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PHASE STABILITY STUDY OF HIGH ENTROPY ALLOYS (HEAs)

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Ph.D

The Hong Kong Polytechnic University 2014



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Phase Stability Study of High Entropy Alloys (HEAs)

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A thesis submitted in partial fulfillment of the requirements for

the degree of Doctor of Philosophy

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CERTIFICATE OF ORIGINALITY

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Abstract

High entropy alloys (HEAs) have been emerging as a new frontier in the metallic materials field. The phase stability of HEAs is of critical significance, but progress in understanding this process has been difficult due to the slow diffusion kinetics, which prevent the completion of diffusion assisted phase transformations toward the equilibrium state. We used a series of thermo-mechanical treatments to investigate the stability of solid solution phases in a high entropy $Al_{0.5}CoCrCuFeNi$ alloy. The solid solution phases were found to be stable, against the intermetallic compounds, at high temperatures > 850°C and at low temperatures < 300°C. At intermediate temperatures, however, the intermetallic σ -phase co-existed with the solid solution phases. Experimental observations were verified by thermodynamic calculation results. The mechanisms of phase stability were investigated, both for the equilibrium state and after quenching-equivalent annealing treatments. The roles of high entropy and slow diffusion kinetics were highlighted.

Phase stability is vitally important for HEAs, but understanding of this phenomenon is very limited. The ability to predict phase stability from the fundamental properties of the constituent elements would greatly benefit our capability for alloy design. We systematically studied the relationship between phase stability and the physicochemical/thermodynamic properties of the alloying components in HEAs. The mixing enthalpy was found to be a key factor in controlling the formation of solid solutions or compounds. The stability of face-centered cubic (fcc) and bodycentered cubic (bcc) solid solutions was well delineated by the valence electron concentration (VEC). Revealing the effect of the VEC on phase stability is vitally important for alloy design and for controlling the mechanical behavior of HEAs.

By applying discoveries concerning the role of VEC, a series of cost-effective Cofree Al_xCrCuFeNi₂ HEAs were developed. The solidification microstructure in these alloys showed some anomalies that are rarely seen in other HEAs or multicomponent alloys. Specifically, submicron rod-like microstructures were found to exist in the eutectic alloy, in spite of the high volume percentage of the rod-like phases. Sunflower-like microstructures existed in the hyper-eutectic alloys, with 200 nm-sized spinodal-decomposed particles densely distributed in the disk florets. We used a combination of thermo-mechanical treatments and thermodynamic calculations to reveal the phase stability of these HEAs, as exemplified by the newly developed Al_{0.5}CrCuFeNi₂ alloy. The metastable nature of the solid solution phases in HEAs was uncovered through thermo-mechanical treatments and induced phase transformations. These results were verified by thermodynamic calculations. In addition, a systematic study of Al_{0.5}CrCuFeNi₂ tensile properties was carried out, and the results were correlated with the alloy's indentation behavior. The tensioncompression asymmetry on plasticity was demonstrated, together with their deviations from Tabor's rule on the relationship between hardness and strength.

List of Publications

- C. Ng, S. Guo, J.H. Luan, Q. Wang, J. Lu, S. Q. Shi and C. T. Liu. Phase stability and tensile properties of Co-free Al_{0.5}CoCrCuFeNi₂ high entropy alloys. *Journal* of Alloys and Compounds 584, pp. 530-537, 2014.
- S. Guo, C. Ng, Z. J. Wang and C.T. Liu. Solid solutioning in equiatomic alloys: Limit set by topological instability. *Journal of Alloys and Compounds 583*, pp. 410-413, 2014.
- 3. S. Guo, C. Ng, C. T. Liu. Sunflower-like solidification microstructure in a neareutectic high-entropy alloy. *Materials Research Letters 1(4)*, pp. 228-232, 2013.
- 4. S. Guo, Q. Hu, C. Ng and C. T. Liu. More than entropy in high-entropy alloys: Forming solid solutions or amorphous phase. *Intermetallics 41*, pp.96-103, 2013.
- S. Guo, C. Ng and C. T. Liu. Anomalous solidification microstructures in Co-free Al_xCrCuFeNi₂ high-entropy alloys. *Journal of Alloys and Compounds 557*, pp. 77-81, 2013.
- C. Ng, S. Guo, J.H. Luan, S. Q. Shi and C. T. Liu. Entropy-driven phase stability and slow diffusion kinetics in an Al_{0.5}CoCrCuFeNi high entropy alloy. *Intermetallics 31*, pp. 165-172, 2012.
- S. Guo, C. Ng, J. Lu and C. T. Liu. Effect of valence electron concentration on stability of fcc or bcc phase in high entropy alloys. *Journal of Applied Physics* 109(10), 103505, pp. 1-5, 2011.

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Abbreviations

AC	As Cast
BCC	Body Centered Cubic
BMG	Bulk Metallic Glass
CALPHAD	Calculation of Phase Diagrams
ССР	Cubic Close Packed
CR	Cold Rolled
DSC	Differential Scanning Calorimeter
DTA	Differential Temperature Analysis
EDS	Energy Dispersive Spectrometer
FC	Furnace Cooling
FCC	Face Centered Cubic
GFA	Glass Forming Ability
G _P	Gibbs Free Energy of Perfect Lattic

НСР	Hexagonal Close Packed
HEAN	High Entropy Alloy Nitride
HEAs	High Entropy Alloys
HE-BMG	High Entropy Bulk Metallic Glass
IM	Intermetallic
MSSAs	Multi-component Solid Solution Alloys
QC	Quench Cooling
SEM	Scanning Electron Microscope
SMAT	Surface Mechanical Attrition Treatment
SS	Solid Solution
ТСР	Topologically Close Packed
TEM	Transmission Electron Microscope
ТМ	Transition Metal
VEC	Valence Electron Concentration

WDS	Wavelength Dispersive Spectroscopy
WQ	Water Quench
XRD	X-Ray Diffractometer
ΔG_{mix}	Mixed Gibbs Free Energy
ΔH_{mix}	Mixed Enthalpy
ΔS_{mix}	Mixed Entropy
Δχ	Electro-negativity Difference

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Chapter 1: Introduction

1.1 Background

High entropy alloy (HEA) is a novel developed alloy family that was first proposed by Yeh et.al in 1995, and is drawing great interest in the metallic materials community [1-3]. As conceived by Yeh, HEAs involve the mixing of at least five principal elements with atomic concentrations between 5% and 35% [4]. The configuration entropies of HEAs, assuming that the alloys mix in a fully random state, are much higher than those of conventional alloys that have one or at most two principal elements [5]. Depending on the alloy compositions, HEAs tend to form simple solid solution phases, such as face-centered cubic (fcc) and body-centered cubic (bcc) phases, with nano-crystalline or even amorphous phases [1, 4, 6-24].

The alloying strategy in HEAs is a breakthrough in the history of physical metallurgy. In the past, alloys normally had only one principle element (e.g. steel, Al or Cu alloys) or two principal elements (e.g. TiAl based alloys). It was presumed that a high concentration of alloying elements would cause the formation of many hard intermetallic compounds, and hence embrittle the materials. Surprisingly, in many HEAs such intermetallic compounds are essentially absent and only simple fcc and/or bcc crystal structures are formed [25-28]. In fact, many unique properties of HEAs originate from the nature of their supersaturated solid solutions, for example, their high temperature precipitation and anti-softening characteristics [6, 29]. After a period of research, researchers have found that HEAs can exhibit a wide variety of properties [1]. Properly designed HEAs are developed with an aim to replace traditional alloys in specific applications [2]. The low thermal conductivity of HEAs makes them good candidates for the thermal management of casting molds. Laser cladding, vacuum coating and sputtering technologies further expands the applications of high hardness, high wear resistance and anti-corrosion HEAs as ideal functional thin films, for example, on the hard-facing of golf club heads, roller surfaces or the walls of steel tubes [15, 17, 23, 24, 30]. Their excellent thermal stability and resistance to softening makes HEAs suitable for use as refractory construction materials, jet engine turbines [2], or diffusion barrier layer between silicon oxide and Cu integrated circuits of silicon wafer [31]. The simple microstructures, versatile properties and broad applications of HEAs are attracting ever-increasing interest from materials scientists and engineers.

A lot of research work has been done in the past decade on developing new alloy systems and improving their mechanical and functional performance. Yet the scientific understanding of HEAs remains very limited, and many interesting, important areas remain to be explored or clarified.

1.2 Aims of this Research Project

 $Al_xCoCrCuFeNi$ is an extensively studied HEA system; $Al_{0.5}CoCrCuFeNi$ has fcc structure in the as-cast condition, comprising mainly two fcc phases in the dendritic and inter-dendritic regions respectively, with some tiny amount of ordered fcc phases,

which can only be detected by transmission electron microscope (TEM) but not by X-ray diffractometer (XRD) [6, 32]. Tong et al. gave an approximate phase diagram for the Al_xCoCrCuFeNi (x = 0 - 3.0) alloys, based on their phase transition temperatures as measured by differential temperature analysis (DTA). According to this analysis, only fcc-typed phases appear in the Al_{0.5}CoCrCuFeNi alloy over the full temperature range [6]. However, the accuracy of this DTA-determined phase diagram is certainly open to question. In fact, when the alloy was cold rolled and then annealed at 900°C, bcc phases started to appear [33], which contradicted the prediction of the phase diagram. When the alloy was cold rolled and then annealed at intermediate temperatures (500°C - 700°C), bcc phases also appeared together with some un-identified phases (see Fig. 10 in Ref. [34]).

The complicacy of the Al_{0.5}CoCrCuFeNi alloy makes it an ideal target alloy for investigating the phase stability of the solid solution phases in HEAs. In conducting this investigation, the work we have done in this project differs from previous work in two main ways. First, we used a much longer annealing time at each temperature we tested. This longer annealing was done to alleviate the kinetic effect on the achievement of the equilibrium phase as much as possible. Second, we performed thermodynamic calculations of the equilibrium phase diagram to verify our experimental observations. The calculated equilibrium phase diagram is critical for HEAs, as it shows their characteristics of slow diffusion, even at elevated temperatures [1]. Without such a calculated diagram, there is no effective way to tell whether the experimentally observed phases have reached their stable states. We expect that this combination of experimental results and theoretical predictions can lead to some convincing conclusions on the phase stability of the high entropy $Al_{0.5}$ CoCrCuFeNi alloy.

A great number of HEAs have been developed so far. However, the scientific understanding of HEAs is still at a preliminary stage, and particularly lack scientific or even empirical principles to guide the design of HEAs in achieving the desired phase constitutions and hence the mechanical properties. For example, although simple solid solution phase can form in HEAs, amorphous phase and intermetallic compounds can also appear [26]. It is thus important for us to predict the stability of phases for a given HEA composition. Assuming that solid solution phases are formed, can we predict whether fcc-type solid solution or bcc-type solid solution will form, for a given HEA composition? We already know that, fully fcc-type HEAs are soft and ductile [35], and those containing bcc phase are generally hard, but tend to be brittle [34]. Therefore, predicting the types of solid solutions is critical for designing HEAs with the mechanical properties appropriate for structural applications. One of the targets of our research was to identify the physical parameters that control the stability of fcc and bcc phases in HEAs.

