predicted</i>)	7.7	9.1	15.7	38.0	29.5	--

Table 5. Phase compositions of the annealed Al₃₀Ni_{17.5}Cr_{17.5}Co_{17.5}Fe_{17.5} HEA determined via TEM-EDS (at.%). The thermodynamically predicted phase chemistries at 700°C and 1050°C are also shown for comparison. The average difference (at. %) between the experimental and predicted values for all of the elements in a given phase are also shown.

Temp.	Phase	Al	Ni	Co	Cr	Fe	Average Difference (at. %)
700°C	B2	35.3 ± 3.0	26.5 ± 0.9	24.9 ± 1.5	1.8 ± 0.1	11.6 ± 1.3	2.0
	B2 (<i>Predicted</i>)	38.0	23.3	23.1	1.9	13.7	--
	BCC	7.8 ± 0.2	6.5 ± 0.3	10.1 ± 0.1	46.5 ± 0.3	29.1 ± 0.1	8.1
	BCC (<i>Predicted</i>)	2.7	0.1	1.3	66.8	29.1	--
1050°C	B2	27.4 ± 1.6	28.8 ± 1.9	23.8 ± 1.5	5.9 ± 1.7	14.0 ± 0.4	4.1
	B2 (<i>Predicted</i>)	35.9	21.9	20.1	6.4	15.1	--
	BCC	1.9 ± 0.3	1.2 ± 0.7	13.1 ± 1.4	52.4 ± 1.7	31.3 ± 0.7	4.7
	BCC (<i>Predicted</i>)	9.6	5.4	10.2	48.5	26.3	--

Figure 1. BSE images with inset higher magnification images of the Al₁₀ HEA after heat treating at 700°C for 1000 hours (a) and 1050°C for 520 hours (b); XRD spectra captured from the heat treated Al₁₀ HEA (c); and calculated phase fractions as a function of temperature for the Al₁₀ HEA using the TCNI8 database in ThermoCalc (d).

Figure 2. STEM-HAADF images of the Al₁₀ HEA annealed at 700°C (a) and 1050°C (f), along with corresponding SADPs (b)-(e) and (g)-(i), respectively.

Figure 3. BSE images with inset higher magnification images of the Al₁₅ HEA after heat treating at 700°C for 1000 hours (a) and 1050°C for 520 hours (b); XRD spectra captured from the heat treated Al₁₅ HEA (c); and calculated phase fractions as a function of temperature for the Al₁₅ HEA using the TCNI8 database in ThermoCalc (d).

Figure 4. STEM-HAADF images of the Al₁₅ HEA annealed at 700°C (a) and 1050°C (e), along with corresponding SADPs (b)-(d) and (f)-(h), respectively.

Figure 5. BSE images with inset higher magnification images of the Al₂₀ HEA after heat treating at 700°C for 1000 hours (a) and 1050°C for 520 hours (b); XRD spectra captured from the heat treated Al₂₀ HEA (c); and calculated phase fractions as a function of temperature for the Al₂₀ HEA using the TCNI8 database in ThermoCalc (d).

Figure 6. STEM-HAADF images of the Al₂₀ HEA annealed at 700°C (a) and 1050°C (f), along with corresponding SADPs (b)-(e) and (g)-(i), respectively.

Figure 7. BSE images with inset higher magnification images of the Al₃₀ HEA after heat treating at 700°C for 1000 hours (a) and 1050°C for 520 hours (b); XRD spectra captured from the heat treated Al₃₀ HEA (c); and calculated phase fractions for the Al₃₀ HEA using the TCNI8 database in ThermoCalc (d).

Figure 8. STEM-HAADF images of the Al₃₀ HEA annealed at 700°C (a) and 1050°C (e), along with corresponding SADPs (b)-(d) and (f)-(i), respectively.

Figure 9. Calculated phase fractions as a function of composition at 1050°C (a) and 700°C (b) for Al_x(NiCoCrFe)_{100-x} alloys where x = 5 to 40 (at. %). Simulations were conducted with the TCNI8 database in ThermoCalc.

Figure 1

Figure 2

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Figure 9