After our research uncovered an empirical rule that governs the stability of fcc and bcc phases in HEAs, we were able to develop a new Co-free $Al_xCrCuFeNi_2$ HEA system. This system can fully replace the expensive Co element with Ni in the extensively studied $Al_xCoCrCuFeNi$ [6]. This thesis also reports our findings on the anomalous solidification microstructures of the $Al_xCrCuFeNi_2$ HEA system, which we believe are not seen in other HEAs and are rarely seen in other conventional non-

equiatomic, multi-component alloys. Furthermore, we have systematically studied the phase stability of $Al_{0.5}CrCuFeNi_2$ through a combination of experimentation and thermodynamic calculations. The tensile properties of the $Al_{0.5}CrCuFeNi_2$ alloys were carefully measured and statistically analyzed in this thesis.

1.3 Outline of the Thesis

This thesis is split into 7 chapters, including a brief introduction in Chapter 1. A review of previous studies, on the unique properties of HEAs, their phase formation, phase stability and sluggish diffusion properties, is given in Chapter 2. The methodologies of materials preparation, microstructure characterization, mechanical testing and thermodynamic calculations, are described in Chapter 3. In Chapter 4, the phase stabilities and mechanical properties of Al_{0.5}CoCrCuFeNi in elevated temperatures are analyzed through a series of systematic thermo-mechanical treatments. The thermodynamic calculations of the equilibrium phase diagram are used to verify the experimental observations. We expect this combination of experimental results and theoretical predictions to produce some convincing conclusions on the phase stability of the high entropy Al_{0.5}CoCrCuFeNi alloy. In Chapter 5, the physical parameters that control the stability of fcc and bcc phases in HEAs are investigated. The effect of the valence electron concentration (VEC) on phase stability has been proven vitally important for alloy design, for controlling the formation of fcc and bcc phases, and, thus for predicting the mechanical behavior of HEAs. In Chapter 6, a series of cost-effective, Co-free Al_xCrCuFeNi₂ HEAs are developed through applying the VEC principle. Also, a detailed analysis of the anomalous solidification microstructures of Al_xCrCuFeNi₂ is carried out. The

mechanism for formation of the pervasive sunflower-like solidification morphologies is clarified. The metastable nature of the solid solution phases in $Al_{0.5}CrCuFeNi_2$ is exposed through the thermo-mechanical treatments to induce phase transformation, and through thermodynamic calculations. In addition, a systematic study of the tensile properties of $Al_{0.5}CrCuFeNi_2$ is carried out and correlated to alloy's indentation behavior. Conclusions and suggestions for future work are given in Chapter 7.

Chapter 2: Literature Review

2.1 Introduction

Metallurgy plays a pivotal role in the civilization of human beings. In the last century, thanks to the rapid progress of technology and the enormous demand for improved materials, new alloy systems, such as Al-, Mg-, Ni- and Ti-based alloys, were designed to cope with challenging working environments in the power, transportation, aerospace and military-related industries [3]. Typical examples include Ni super alloys, wrought Al alloys and stainless steels. Most of the conventional designed alloy systems are based on one or two principal elements as the matrix, with small amounts of other elements to improve the mechanical and chemical properties of the master metal. In 1960, Klement et al. successfully synthesized the amorphous Au₇₅Si₂₅ alloy [36]. The high mechanical strength and corrosion resistance of amorphous alloys, including Pd-, La-, Zr-, Fe- and Mg-based alloys [37]. Until 2009, the design concept of bulk amorphous alloys was still based on using one or two principal elements [6].

The main reason why metallurgists have avoided incorporating multi-principal elements into alloy preparation is the anticipated formation of many inter-metallic compounds. The brittleness and difficulty in processing or analyzing such alloys, due to the formation of inter-metallic compounds, discouraged metallurgists from designing or synthesizing new alloys with multi-principal elements.

In 1995, the development of HEAs provided a novel alloy design concept that significantly expanded the scope of traditional alloy design [4]. As proposed by Yeh et al., HEAs typically consist of at least five principal metallic elements in near-equimolar ratios. These alloys form a single solid-solution structure, instead of the many intermetallic compounds that were expected according to general physical metallurgy principles [1]. In addition to forming simple solid solutions, some well-designed HEAs also developed nano-scaled precipitates or even formed amorphous structures without the need for special process treatments [6, 14]. HEAs were shown to possess many excellent mechanical properties such as high strength and hardness [4, 32, 38, 39], high wear resistance [40, 41], and resistance to softening at high temperatures [12]. These alloys have found many functional applications such as hydrogen storage [42], diffusion barrier [31], and even biomedical applications [43].

In this chapter, we review the previous studies of HEAs. Based on the findings of this literature review, the achievements of previous studies are summarized. The objectives of our research are clarified as well.

2.2 High Entropy Alloys

2.2.1 Definition of High Entropy Alloys (HEAs)

In a thermodynamic point of view, a system tries to minimize its Gibbs free energy (ΔG_{mix}) to achieve a metastable or stable equilibrium state [5]. Equation 2.2.1-1 is the formula of the Gibbs free energy [44].

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \qquad (Equation 2.2.1-1)$$

It can be seen that the mixed enthalpy (ΔH_{mix}) and mixed entropy (ΔS_{mix}) have a direct relationship with Gibbs free energy in determining the equilibrium state at a given temperature (T), in Kelvin. As depicted by Equation 2.2.1-1, either decreasing the mixed enthalpy or increasing the mixed entropy can reduce the Gibbs free energy, and make the system stable. In a high temperature environment, the T ΔS_{mix} term becomes a dominant factor. Therefore, HEAs are expected to significantly extend the solubility range in their alloy systems, and to form simple multi-element solution phases [1].

Following Boltzmann's hypotheses, the mixing entropy or configuration entropy of N-element as regular liquid can be expressed with Equation 2.2.1-2, and the entropy would reach a maximum when the alloy is in the equi-atomic ratio as expressed in Equation 2.2.1-3.

$$\Delta S_{mix} = -R \sum_{i=1}^{N} c_i \ln c_i \qquad (\text{Equation 2.2.1-2})$$

$$\Delta S_{mix} = R \ln N \qquad (\text{Equation } 2.2.1-3)$$

Where *R* is the gas constant, 8.31 $\left(\frac{J}{K-Mol}\right)$; and where; c_i and *N* are the atomic percentages of the *i*th element and the total number of elements involved respectively. By increasing the total number of elements (*N*), the mixing entropy increases correspondingly. Based on equation 2.2.1-3, Yeh et al. plotted a chart of mixing entropy versus the number of elements in equimolar alloys (Fig. 2.2.1-1) [1]. They found that the mixing entropy of five elements was high enough to counterbalance the mixing entropy in most alloy systems, and to favor the formation of solid solution phases. Furthermore, increasing the number of elements to over five gave a limited contribution for increasing the mixing entropy. Therefore, Yeh proposed the definition of HEAs as alloys containing at least five principal elements with atomic concentrations between 5% and 35%. Another definition was that the value of mixing entropy for the synthesis alloys was equal to or higher than 13.37 $\left(\frac{J}{K-Mol}\right)$ [4].



Fig. 2.2.1-1: The mixing entropy as a function of the number of elements in equimolar alloys (after [1])
Zhang et al. used mixing enthalpy to characterize the chemical compatibility among the principal components of HEAs [27]. The variable ΔH_{mix} (kJ/mol) was calculated based on the extended regular solution model (Miedema's macroscopic model) [45-48], as shown in Equation 2.2.1-4

$$\Delta H_{mix} = \sum_{i=1, i \neq j}^{n} \Omega_{ij} c_i c_j \qquad (\text{Equation 2.2.1-4})$$

Where $\Omega_{ij} = 4\Delta H_{AB}^{mix}$ is the regular melt-inter-action parameter between i^{th} and j^{th} elements, and ΔH_{AB}^{mix} is the mixing enthalpy of binary liquid AB alloys, as seen in reference [45]. The variables c_i and c_j are the composition of the i^{th} element and j^{th} element respectively.

Indeed, mixing entropy and mixing enthalpy are two important parameters that are vital in HEA research. Solid solutions are formed, as the HEAs possess high mixing entropy with reduced negative mixing enthalpy. If the mixing entropy is not high enough to compete with the mixing enthalpy, inter-metallic compounds tend to form in HEAs [27, 49]. Detailed explanations of solid solution, inter-metallic compounds and amorphous structure formations in HEAs are introduced in Section 2.3 of this chapter.

2.2.2 Unique Properties of HEAs

High mixing entropy, severe lattice distortion, sluggish diffusion kinetics and cocktail effects are four unique properties of HEAs [1].

Following Boltzmann's hypotheses, the mixing entropy of HEAs is high due to the multi-principal elements mixed in near-equimolar ratios [4]. In alloy systems, the high mixing entropy competes with enthalpy to lower the Gibbs free energy and promote the formation of simple solid solutions. High mixing entropy also inhibits the formation of inter-metallic compounds. Fig. 2.2.2-1 shows comparisons of the X-ray diffraction (XRD) patterns of an equimolar HEA series of Cu-Ni-Al-Co-Cr-Fe-Si, ranging from two up to seven elements in the as-cast condition [50]. This analysis demonstrated that only simple fcc and bcc phases can be detected. The result revealed that high mixing entropy can effectively inhibit the formation of brittle and complex inter-metallic compounds, and this inhibition effect helps to simplify the phase and structural analysis of HEAs.



Fig. 2.2.2-1: XRD diffraction patterns of an equimolar HEA series of Cu-Ni-Al-Co-Cr-Fe-Si, from two up to seven elements in the as-cast condition (after [50])

There is no host metallic element in HEAs. Every metallic element can be treated as a solute, and possesses the same probability of occupying the lattice to form a solid solution. Consequently, multi-element lattices are distorted due to the different atomic sizes among the solute atoms involved. A schematic illustration of a bcc crystal structure altered from a perfect bcc lattice to a distorted lattice is shown in Fig. 2.2.2-2 [51]. The severe lattice distortion in HEAs causes high solid solution hardening and high thermal resistance effects. As we know, thermal conduction can be carried out by the vibrations of phonons and electrons [52], and severe lattice distortion reduces the efficiencies of thermal conduction induced by the electrons. As a result, the thermal conductivity in HEAs is low compared to that of lower-entropy alloys. An experimental comparison of the thermal conductivities of HEA A (Fe-Co-Ni-Cr-Si-Cu-Al), HEA B (Co-Cr-Cu-Fe-Ni-Si-Zr), and SKD61 steel, as measured by the hot disk method, is summarized in Table 2.2.2-1 [2]. This experimental result demonstrated the low thermal conductivity in HEAs, which is consistent with the theoretical explanation that the severe lattice distortion in HEAs increases their thermal resistance. In functional coating applications, HEAs are good coating material on the mold surface. They enable thermal management due to their low thermal conductivity and high thermal stability.



Fig. 2.2.2-2: Schematic illustration of a bcc structure: (a) perfect Cr lattice; (b) seriously distorted lattice caused by many kinds of different-sized atoms randomly distributed in the crystal lattice with the same probability to occupy the lattice sites in multi-principal solid solutions (after [51]).

Table 2.2.2-1: Thermal conductivities of HEA A (Fe-Co-Ni-Cr-Si-Cu-Al), HEA B (Co-Cr-Cu-Fe-Ni-Si-Zr) and SKD61 steel, as measured by the hot disk method (after [2]).

Material		HE alloy A	HE alloy B	SKD61
Thermal conductivity (W/mK)	Bulk	7.94	6.69	28
	Coating	3.24	3.14	

The severe lattice distortion of multi-principal elements in HEAs leads to sluggish diffusion kinetics. In casting HEAs, the phase separation during cooling is often inhibited at higher temperatures, and delayed at room temperature. As a result, nano-precipitates are easily precipitated in as-cast HEAs due to the sluggish diffusion kinetics. This formation of nano-precipitates due to a sluggish diffusion kinetics mechanism can be easily revealed by investigating the structural image of as-cast FeCoNiCrCuAl, as captured by transmission electron microscope (TEM) in Fig. 2.2.2-3. The ε -particle is the nano-precipitate in the spinodal decomposition ordered bcc phase plate [6]. The precipitation of nano-crystalline structure definitely promotes the mechanical strength of HEAs.

Observers may point out that the above example does not reflect the mechanism of diffusion kinetics in HEAs directly. To deal with this concern, Tsai et al. used a quasi-binary HEA couples method to test the diffusion kinetics in an argon-filled quartz tube, with the samples annealed at high temperatures (Fig. 2.2.2-4) [53]. The results, in terms of measured temperature dependence diffusion coefficients, are

plotted in Fig. 2.2.2-5. As expected, HEAs demonstrated lower diffusion kinetics compared to the low- or medium-entropy alloys [53]. Their thermally stable and sluggish diffusion kinetics properties make HEAs good candidates for thermal diffusion barrier applications. Chang et al. coated a 10 nm-thick (AlCrTaTiZr)N film as a barrier layer between SiO₂ and Cu interconnect circuit, and annealed the film stack sample at 900°C for 30 minutes in a vacuum of 2×10^{-5} torr (Fig. 2.2.2-6). This experiment proved that high entropy alloy nitride (HEAN) film acts an effective diffusion barrier layer [31]. A similar experiment was conducted by Tsai et al. They deposited a 1 µm-thick AlMoNbSiTaTiVZr film between layers of Si and Cu, and annealed the sandwich stack sample at temperatures up to 700°C for 30 minutes in a vacuum [15]. Tsai et al. found that the HEA layer was effective as a diffusion barrier at 700 $^{\circ}$ C, but failed at temperatures above 750 $^{\circ}$ C (Fig. 2.2.2-7) [15]. The experiments conducted by Chang and Tsai demonstrated that HEA film is an effective diffusion barrier layer due to its excellent high-temperature chemical and structural stability, and its intrinsically sluggish diffusion kinetics properties.



Fig. 2.2.2-3: TEM microstructure of as-cast FeCoNiCrCuAl, α : disordered bcc phase with 70 nm in thickness, β : ordered bcc phase with 100 nm in thickness, ϵ : nano-

precipitate in plates (after [6]).



Fig. 2.2.2-4: Schematic diagrams showing the assembly of the diffusion couples (after [53]).



Fig. 2.2.2-5: Temperature dependence of the diffusion coefficients (D) for Cr, Mn, Fe, Co, and Ni in different alloys (after [53]).



Fig. 2.2.2-6: (a) TEM bright field image of 900°C annealed SiO₂/HEAN/Cu film stack; (b) Lattice image at the SiO₂/HEAN interface (circled: lattices of nanocrystallites) (after [31]).



Fig. 2.2.2-7: XRD spectrum from the Cu/HEA/Si structure before and after annealing at 700°C, 750°C and 800°C for 30 minutes, respectively (after [15]).

Incorporating multi-principal elements, HEAs can be viewed as an atomic-scale composite. If more light elements are used, the overall density of HEA will be low. If more oxidation resistant elements are used, the oxidation resistance of the synthesized HEA at high temperatures will be improved. Yeh defined such composite effects as cocktail effects in HEAs [1].

The chemical and mechanical properties of HEAs can be varied by synthesizing HEAs in different recipes. Some HEAs demonstrate high hardness, but low ductility.

Some of them show low hardness, but high ductility and wear resistance [1]. Based on previous studies, the hardness of HEAs can vary from HV 160 to HV 1100 [6, 30, 54]. A wide variety of mechanical features make this novel alloy family suitable for adaptation to various tasks in industry. For example, the high hardness, high temperature softening resistance (Fig. 2.2.2-8) and oxidation resistance of HEAs make them excellent candidates for use in the mold manufacturing industry as new thermal-barrier coatings [2, 4]. The low thermal conductivity of HEAs keeps molten liquid hot and slows down the rate of solidification. Therefore, larger area and thinner gage casting is possible. To date, significant efforts have been devoted to developing new HEAs with improved properties.



Fig. 2.2.2-8: Comparison of hardness in as-cast and fully annealed (at 1000°C for 12 hours) HEAs and in commercial alloys (after [4]).

2.3 Phase Formation in HEAs

In HEAs, the commonly used alloying elements include fcc-type Cu, Al or Ni, bcctype Fe, Cr, Mn, Mo or V and hexagonal close-packed (hcp)-type Ti or Co. Normally, there is high ductility but low mechanical strength, if the alloy possesses A1-type solely dimple disordered fcc phase. If the alloy possesses A1-type disordered fcc phase mixed with L1₂-type ordered fcc phase, the mechanical strength increases dramatically, accompanied by high plasticity. One typical example is Ni super alloy [55]. If an alloy possesses solely simple A2 disordered bcc phase, the mechanical strength is higher than if it has A1-type disordered fcc phase, but the ductility is poorer than A1-type disordered fcc phase. Alloys with B2-type ordered bcc phase and hcp phase are hard, but brittle.

Over the years, remarkable efforts have been devoted to the development of new HEA systems with improved mechanical and functional properties. However, the scientific understanding of HEAs has been very limited, and some of the most fundamental aspects of HEAs remain unknown. How do the alloying atoms arrange themselves in an HEA complex solid solution? What is the key factor controlling the formation of fcc or bcc solution? Can we predict the phase selection from a given alloy compositions?

In this section, we review the previous research on phase formation in HEAs. A simple solid solution is not the only final result seen in HEAs. Inter-metallic compounds also exist in some synthesized HEAs, such as Laves or sigma phases, and amorphous phase is also possible in HEAs [10, 14, 18, 38, 49, 56-59].

2.3.1 Solid Solution Forming HEAs

It is easy to identify fcc, bcc or hcp phase in pure metals. However, it is not an easy task to predict the final phases in synthesizing alloys with several metallic elements. Cantor et al. mixed an alloy containing 5-component Fe(bcc)-Cr(bcc)-Mn(bcc)-Ni(fcc)-Co(hcp) in an equi-molar ratio. They found that simple fcc solid solution was solidified dendritically in the as-cast alloy [3]. Then they expanded the 5component alloy to a 6-component alloy by adding Nb(bcc), Cu(fcc) or V(bcc). Simple fcc solid solutions still formed in the as-cast alloy but with different lattice parameters. When adding cubic close-packed (ccp)-type Ge or hcp-type Ti, mixed fcc with bcc solid solutions formed. Another typical example is the Al_xCoCrCuFeNi (in atomic portions) system studied by Tong et al. [6]. As-cast CoCrCuFeNi has pure fcc structure, whereas AlCoCrCuFeNi has fcc + bcc structures. By progressively increasing the Al atomic ratio from 0 to 3, the Al_xCoCrCuFeNi system was able to adjust the crystal structure from fcc to fcc + bcc, and finally to a solely bcc structure [6]. The hardness and strength of Al_xCoCrCuFeNi increased following the phase transformation from fcc to bcc, but the alloys became brittle at room temperature as the percentage of bcc phase was increased.

Cantor and Tong reported only the final results of the phase formations of particular HEA systems. Neither of them established a rule concerning phase selection in the multi-component HEAs. It is of interest to learn whether the experimentally observed solid solution phases are stable, or are metastable phases. The energy landscape fundamentally accounts for the phase stability, and hence the phase selection, when cooling the molten alloy to room temperature.

Li et al. calculated the value of ΔG_{mix} for the formation of solid solutions or intermetallic compounds by using Miedemas's model [60]. They found that the value of ΔG_{mix} in AlCrCuFeNi was smaller than that in inter-metallic compounds. Therefore, the conclusion has been drawn that HEAs form solid solutions more easily than inter-metallic compounds due to the low value of ΔG_{mix} . However, Li et al. only used a quinary HEA to compare with several binary inter-metallic compound systems. Such a comparison is an inadequate basis for drawing at conclusion that the reason AlCrCuFeNi favors the solid solution formation is because its value of ΔG_{mix} is low.

The phase formation competition between solid solutions and inter-metallic compounds is empirically governed by the famous Hume-Rothery rule [61]. However, the Hume-Rothery rule is based on the traditional metallurgy system, and not all of the criteria suggested by the Hume-Rothery rule are applicable to solid solution formation in HEAs. For example, the Hume-Rothery rule suggests that the type of crystal structures must be the same to form solid solution. However, a great

deal of research work on HEAs demonstrated that the alloys synthesized by different crystal structure elements can form simple fcc or bcc solid solutions. The criterion of small atomic size differences suggested by the Hume-Rothery rule is well reflected in the formation of solid solutions in HEAs [6, 62]. However, it remains an interesting scientific puzzle for researchers to predict the solid solution formation in HEAs.

In 2008, Zhang et al. summarized the structural characteristics of several HEAs in terms of their magnified atomic size difference (delta, δ), mixing entropy (ΔS_{mix}) and mixing enthalpy (ΔH_{mix}). They predicted the phase formation in various HEAs, inter-metallic compounds and amorphous metallic glasses [27]. Equation 2.3.1-1 shows the parameter δ which is used to describe the comprehensive effect of the atomic size difference in HEAs.

$$\delta = 100 \times \sqrt{\sum_{i=1}^{N} c_i (1 - \frac{r_i}{\bar{r}})^2}$$
 (Equation 2.3.1-1)

Where *N* is the number of involved elements in an alloy system, c_i is the atomic percentage of i^{th} element, $\bar{r} = \sum_{i=1}^{N} c_i r_i$ is the average atomic radius, and r_i is the atomic radius, as obtained in reference [63]. Zhang et al. summarized δ and ΔH_{mix} in analyzed alloys, and plotted their relationships as shown in Fig. 2.3.1-1. They concluded that at solid solution tends to form in the region delineated by -15kJ/ $mol \leq \Delta H_{mix} \leq 5kJ/mol$ and $1 \leq \delta \leq 5$ [27]. In accordance with data presented in Fig. 2.3.1-2, Zhang et al. drew the conclusion that with high mixing entropy (equal to or larger than $12\frac{J}{K \cdot mol}$), the solid solution is easily formed with the boundary conditions of δ and ΔH_{mix} , as is described in Fig. 2.3.1-1. In other words, solid solution tends to form in an alloy system where the atomic size difference among the solute elements is small, the value of entropy is high, and the value of enthalpy is less positive or negative.



Fig. 2.3.1-1: Relationship between δ and ΔH_{mix} in HEAs (note on the symbol key: "solid solution" indicates that the alloy contains only solid solution, "ordered solid solution" indicates a minor ordered solid solution precipitate with a solid solution, and "intermediate phase" indicates that there is precipitation of inter-metallic compounds) (after [27]).



Fig. 2.3.1-2: The effect of ΔS_{mix} on the phase formation in HEAs (after [27]).

2.3.2 Intermetallic Compound Forming HEAs

As mentioned in Section 2.3.1, when blending more than five components to synthesize HEAs, the high mixing entropy inhibits the formation of brittle intermetallic compounds. However, from a thermo-dynamic point of view, apart from the mixing entropy, the mixing enthalpy plays a decisive role in determining the phase formation. Moreover, HEAs synthesized by elements with large differences in atomic sizes have and increased degree of lattice distortion, which triggers the phase transformation to a lower level of Gibbs free energy. Zhou et al. analyzed a CoCrFeNiCu_xAl_{1-x} system using the Gibbs free energy calculation method, and proved that the phase transformation from fcc to bcc can effectively lower the Gibbs free energy and restore the alloy to a stable state [11]. Generally, the larger the

lattice distortion in an HEA, the higher its mechanical strength will be, but its ductility will be sacrificed.

Fe, Ni, Cr, Co, Cu, Mo, Al, Ti and Zr are the most commonly used raw materials to synthesize HEAs. Table 2.3.2-1 shows the radii and the mixed binary enthalpy of the above mentioned elements [63]. The atomic radii of Fe, Ni, Cr, Co and Cu are comparatively small and are similar. Their mixing enthalpies are less negative, and their mixing entropies become the dominant factors for lowering the Gibbs free energy. As a result, the final blended HEAs have the tendency to form simple fcc solid solutions, as which has been proven by Chen et al. [64]. However, a simple disordered fcc solid solution with a lower mechanical strength in HEAs is not attractive in many functional applications. Chen doped large atomic size Al into a CoCrCuFeNi alloy to increase the lattice distortion. As Al doping increased from an atomic ratio of 0.3 to 0.8, the lattice distortion became serious, which was reflected by the increase in the lattice constant. As the amount of Al increased, the simple fcc solid solution transformed to a mixed fcc and bcc solid solution. The hardness values also increased with more Al doping, which aligned well with the phase transformation result. The relationships between lattice distortion, phase transformation and hardness values are displayed in Table 2.3.2-2 [64].

Element (atomic size, Å)	Fe	Ni	Cr	Со	Cu	Мо	Al	Ti	Zr
Fe (1.241)		-2	-1	-1	13	-2	-11	-17	-25
Ni (1.246)	-2		-7	0	4	-7	-22	-35	-49
Cr (1.249)	-1	-7		-4	12	0	-10	-7	-12
Co (1.251)	-1	0	-4		6	-5	-19	-28	-41
Cu (1.278)	13	4	12	6		19	-1	-9	-23
Mo (1.363)	-2	-7	0	-5	19		-5	-4	-6
Al (1.432)	-11	-22	-10	-19	-1	-5		-30	-44
Ti (1.462)	-17	-35	-7	-28	-9	-4	-30		0
Zr (1.603)	-25	-49	-12	-41	-23	-6	-44	0	

Table 2.3.2-1: The mixing enthalpies of the atomic pairs among the alloying elements, kJ/mol (after [45, 63])

Alloy	Crystal structure and lattice constant (Å)	Hardness (HV)
CoCrCuFeNi	FCC (3.58)	133±20
Al _{0.3} CoCrCuFeNi	FCC (3.58)	180±20
Al _{0.5} CoCrCuFeNi	FCC (3.59)	208±20
Al _{0.8} CoCrCuFeNi	FCC (3.60) + BCC (2.87)	271 <u>±</u> 20
AlCoCrCuFeNi	FCC (3.60) + BCC (2.87)	406 <u>±</u> 20

Table 2.3.2-2: The crystal structure, lattice constant, and hardness of

Al_xCoCrCuFeNi (after [64])

It seems a good idea to dope elements that have large atomic sizes into Fe, Co, Ni, Cr and Cu based HEA to increase the mechanical strength, and to maintain simple solid solution phases in the synthesized HEAs. Li et al. replaced Al with the larger atomic-sized Zr, to synthesize an FeNiCrCuZr HEA. The hardness value of FeNiCrCuZr increased almost 43% compared to that of FeNiCrCuAl (see Table 2.3.2-3) [65]. However, apart from the bcc phase, intermetallic compounds also precipitated in FeNiCrCuZr. The high hardness value of FeNiCrCuZr resulted from both the phase transformation from fcc to bcc and the chemical bonded intermetallic

compounds [65]. Li explained the formation of inter-metallic compounds in FeNiCrCuZr as due to the strong compound formation tendency of Zr with other metals. This explanation aligned well with measurements showing that the mixing enthalpies of Zr and other metals are too negative (Table 2.3.2-1). As a result, the mixing enthalpy became another dominant factor to promote the formation of intermetallic compounds in FeNiCrCuZr.

Observers may ask about the effects of doping Ti instead of Zr. In 2006, Wang et al. selected Ti doping in the CoCrCuFeNiTi_x system. Only simple fcc solid solution formed, as the atomic ratio of Ti is less than or equal to 0.5 [66]. However, the Laves phase of the Fe₂Ti (inter-metallic compound) mixed with the fcc solid solution as the atomic ratio of Ti increased to 0.8 or higher values. In the same year, Chen et al. investigated the properties of Al_{0.5}CoCrCuFeNiTi_x (x = $0 \sim 2.0$) [67]. As Fig. 2.3.2-1 shows, when $x \le 0.2$, simple fcc phase formed; when $0.4 \le x \le 0.6$, a mixture of fcc and bcc phases formed; when $0.8 \le x \le 1.2$, apart from the mixed fcc and bcc phases, a CoCr-like structure (σ phase) and a Ti₂Ni-like structure (TL phase) were also precipitated. With further increases the Ti content over 1.2 in atomic ratio, the σ phase disappeared, yet the mixed fcc, bcc and TL phases remained. Chen also found that the hardness of the testing alloy system increased from HV 225 to HV 660 in correspondence with the increase in the atomic ratio of Ti from 0 to 2.0 (Fig. 2.3.2-2). The increased mechanical strength in this HEA system resulted mainly from the phase transformation from fcc to bcc and from the precipitation of inter-metallic compounds, as in the σ and TL phases.

The Zr and Ti doping experiments demonstrated that a high entropy effect can promote the formation of simple solid solution. Solid solution hardening effect in HEAs can effectively strengthen the mechanical properties of HEAs. However, doping high chemical bonding elements into the HEA system significantly lowers the enthalpy value and favors the formation of inter-metallic compounds. Hsu et al. studied the AlCo_xCrFeMo_{0.5}Ni HEA system and found that the inter-metallic compound σ -phase always exists in this system. However it was interesting to learn that Co was an effective element for suppressing the σ phase, but promoting the fcc phase [68]. As shown in Fig. 2.3.2-3, the σ phase decreased, but the fcc phase increased with the rising atomic ratio of the Co contents in the AlCo_xCrFeMo_{0.5}Ni HEA system.

Alloy	Structure	Hardness (HV)
FeNiCrCuCo	FCC	286
FeNiCrCuMo	FCC	263
FeNiCrCuAl	FCC + BCC	342
FeNiCrCuMn	FCC + BCC	296
FeNiCrCoAl	BCC	395
FeNiCrCoAl _{1.5}	BCC	402
Fe NiCrCoAl ₂	BCC	432
FeNiCrCoAl _{2.5}	BCC	487
FeNiCrCoAl ₃	BCC	506
FeNiCrCuZr	BCC + compounds	566

Table 2.3.2-3: The hardness of synthesized HEAs (after [65])



Fig. 2.3.2-1: XRD analysis of $Al_{0.5}$ CoCrCuFeNiTi_x alloys with different Ti contents (x value in molar ratio); (a) x = 0 to 0.6; (b) x = 0.8 to 1.2; (c) x = 1.4 to 2.0 (after

[67]).



Fig. 2.3.2-2: Vickers hardness and wear resistance of $Al_{0.5}CoCrCuFeNiTi_x$ alloys with different Ti contents (after [67]).



Fig. 2.3.2-3: XRD patterns of AlCoxCrFeMo_{0.5}Ni with various Co contents (after

[68]).

2.3.3 Amorphous Phase

Bulk metallic glass (BMG) is an amorphous metallic alloy. In the past 30 years, BMG has attracted growing interest from academics and engineers in the field of advanced metallic materials, due to its unique structures and properties, which are superior to those of conventional crystalline alloys [37].

In 1993, Greer proposed a "confusion principle" to explain the high glass forming ability (GFA) of BMG [69]. This confusion principle holds that the more alloying elements are involved, the lower the chances are that the alloy can form well-defined crystal structures. This principle was used with success to explain that the amorphous phase formation is easier (or it has a lower critical cooling rate to achieve the fully amorphous state from the molten liquid) in multi-component alloys that have more than three alloying elements, and have a mixing entropy that is higher than in simpler alloy systems.

Naturally, the confusion principle raises a question. In conditions where more alloying elements are involved and mixing entropy is high, will an amorphous phase form easily in HEAs? Cantor et al. found that alloys containing 16 or 20 components in equal proportions are multiphase, and can use either as-cast or melt spinning manufacturing processes [3]. Zhang et al. tried to explain the contradiction between the of phase formation in HEAs and the confusion principle by using the

Adam-Gibbs energy equation, correlated to the viscosity and the configuration entropy S_c (mainly related to ΔS_{mix}) [27].

$$\eta = \eta_0 \cdot \exp\left[\frac{c}{TS_c(T)}\right]$$
 (Equation 2.3.3-1)

Where, *C* is an enthalpy-free barrier to cooperative rearrangements. According to Equation 2.3.3-1, high ΔS_{mix} leads to low viscosity, with high mobility of the atoms in the liquid, and thus a lower glass forming ability.

Based on the extensive data generated on the synthesis of BMGs, Inoue proposed three empirical rules that have proven useful. These rules concern multi-component systems, significantly large atomic size differences and negative heat of mixing among the constituent elements [70]. Moreover, a fast cooling rate and an oxygenfree atmosphere are the basic requirements in synthesizing BMGs. In 2011, Takeuchi et al. successfully synthesized high entropy bulk metallic glass (HE-BMG) composed of Pd₂₀Pt₂₀Cu₂₀Ni₂₀P₂₀ in a 10 mm diameter cylinder (Fig. 2.3.3-1) [14]. This HE-BMG has been developed based on a ternary prototype of $Pd_{40}Ni_{40}P_{20}$ BMG. Building on this ternary prototype, Takeuchi developed a model for Pd₂₀Pt₂₀(TM1)₂₀(TM2)₂₀P₂₀ alloys in nominal atomic percentages, in which TM1 and TM2 were transition metals from Fe, Co, Ni and Cu. Through trial-and-error experiments, Takeuchi found the possible combinations to form HE-BMG (Fig. 2.3.3-2) [14]. In the same year, Zhao et al. found another HE-BMG recipe, but with a low glass transition temperature (323K). This $Zn_{20}Ca_{20}Sr_{20}Yb_{20}(Li_{0.55}Mg_{0.45})_{20}$ HE-BMG, drop-cast in a 3 mm diameter cylinder, demonstrated low density and polymer-like thermoplastic manufacturability [10]. This HE-BMG can be compressed 70% from its original height without shear lines or cracking. Interestingly, even after 70% compression deformation, the alloy retains an amorphous structure (see Fig. 2.3.3-3) [10]. Moreover, Gao and Zhao synthesized two more HE-BMG alloys in the same year by fine tuning the elemental compositions of $Zn_{20}Ca_{20}Sr_{20}Yb_{20}(Li_{0.55}Mg_{0.45})_{20}$ [56]. The amorphous XRD patterns of the newly synthesized $Sr_{20}Ca_{20}Yb_{20}Mg_{20}Zn_{10}Cu_{10}$ and $Sr_{20}Ca_{20}Yb_{20}Mg_{20}Zn_{20}$ can be seen in Fig. 2.3.3-4 [56].



Fig. 2.3.3-1: (a) Outer surface and cross-sectional images, (b) XRD pattern of Pd₂₀Pt₂₀Cu₂₀Ni₂₀P₂₀ with 10mm in diameter cylinder prepared by water quenching with B₂O₃ fluxed treatment (after [14]).



Fig. 2.3.3-2: XRD patterns of $Pd_{20}Pt_{20}(TM1)_{20}(TM2)_{20}P_{20}$ with 3 and 5 mm diameters prepared by copper mold casting. (TM1, TM2) = (Co, Cu), (Co, Fe), (Fe, Cu) and (Cu, Ni) (after [14]).



Fig. 2.3.3-3: (a) XRD patterns of $Zn_{20}Ca_{20}Sr_{20}Yb_{20}(Li_{0.55}Mg_{0.45})_{20}$ in as cast and after 70% compression deformation; (b) the stress-strain curves for $Zn_{20}Ca_{20}Sr_{20}Yb_{20}(Li_{0.55}Mg_{0.45})_{20}$ at strain rates of 10^{-4} and 10^{-5} s⁻¹; (c) the photos of compressed samples (after [10]).



Fig. 2.3.3-4: (a) XRD patterns of Zn₂₀Ca₂₀Sr₂₀Yb₂₀(Li_{0.55}Mg_{0.45})₂₀,

 $Sr_{20}Ca_{20}Yb_{20}Mg_{20}Zn_{10}Cu_{10}$ and $Sr_{20}Ca_{20}Yb_{20}Mg_{20}Zn_{20}$ alloys in plate form respectively; (b) $Sr_{20}Ca_{20}Yb_{20}Mg_{20}Zn_{10}Cu_{10}$ alloy in rods with diameters up to 5 mm. The word "cooled" indicated that the copper mold was cooled before hand by liquid nitrogen (after [56]).

Indeed, HE-BMG research is a new hot spot in the science of advanced metallic materials. To date only a limited quantity of HE-BMGs have been synthesized [10, 14, 37, 56]. However, the funding investment threshold for entering this area is high; and therefore it is not included in the scope of this project.

2.4 Phase Stability in HEAs

The thermo-mechanical treatment and element doping methods are two common ways to control the phase stability in alloy systems. Both of these methods can effectively control the phase formation and phase transformation in an alloy system.

The solid solution phases formed in as-cast HEAs have recently been shown to be essentially metastable. They are indeed the first formed solid state phases to appear upon solidification, which are then retained to the ambient temperature due to the sluggish diffusion kinetics of HEAs. In 2009, Tsai et al. introduced the thermomechanical treatment method to study the phase transformation of Al_{0.5}CoCrCuFeNi at different annealing temperatures [33]. Interestingly, the solely fcc phase that existed in as-cast Al_{0.5}CoCrCuFeNi was transformed to mixed fcc and bcc phases in samples as-forged at 900°C (Fig. 2.4-1) [33]. However, when the as-forged alloy was annealed at 1100°C for 24 hours, followed by water quench cooling, the bcc phase disappeared. In 2010, Tsai et al. further investigated the phase stability of Al_{0.5}CoCrCuFeNi at medium temperature ranges (500 $^{\circ}$ C, 600 $^{\circ}$ C and 700 $^{\circ}$ C). They found that after annealing the specimens for 10 hours, they got the same result found in as-forged specimens at 900°C. Both the mixed fcc and bcc phases precipitated (Fig. 2.4-2) [34]. It is believed that the solely fcc phase of as-cast Al_{0.5}CoCrCuFeNi is a metastable state due to the sluggish kinetics of HEAs. Tsai's findings updated the phase diagram of Al_{0.5}CoCrCuFeNi as predicted by Tong et al. [6] in 2005, and corrected the conclusion that only fcc phase was available in Al_{0.5}CoCrCuFeNi over

the whole temperature range. Tong et al. had been misled in their conclusion by their DTA analysis results (Fig. 2.4-3) [6].



Fig. 2.4-1: XRD patterns of Al_{0.5}CoCrCuFeNi in as-cast, as-forged at 900°C, ashomogenized at 1100°C followed by furnace cooling (FC) and as-homogenized at 1100°C followed by water quench cooling (QC) (after [33]).

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Fig. 2.4-2: XRD patterns of rolled Al_{0.5}CoCrCuFeNi annealed at 500 $^\circ\!C$, 600 $^\circ\!C$ and

700°C for 10 hours (after [34]).



Fig. 2.4-3: Predicted phase diagram of Al_xCoCrCuFeNi alloy system with differentAl contents (x values). L: liquid phase. The phase transition temperatures of the alloys were measured by DTA (after [6]).

Most metallurgical materials are metastable in one way or another. During the casting process, the water-cooled copper mold quickly removes thermal energy from molten HEA and freezes the alloy to a metastable state. In the liquid state, the mixed elements are soluble in each other and have an amorphous structure. As the temperature drops dramatically to freeze the HEAs, they form dendritic and inter-dendritic structures accompanied with nano-precipitates in a solidified matrix, due to the sluggish atomic diffusion and phase separation [1]. By introducing rapid solidification methods, such as splat quenching and melt spinning, highly metastable HEAs are easily obtained in round, flattened sheets or thin ribbons. Even though the

cooling rate of drop-casting in a water-cooled copper mold is much lower than in splat quenching or melt spinning, the cooling rate is still high enough to freeze the phases of the solidified alloy as formed at high temperatures. To learn the phase stability of a tested alloy, the thermo-mechanical treatment method is an effective way to analyze the equilibrium phases of the tested HEAs at particular temperatures.

In the element doping mechanism, the phases in the testing alloy are transformed due to severe lattice distortion caused by doping different sized atoms into the alloy system. Wang et al. discussed the reason for adding Al into the $Ti_{0.5}CrFeCoNiAl_xCu_{1-x}$ alloys, causing structural transitions from fcc to bcc [71]. These researchers claimed that the alloying effect of doping with large atom sized Al introduces high lattice distortion energy. The packing factor of the fcc structure is 0.74, but the packing factor of the bcc structure is 0.68. Therefore, the fcc structure is more closely packed than the bcc structure. In doping large Al atoms into an fcc structure alloy, the original fcc lattice is distorted and transformed into a more stable bcc lattice. Zhou et al. explained this mechanism by using Gibbs free energy in their model of phase transformation induced by lattice distortion in the CoCrFeNiCu_xAl_{1-x} alloy system (Fig. 2.4-4) [11]. According to this elastic model, Gibbs free energy can be expressed as:

$$G = G_P + K x (\Delta V)^2 D$$
 (Equation 2.4-1)

Where G_P is Gibbs free energy of perfect lattice, *K* is a constant and *x* is the Al content. The $\Delta V = V_{Al} - V_{Cu}$, in which V_{Al} and V_{Cu} are the atomic volumes of Al and Cu, respectively, and *D* is the atomic packing efficiency (*D* is 0.74 for the fcc,

and 0.68 for the bcc structure). According to Equation 2.4-1, as $D_{fcc} > D_{bcc}$, the phase transformation from fcc to bcc could effectively lower the value of *G* and obtain a stable state.



Fig. 2.4-4: Schematic illustration of lattice distortion and phase transformation caused by component substitution in multi-component solid solution alloys (MSSAs) (after [11]).

Apart from the effect of different atomic sizes on phase transformation, the intrinsic phase formation properties of particular elements also play pivotal roles in phase formation and transformation. Ke et al. studied the $Al_xCo_yCr_zCu_{0.5}Fe_vNi_w$ system, and found that Ni and Co are fcc stabilizers, but Al and Cr are bcc stabilizers [19]. In this system, 1.11 Co is equivalent to Ni as an fcc stabilizer, and 2.23 Cr is equivalent to Al as a bcc stabilizer [19]. This empirical rule for controlling phase formation is useful, but such a rule is limited to specific alloy systems. Therefore, building a scientific principle for controlling crystal structure and phase formation mechanism in HEAs can contribute to better design of new HEA systems.
2.5 Summary

The solid solution in equi-atomic alloys has become an interesting and timely topic, considering the current intensive interest at HEAs by the material community. In circumstances where there is no such differentiation of the solvents and solutes, the high entropy is claimed to favor the formation of solid solution phases. However, recent studies have shown that inter-metallic compounds or amorphous structures are also possible in HEAs [14, 18, 38, 49, 58, 59, 66, 72, 73].

Despite the remarkable efforts devoted to the development of new HEA systems with improved mechanical and functional properties, scientific understanding of HEAs remains very limited. Previous studies of thermal stability in HEAs have not investigated deeply enough to reveal the complete sequences of phase formations and transformations at different temperatures. More detailed work is required to refine the phase stability analysis. Various structural features make distinct contributions to the mechanical properties, but the key factor in the phase selection mechanism between the fcc or bcc phase in HEAs is unknown. From an alloy design perspective, it is critical to be able to control the incidence and volume percentage of phase formation.

Chapter 3: Methodology

3.1 Materials Preparation

3.1.1 Al_{0.5}CoCrCuFeNi Slabs

The Al_{0.5}CoCrCuFeNi (in atomic proportion) alloys were prepared by arc-melting a mixture of the constituent elements with purity better than 99.9 wt.%, in a Tigettered high-purity argon atmosphere. The melting was repeated five times to achieve a good chemical homogeneity of the alloy. The molten alloy was drop-cast into a 50mm (length) \times 15mm (width) \times 3mm (thickness) copper mold. The 3mm-thick as-cast (AC) alloy was cold rolled (CR) to a 1 mm thickness (a reduction of 66.7%) intermittently, with two high vacuum annealing treatments first at 900°C for 1 hour when rolled to 1.7mm, and then at 900°C for 2 hours when rolled to 1.4mm. After annealing, the samples cooled down inside the furnace. One piece of the 1.7mm-thick samples was water quenched (WQ) after being annealed at 900°C for 1 hour, as a test of the cooling rate effect on phase formation. The 1 mm-thick cold rolled samples were then annealed in the high vacuum at 700°C, 900°C and 1100°C for 1 day, 5 days and 20 days, respectively. All of the annealed samples were cooled down inside the furnace.

3.1.2 Co-free $Al_xCrCuFeNi_2$ (x = 0.2 ~ 2.5) Cylinders

The Al_xCrCuFeNi₂ (x= $0.2 \sim 2.5$) alloys (in atomic proportion) were prepared by arcmelting a mixture of constituent elements with purity better than 99.9 wt.% in a Tigettered high purity argon atmosphere. The melting was repeated at least five times to improve the chemical homogeneity of the alloys, and finally the molten alloys were drop-cast into a 10mm diameter copper mold.

3.1.3 Al_{0.5}CrCuFeNi₂ Slabs

The alloys, with a nominal composition of $Al_{0.5}CrCuFeNi_2$ (elements in atomic ratio), were prepared by arc-melting a mixture of the constituent elements with purity better than 99.9 wt.%, in a Ti-gettered high-purity argon atmosphere. The melting was repeated five times to achieve a good chemical homogeneity of the alloy. The molten alloy was drop-cast into a 50mm (length) × 15mm (width) × 3mm (thickness) copper mold. The 3mm-thick as-cast alloys were cold rolled to a thickness of 1.7 mm (a reduction of 43.3%). Further cold rolling caused cracking of the specimens. Despite the cracking, one sample was cold rolled to 1 mm (a thickness reduction of 66.7%) to test the phase stability of the alloy upon thermo-mechanical treatments. The 1.7 mm thick cold rolled samples were annealed in the argon atmosphere at 700 $^{\circ}$ C, 900 $^{\circ}$ C and 1100 $^{\circ}$ C for 1 day and 5 days, respectively. All of the annealed samples were cooled down inside the furnace.

3.2 Phase and Microstructure Characterization

3.2.1 Al_{0.5}CoCrCuFeNi Slabs

The phase constitutions of annealed samples were identified using the Bruker AXS D8 Discover X-ray diffractometer (XRD) with a Co target. The microstructure of the alloys was characterized using a JEOL JSM-6490 scanning electron microscope (SEM) installed with an energy dispersive spectrometer (EDS), operating at 20kV. For the microstructure observations, the sample surface was sequentially polished down to 0.3 µm grit alumina suspension finish.

3.2.2 Co-free $Al_xCrCuFeNi_2$ (x = 0.2 ~ 2.5) Cylinders

Phase constitutions of the Al_xCrCuFeNi₂ ($x = 0.2 \sim 2.5$) alloys were examined by the XRD using the Co radiation (Bruker AXS D8 Discover). To facilitate the microstructure observation, the sample surfaces were sequentially polished down to 0.3µm grit alumina suspension finish, and then electrochemically etched using the Cica-Reagent, Kanto Chemical (ammonium chloride: 250g, water: 1150ml, glycerin: 600ml). The microstructures of the alloys were examined using the SEM, JEOL JSM-6490. The chemical composition was analyzed using the electron microprobe (JEOL JXA-8230) with wavelength dispersive spectroscopy (WDS). The chemical composition for the fine features was analyzed using a transmission electron microscope – energy dispersive spectroscopy (TEM-EDS), Philips CM20. TEM specimens were prepared by mechanical thinning, followed by twin-jet electrochemical polishing till perforation, with 10 vol.% perchloric acid – 90 vol.% ethanol solution.

3.2.3 Al_{0.5}CrCuFeNi₂ Slabs

The phase constitution of annealed samples was identified using the Bruker AXS D8 Discover XRD with a Co target. The microstructure of the alloys was characterized using the JEOL JSM-6490 SEM equipped with EDS, operating at 20 kV. For the microstructure observation, the sample surface was sequentially polished down to 0.3 μ m grit alumina suspension finish, and then electrochemically etched using the Cica-Reagent, Kanto Chemical. The finer microstructure was characterized using a TEM, JEOL-2100F operating at 200 kV. For the TEM observations, the specimens were first mechanically thinned to less than 80 μ m in thickness and then twin-jet electrochemically polished till perforations, using the 10 vol.% perchloric acid – 90 vol.% ethanol solution.

3.3 Mechanical Testing

3.3.1 Al_{0.5}CoCrCuFeNi Slabs and Al_xCrCuFeNi₂ (x = $0.2 \sim 2.5$) Cylinders

Vickers hardness was measured on the polished surfaces by applying a load of 1kg for 15 seconds dwell time using a Future-Tech microhardness tester.

3.3.2 Al_{0.5}CrCuFeNi₂ Slabs

Vickers hardness was measured on the polished surfaces by applying a load of 1kg for 15 seconds dwell time using a Future-Tech microhardness tester. For the tensile tests, the bar-shaped specimens were wire cut from the as-cast and 1-day annealed alloys, with a gauge length of 12.5mm, a width of 3.2mm and a thickness of around 1mm. Both sides of the specimens were carefully polished (see Fig. 3.3.2-1). The tension specimens were tested to failure at a strain rate of 1×10^{-3} s⁻¹ on an 810 MTS instrument. At least three specimens were tested for each condition to obtain statistical distributions of the tensile properties. The melting point of the alloy was measured using a TA Instruments SDT Q600 differential scanning calorimeter (DSC) in an argon atmosphere, and the heating rate was 20° C/min.



Fig. 3.3.2-1: Tension specimen of Al_{0.5}CrCuFeNi₂.

3.4 Thermodynamics Calculations

The Thermo-Calc program, based on the CALPHAD (calculation of phase diagrams) method [74], was used to evaluate phase constitutions in the multi-component HEAs tested in this project. Thermodynamics describes the equilibrium state of a system, and this is well delineated by the CALPHAD method through implementing the concept of lowering Gibbs free energy. The function for calculating the Gibbs free energy for an individual phase depends on temperature, pressure and composition. The Gibbs free energy function is expressed as Equation 3.4.1 [75]. By setting $\frac{\partial G}{\partial x^{\theta}}$ = 0, the minimization of the total Gibbs free energy under given conditions can be calculated. For a system in isothermal and isobaric conditions, the second law of thermodynamics indicates that equilibrium is attained when the Gibbs free energy reaches its minimum value. After comparing the calculated Gibbs free energy among the selected phases from the well-established thermodynamic databases, the equilibrium phases with the lowest Gibbs free energy values are precipitated in the system. In this project, the calculations of equilibrium phases for Al_{0.5}CoCrCuFeNi and Al_{0.5}CrCuFeNi₂ were based on the TTNI8 Database, which was developed for Ni-based alloys.

$$G = \sum_{\phi} N^{\phi} G_m^{\phi} (T, P, x_i^{\phi})$$
 (Equation 3.4.1)

Where *G* is the total Gibbs free energy, N^{ϕ} is the total number of moles of phase ϕ , G_m^{ϕ} is the Gibbs free energy per mole of components of phase ϕ , *T* is the absolute temperature, *P* is the pressure, and x_i^{ϕ} is the mole fraction of component *i* of phase ϕ .

Chapter 4: Metastability of Solid Solution Phases in Al_{0.5}CoCrCuFeNi HEAs

4.1 Introduction

High entropy alloys (HEAs), are defined as alloys made of multiple (normally \geq 5) principle elements and these principle elements are normally mixed in an equal or nearly-equal atomic ratios [4]. This type of alloy represents a new concept that is distinct from traditional metallic alloys such as steels, Al alloys, or NiAl- and TiAl-based alloys, in which one or at most two elements predominate. The new alloys are termed high entropy alloys because their equal atomic ratio means that the configuration entropy is high, according to Boltzmann's definition of entropy in mixing [5]. One of the interesting characteristics of HEAs is their relatively simple phase constitution. Quite often, only single-phase or dual-phase solid solution phases form (fcc and/or bcc types), without any formation of the intermetallic compounds, expected in traditional theories of physical metallurgy. HEAs can possess some unique mechanical and functional properties, such as high hardness, high wear resistance, high resistance to temperature softening, good resistance to oxidation or corrosion, and low thermal conductivity [1, 2]. As a result, HEAs are attracting ever-increasing interest from materials scientists and engineers.

A great number of HEAs have been developed so far. However, the scientific understanding of HEAs is still at a preliminary stage. Researchers presently lack scientific or even empirical principles for guiding the design of HEAs. More work must be done to achieve the desired phase constitutions and produce enhanced mechanical properties. For example, although simple solid solution phases often form in HEAs, amorphous phase and intermetallic compounds can also appear [26]. (Note that all of the phase constitutions in HEAs are referred to in terms of the ascast state here and afterward, if not otherwise specified.) It is thus important for us to predict the stability of phases (solid solution, amorphous phase or intermetallic compound) from a given HEA composition. Assuming that solid solution phases are formed, can we predict whether fcc-type solid solution or bcc-type solid solutions will form, in a given HEA composition? As we already know, fully fcc-type HEAs are soft and ductile [35], and the HEAs containing bcc phases are generally hard, but tend to be brittle [34]. Therefore, learning how to predict and manage the forms of solutions is critical for designing the mechanical properties of HEAs for structural applications. In the previous section we addressed these important issues, considering the fundamental properties of the constituent elements including the aspects of atomic size mismatch, mixing entropy, mixing enthalpy, electronegativity and electron concentration. Some useful information, although still not definitive, has been extracted from our analyses. For example, we have found that the valence electron concentration (VEC) can critically determine the fcc or the bcc solid solution formation. For further investigation of this factor, please see Chapter 5.

This overview of research to date brings us to a reasonable starting point, considering that most of the reported HEAs are in the as-cast condition. In furthering this research, our first priority was to see how stable the solid solution phases in HEAs are (fcc vs. bcc, or solid solution vs. amorphous phase and

intermetallic compounds). In this area, we do have some validated evidence showing that the solid solution phases in HEAs are quite stable [12, 76-78]. These findings tempt us to think that the phase stability of the as-cast condition represents a broader pattern of conditions across the range of temperature and time. However, we are also aware that in some alloy systems, the as-cast phases can change after undergoing thermo-mechanical treatments and new solid solution phases, or even intermetallic phases can appear [29, 34, 79]. The stability of the solid solution phases in HEAs is hence an inclusive issue, which becomes critical for the study of this class of alloys.

For our research, in clarifying the deterministic factors that control the phase stability in HEAs, we used Al_{0.5}CoCrCuFeNi, an extensively studied HE alloy [6]. This alloy can exemplify the effect of thermo-mechanical treatments on the stability of the solid solution phases. Al_{0.5}CoCrCuFeNi has fcc structure in its as-cast condition. This condition comprises two main fcc phases which appear in the dendritic and inter-dendritic regions, respectively [6, 32], along with some very minor ordered fcc phases that, can be detected only by a TEM, but not by an XRD [6]. Tong et al. gave an approximate phase diagram for the Al_xCoCrCuFeNi (x = 0 – 3.0) alloys, based on the phase transition temperatures as measured from the DTA. According to these measurements, only fcc-type phases appeared across the full temperature range in the Al_{0.5}CoCrCuFeNi alloy [6]. The accuracy of this DTA-determined phase diagram is certainly open to question. In fact, when the alloy was cold rolled and then annealed at 900°C, bcc phases started to appear [33], which contradicted the prediction of the phase diagram. When the alloy was cold rolled

and then annealed at intermediate temperatures ($500 - 700^{\circ}$ C), bcc phases also appeared, together with some unidentified phases (at least at temperatures of 600° C and 700° C, see Fig.2.4-2 or Fig. 10 in Ref. [34]). The complicacy of the Al_{0.5}CoCrCuFeNi alloy makes it an ideal target alloy for investigating the phase stability of the solid solution phases in HEAs.

The research done in this project differs from previous work in two main ways. First, we used a much longer annealing time (up to 20 days) at each selected temperature, to alleviate the kinetic effect on the achievement of the equilibrium phase as much as possible. Second, we performed thermodynamic calculations of the equilibrium phase diagram to verify our experimental observations. The calculated equilibrium phase diagram was critical for determining the HEA's characteristics of slow diffusion at even elevated temperatures [1]. Otherwise, there was no effective way to tell whether the experimentally observed phases had reached their stable states. To the best of our knowledge, this investigation was the first to present an equilibrium phase diagram for HEAs based on the thermodynamic calculations. We expected that a combination of experimental results and theoretical predictions could produce some convincing conclusions on the phase stability of the high-entropy $Al_{0.5}CoCrCuFeNi$ alloy.

4.2 Effect of Thermo-mechanical Treatment

4.2.1 Phase Analysis

Fig. 4.2.1-1 shows the XRD patterns for the cast alloys fabricated through intermittent cold rolling and annealing to the 1 mm-thick cold rolled state. Two fcc phases (fcc1 and fcc2) appeared in the as-cast alloy. After cold rolling to 1.7 mm, the strain-induced peak broadening masked the two fcc phases, and only one set of fcc peaks could be observed. Apparently, these peaks were not symmetric. The bcc phase started to appear after annealing at 900°C for 1 hour, which was similar to what Tsai et al. reported previously [33]. The ordered bcc phase also already appeared at this stage. A faster cooling rate through water quenching from 900 $^{\circ}$ C did not prevent the bcc phases from being formed, although the formation of bcc phases in the water quenched condition appeared to be less than those found in the furnace cooled condition, judging from their relative diffraction intensities. However, Tsai et al. reported that water quenching from 1100°C could prevent the formation of the bcc phase in the same alloy, and that furnace cooling of the same alloy could not. This finding probably indicates that the temperature affects the phase stability more significantly than the kinetic effect. We will come back to this point later in the Thermodynamic Calculations section. In a further step to this experiment, no new phase appeared with additional cold rolling and annealing.



Fig. 4.2.1-1: XRD patterns for $Al_{0.5}$ CoCrCuFeNi alloys measured as-cast, when intermittently cold rolled and annealed, and finally when cold rolled to 1 mmthickness.

The 1 mm-thick cold rolled samples were then annealed at 700°C, 900°C and 1100°C, for 1 day, 5 days and 20 days, respectively. The corresponding XRD patterns are given in Fig. 4.2.1-2. As this figure shows, an extended annealing at 900°C did not essentially change the phase constitution, and two fcc phases (the bcc phase and ordered bcc phase) remained in existence. This result, together with other evidence to be provided later, actually suggested that the solid solution phases were kinetically quite stable in some particular higher temperature ranges. Annealing at 700°C resulted in the formation of two fcc phases, a bcc phase and an ordered bcc phase,

with the additional formation of an intermetallic σ -phase. To our knowledge, this was the first report of an intermetallic phase forming in the Al_{0.5}CoCrCuFeNi alloy. As mentioned in the Introduction section, Tsai et al. did the annealing for this alloy at 600°C and 700°C for 10 hours, and from the XRD patterns they collected (Fig. 10 in Ref. [34]), an intermetallic phase also formed. However, Tsai et al. apparently ignored those weak peaks that corresponded to the σ -phase. By combining the crystallography information with the matching alloying elements, the σ -phase could be CoCr, CrFe, CoNiCr, or more probably the CoCr-, CrFe-, CoNiCr-based solid solutions [68]. Annealing at 1100°C, however, led to another phase constitution in which only fcc-type phases existed: two fcc phases and an ordered fcc phase. This phase constitution was similar to that seen in the as-cast state, except that the extent of the fcc2 phase had increased, and the ordered phase had grown sufficient for detection by XRD.



Fig. 4.2.1-2: XRD patterns for the Al_{0.5}CoCrCuFeNi alloys after annealing at 700 $^{\circ}$ C, 900 $^{\circ}$ C and 1100 $^{\circ}$ C for 1 day, 5 days and 20 days, respectively.

4.2.2 Microstructure Characterization

The microstructures for the as-cast and 1 mm-thick cold rolled alloys are shown in Fig. 4.2.2-1. The as-cast alloy had a clear dendritic structure, and the inter-dendritic region had significant Cu segregation, mainly due to the positive mixing enthalpy between Cu and other alloying elements (see Table 2.3.2-1) [6, 47]. The EDS results for the average chemical compositions in the dendritic regions and inter-dendritic regions (Regions I and II, respectively, as marked in Fig. 4.2.2-1(a)) are given in Table 4.2.2-1. Concerning the phase analysis given in Fig. 4.2.1-1, both the dendritic regions and inter-dendritic regions had the fcc-type structure, and more specifically they corresponded to the fcc1 and fcc2 phases, respectively, as inferred from their relative amounts. The Cu-rich fcc2 phase had a larger lattice constant than that of the main fcc1 phase, as revealed from their relative peak positions.



Fig. 4.2.2-1: Back scattering electron images for the (a) as-cast and (b) 1 mm-thick cold rolled $Al_{0.5}$ CoCrCuFeNi alloys.

Material	Region	Al	Со	Cr	Cu	Fe	Ni
	nominal	9.0	18.2	18.2	18.2	18.2	18.2
AC	Ι	8.0	20.6	21.0	11.5	19.7	19.2
3mm	Π	13.3	6.2	6.4	55.7	5.9	12.5
	Ι	6.3	20.6	22.5	11.9	22.6	16.2
CR 1mm	Π	10.5	6.1	6.4	59.0	5.9	12.1
	III	28.2	11.2	8.1	14.1	9.2	29.2

Table 4.2.2-1: EDS analysis for the as-cast and 1 mm-thick cold rolled

Al_{0.5}CoCrCuFeNi alloys.

Compared to the as-cast alloy, the 1 mm-thick cold rolled alloy showed elongated structures in the dendritic regions, but the inter-dendritic regions became discontinuous. The cold rolled alloy showed three distinguishable and chemically different regions (regions I, II and III, as seen in Fig. 4.2.2-1(b)), rather than the two regions that appeared in the as-cast state. Naturally, this finding also related to the phase analysis given in Fig. 4.2.1-1. In addition to the fcc1 and fcc2 phases in the

as-cast state, a bcc phase had formed, which corresponded to Region III in Fig. 4.2.2-1(b). As seen from the EDS analysis given in Table 4.2.2-1, the bcc phase was rich in Ni and Al, and the amounts of Ni and Al were almost equal. In total, Ni and Al accounted for around 60 at.% of the total alloying elements in this bcc-type phase. The nearly equal atomic ratios of Ni and Al in the bcc phase could also be responsible for the ordered bcc phase that was detected by the XRD: Tong et al. had already shown that the ordered bcc phase had a NiAl-like (B2) crystal structure [6].

Starting from the 1 mm-thick cold rolled state, the alloy samples were annealed at 700° C, 900° C and 1100° C for 1 day, 5 days and 20 days, respectively. The resulting microstructures are shown in Fig. 4.2.2-2. For the 700°C annealed conditions, the elongated dendrites progressively transformed to poly-grained structures as the annealing time increased. There were still some long dendrites left after 20 days of annealing at this temperature, which suggested that the full re-crystallization had not been completed. From the phase analysis given in Fig. 4.2.1-2, we know that compared to the starting state, an additional intermetallic σ -phase also formed. Judging from Fig. 4.2.2-2 (a – c), this σ -phase very possibly corresponded to the rodlike precipitates indicated by the blue arrows. Although the sizes of these intermetallic compounds may have prevented a meaningful EDS measurement of their chemical composition (the probe size of SEM/EDS was no better than 1 μ m), the darker contrast as shown in the back scattering electron images indicated that they could be CrFe- or CoCr- based solid solutions. This possibly was also suggested by the crystallography information that was obtained from the phase analysis. In the 900°C annealed alloys, the rod-like σ -phase did not exist, which

agreed with the XRD results. In the 900 $^{\circ}$ C annealed samples, the microstructure was almost fully poly-grained, and no obvious elongated dendrites existed after one day of annealing at this temperature. Three regions of distinctive chemical contrast were clearly observable, and their compositions were very similar to those of the corresponding regions in the 1 mm-thick cold rolled alloy (see Tables 4.2.2-1 and 4.2.2-2). The 1100°C annealed alloys had a similar microstructure to that of the ascast alloy, which was reasonable in that both alloys had the same phase constitutions (mainly fcc1 and fcc2). The difference was that in the 1100° C annealed alloys, a fully poly-grained structure replaced the dendritic structure found in the as-cast alloy. The amount of the fcc2 phases also increased in the 1100°C annealed alloys, as can be seen from a comparison between Figs. 4.2.2-1 (a) and 4.2.2-2 (g - i), and between the XRD patterns in Figs. 4.2.1-1 and 4.2.1-2. The chemical compositions of the fcc1 and fcc2 in all of the 1100° C annealed samples, regardless of the annealing time, were very close to those in the as-cast alloy, as seen from the EDS results given in Table 4.2.2-2. Grain growth occurred in both the $(900^{\circ}C \text{ and } 1100^{\circ}C)$ annealed alloys, although ideally a detailed linear intercept method would be required to analyze the grain sizes, and secondary electron images of the etched samples are preferred than the back scattering electron images as provided in Fig. 4.2.2-2 (the grain boundary can be better revealed), a rough estimate of the grain size in the 1100 $^{\circ}$ C annealed samples indicated that the grain growth was not significant. The grain sizes changed from ~ 10 μ m in the 1-day annealed sample, to ~ 20 μ m in the 20-day annealed sample. We thus concluded that the contribution of grain size variation to the sample's mechanical properties was limited.



Fig. 4.2.2-2: Back scattering electron images for the Al_{0.5}CoCrCuFeNi alloys after annealing, (a) 700°C/1D; (b) 700°C/5D; (c) 700°C/20D; (d) 900°C/1D; (e) 900°C/5D; (f) 900°C/20D; (g) 1100°C/1D; (h) 1100°C/5D; (i) 1100°C/20D.

Table 4.2.2-2: EDS results for the Al $_{0.5}$ CoCrCuFeNi alloys annealed at 700°C,

 $900^\circ\!\mathrm{C}\,$ and $1100^\circ\!\mathrm{C}\,$ for 1 day, 5 days and 20 days, respectively.

Element (at. %)									
Material		Region	Al	Со	Cr	Cu	Fe	Ni	
		nominal	9.0	18.2	18.2	18.2	18.2	18.2	
700°C	1D	Ι	6.4	21.5	22.9	9.7	21.9	17.6	
		Π	6.6	7.6	7.6	60.6	7.7	9.8	

Element (at. %)								
Material		Region	Al	Co	Cr	Cu	Fe	Ni
		nominal	9.0	18.2	18.2	18.2	18.2	18.2
		III	30.1	11.7	6.3	10.8	9.3	31.7
		Ι	5.7	21.8	21.0	10.1	23.0	17.5
	5D	Π	7.5	5.3	4.5	66.9	5.1	10.7
		III	31.1	11.4	5.3	7.8	9.2	35.3
		Ι	5.9	21.4	22.3	10.5	22.4	17.6
	20D	Π	7.7	5.2	4.1	69.1	4.3	9.6
		III	30.0	11.3	5.9	9.7	9.3	33.8
D°00€		Ι	6.5	21.3	23.4	8.9	23.3	16.5
	1D	Π	9.3	5.1	4.9	64.4	5.1	11.1
		III	29.0	12.1	7.4	10.8	10.0	30.7
	5D	Ι	5.5	23.4	25.3	5.0	23.8	17.1
		Π	9.1	7.6	7.7	55.3	7.7	12.7
		III	29.3	12.0	7.3	9.9	9.6	31.9
	20D	Ι	5.2	23.8	24.9	4.7	23.9	17.5
		Π	9.7	4.1	3.4	67.6	3.7	11.5

Element (at. %)								
Material		Region	Al	Со	Cr	Cu	Fe	Ni
		nominal	9.0	18.2	18.2	18.2	18.2	18.2
		III	30.7	10.6	4.8	11.4	8.5	34.0
1100°C	1D	Ι	8.6	19.7	20.5	13.2	19.7	18.5
		Π	12.0	6.9	5.7	53.9	6.5	15.1
	5D	Ι	8.0	19.9	20.7	12.6	19.9	18.9
		Π	12.1	5.7	4.4	57.6	5.5	14.7
	20D	Ι	8.3	19.4	20.9	13.3	20.4	17.7
		Π	11.4	6.1	5.0	57.8	6.0	13.6

4.2.3 Mechanical Behavior

The hardness variation from the as-cast state, to the 1 mm-thick cold rolled state, through intermittent cold rolling and annealing, is given in Fig. 4.2.3-1. The hardness of the as-cast sample was HV 212, and this increased to HV 362 after the sample was cold rolled to 1.7 mm (~ 43.3% reduction in thickness). One hour of annealing at 900°C decreased the hardness to ~ HV 341, due to the reduced effect of cold rolling. However, this weakening was partially compensated by the strengthening effect of the newly formed bcc (and ordered bcc) phases. This factor could also explain why a lower hardness of HV 302 was obtained in the water

quenched alloy, in which lesser amounts of the bcc phase were formed. The further increases and decreases in hardness after cold-rolling and annealing of alloys were understandable, as these effects were all caused by variations in the strain stored in the materials, and no noticeable phase transformations were involved. The 1 mm-thick cold rolled alloy had a hardness of HV 341. After the first annealing at 900°C for 1 hour, further cold rolling and annealing produced relatively slow changes in hardness.



Fig. 4.2.3-1: Vickers hardness for $Al_{0.5}$ CoCrCuFeNi alloys measured as-cast, after being intermittently cold rolled and annealed, and finally after being cold rolled to 1 mm-thick.

The hardness changes for the alloys annealed at 700 $^{\circ}$ C, 900 $^{\circ}$ C and 1100 $^{\circ}$ C for 1 day, 5 days and 20 days are shown in Fig. 4.2.3-2. In the 700 $^{\circ}$ C annealed conditions, the hardness first increased from HV 341 to HV 362, mainly due to the contribution of the newly formed σ -phase. The amount of the σ -phase did not change significantly with longer annealing time, as seen from both the XRD patterns in Fig. 4.2.1-2 and the microstructures in Fig. 4.2.2-2 (a - c). However, the extended annealing at this temperature induced a progressive structural transformation from the dendrite to the poly-grained structure. The release of strain energy reduced the hardness to HV 341 after 5 days, and to HV 307 after 20 days of annealing. For the 900°C annealing conditions, the hardness initially decreased to HV 261 after 1 day, then decreased more slowly to HV 254 and HV 248, respectively, after 5 days and 20 days of annealing. This decrease was reasonable, as neither significant phase transformations (see Fig. 4.2.1-2) nor microstructure evolutions (see Fig. 4.2.2-2 (d f)) occurred during the extended annealing at this temperature. As for the 1100° C annealing conditions, the hardness changed from HV 341 to HV 265 after 1 day of annealing. We noted that both at phase transformation (the bcc phase disappeared) and the microstructure variation (from dendrites to poly-grains) occurred during this process. The hardness decreased slowly to HV 245 after 5 days of annealing, as with the 900°C annealed alloys, but then the hardness increased to HV 284 after 20 days of annealing. This increase in hardness must be accredited to a growing amount of the fcc2 phase (and very possibly of the ordered fcc phase), as is seen clearly in the XRD pattern in Fig. 4.2.1-2, although this is less sensitively reflected in the microstructures shown in Fig. 4.2.2-2 (i).



Fig. 4.2.3-2: Vickers hardness for the Al_{0.5}CoCrCuFeNi alloys after annealing at 700 °C, 900°C and 1100°C for 1 day, 5 days and 20 days, respectively. The hardness for the as-cast and 1 mm-thick cold rolled alloys are also given as reference.

4.3 Thermodynamics Calculations

As mentioned in the Introduction section, it was difficult to determine whether the phases existing after the thermo-mechanical treatments reached their equilibrium states, as the sluggish diffusion in HEAs [1] would probably require a fairly long time to complete the phase transformation process. Thermodynamic calculations, however, are not affected by the diffusion kinetics. These calculations can supplement the experimental observations, and provide a prediction of the equilibrium phases and their fractions over the full temperature range. The Thermo-

Calc program, which has validated databases for thermodynamic calculations of phase equilibrium and uses the CALPHAD method, has been widely applied in the evaluation of phase stability in complex multi-component alloy systems [80]. We used the Thermo-Calc program to form a preliminary estimation of the equilibrium phase diagram (phase constitution vs. temperature) for the $Al_{0.5}CoCrCuFeNi$ alloy. The obtained results served to evaluate the equilibrium phase relationship for the multi-component alloys with equal or nearly-equal atomic ratios. As both Cu and Co can form continuous solid solutions with Ni over almost the full composition range [81], we approximated the $Al_{0.5}CoCrCuFeNi$ alloy as a Ni-based alloy, and did the preliminary calculations based on the TTNI8 database for Ni-based alloys.

4.3.1 Equilibrium Phase

The aim of our research was to verify the stability of the solid solution phases in HEAs, and to do this we used a series of thermo-mechanical treatments. As shown in Figs. 4.2.1-1 and 4.2.1-2, the solid solution phases (fcc1 + fcc2) in the as-cast Al_{0.5}CoCrCuFeNi alloy were not thermally stable, at least when they were annealed at between 700°C and 900°C. Interestingly, when annealed at a higher temperature of 1100°C (which is close to this alloy's melting temperature of ~ 1279°C) [6], the phase constitution was the same as that found in the as-cast condition, although the relative amount of each phase varied. We also noted that the extended annealing at a fixed temperature for up to 20 days did not change the phase constitution. These phenomena naturally led us to propose the following scenario. The phases we obtained after annealing at 700°C, 900°C and 1100°C were actually the equilibrium

phases at these corresponding temperatures, and they were frozen to the room temperature because the annealing of HEAs was somehow equivalent to a quenching process for conventional alloys. There are two premises that could support this conceptual scenario. First, the equilibrium phases at these relevant temperatures were in agreement with what we saw experimentally. Second, the equivalence of annealing to quenching is valid for HEAs.

The proposed sluggish diffusion features in HEAs [1] may be responsible for an equivalence of annealing to quenching, although we still lack exact diffusion data for the HEAs to support this claim. This problem, however, can be conceptually understood by considering the phase transformation process which requires the cooperative diffusion of elements to achieve the equilibrium partitioning among different phases. The severe lattice distortion that occurs in the HEAs [1, 50] in fact hinders the atomic movement by which diffusion occurs. In other words, although the alloys in our annealing experiments cooled down to room temperature inside the furnace, the cooling time scale can still be regarded as rapid enough, compared to the time scale that would be required for diffusion to complete the phase transformation before solidification. The annealing is hence equivalent to a quenching process in this sense.

We then come back to the first premise. Are the phases we observed experimentally the equilibrium ones at the relevant temperatures? To answer this question, we used the Thermo-Calc software to calculate the equilibrium phase diagram (phase constitution vs. temperature) for the $Al_{0.5}$ CoCrCuFeNi alloy, and the results are

shown in Fig. 4.3.1-1. As seen in this figure, the prediction from the calculations was in good agreement with the experimental observations. At 700°C, the predicted phases were fcc + ordered fcc + ordered bcc + σ -phase, and we observed a progression of fcc1 + fcc2 + bcc + ordered bcc + σ -phase. At 900°C, the predicted phases were fcc + ordered fcc + ordered bcc, and we observed fcc1 + fcc2 + bcc + ordered bcc. At 1100°C, the predicted phases were fcc + ordered bcc, and we observed fcc1 + fcc2 + bcc + ordered bcc. At 1100°C, the predicted phases were fcc + ordered fcc - (a tiny amount of) ordered bcc, and we observed fcc1 + fcc2 + ordered fcc. For convenience, this comparison of the phase constitution between experiments and thermodynamic calculations is shown in Fig. 4.3.1-2.

The discrepancy between the prediction and the experimental results appeared mainly in the fcc2 phase and in the ordering of the fcc and bcc phases. The fcc2 phase formed due to Cu segregation, as explained in Sections 4.2.1 (phase analysis) and 4.2.2 (microstructure characterization). This discrepancy was not a major concern. The discrepancy in the ordering between the prediction and experimental observations could possibly arise from two causes. First, in our experimental results, we identified the disordered or ordered solid solution phases mainly by relying on the XRD patterns. However, the XRD method is inaccurate in measuring the quantitative information on the relative amount of disordered or ordered phases in HEAs, as the diffraction intensities decrease sharply due to the crystalline planes' being distorted by solid solutioning [50]. Singh et al., for example, analyzed the XRD pattern in an as-cast Al_{1.0}CoCrCuFeNi alloy, and detected little indication of ordered bcc phases. However, the TEM images showed bcc phases in this alloy that were mainly ordered [82]. Of course, it is highly possible that the slow kinetics in

HEAs inhibited or at least slowed down the ordering process. Certainly, the ordering information generated from our preliminary calculation needs further refinement.



Fig. 4.3.1-1: Calculated phase diagram (phase constitution vs. temperature) for the Al_{0.5}CoCrCuFeNi alloy using the Thermo-Calc software. The dash-dotted lines indicate the three annealing temperatures used in this project. Symbols in the plot:
A1 for disordered fcc phase, A2 for disordered bcc phase, B2 for ordered bcc phase,

 γ' for ordered fcc phase, σ for σ -phase, and L for liquid phase.



Fig. 4.3.1-2: A comparison of the phase constitution between the experimental observations and the thermodynamic calculations.

In spite of the discrepancy acknowledged above, the very reasonable agreement between the experimental observations and the calculated prediction was encouraging. These results supported our proposed scenario, in which the annealinginduced phases were actually the equilibrium phases at the relevant annealing temperatures, and the cooling from annealing of HEAs could be treated as a quenching process. From Fig. 4.3.1-1, we also see that the intermetallic σ -phase appeared in the temperature range between ~ 300 °C and ~ 850 °C. Below this temperature, the phase constitution was of purely solid solution phases. Above ~ 1100°C and below the melting point, only fcc-type solid solution phases (disordered and ordered) existed. The calculated equilibrium phase diagram is expected to give useful guidance on the design of thermo-mechanical treatments to control the phase constitution in HEAs.

4.3.2 Entropy-driven Phase Stability

In the above section, we proposed that the slow diffusion kinetics in HEAs ensures that the equilibrium phases at elevated temperatures can be frozen to the room temperature even by conventional annealing treatments. The stability of the solid solutions, and particularly the random or disordered solid solutions at high temperatures (in this case above ~ 850° C), is still of interest in considering the phase competition between the solid solution phases and potential intermetallic compounds. In other words, it is important to understand that the thermodynamic nature of the phase stability in the solid solution (SS) phase competes with the intermetallic compound (IM) phase during the solidification process from the liquid state. From an energy perspective, which ultimately determines the phase stability, the formation energy (Δ G) of the SS phase has to be lower than that of the intermetallic compound for the SS phase to win the competition.

The formation energy, ΔG , for a solid solution phase can be defined as the free energy change from the elemental state to the alloy state. The ΔG is related to the enthalpy of mixing, ΔH , and the entropy of mixing, ΔS , as indicated in the equation $\Delta G = \Delta H - T\Delta S$ [44]. As can be perceived from the equation, the contribution from ΔS to ΔG becomes more important (lowering ΔG) at elevated temperatures. This effect is even more significant in HEAs, as the ΔS in HEAs is much higher than that of low entropy alloys [27]. Thus, it is reasonable to attribute the stability of the SS phase at high temperatures to the high entropy effect. This claim is supported by a more refined thermodynamic calculation on the ΔG of the SS phase and IM phase in the AlCrCuFeNi alloy, using the Miedema model. However, it should be pointed out that the high entropy effect in stabilizing the SS phase should not be over exaggerated. If the ΔH is very negative, the IM phase will form anyway [26].

At intermediate temperatures, such as between 300 $^{\circ}$ C and 850 $^{\circ}$ C in the Al_{0.5}CoCrCuFeNi alloy, the contribution of Δ S to Δ G is less significant. As a result, the Δ G of the SS phase is not universally lower than that of the IM phase across a wide composition range. This factor leads to the co-existence of the SS and the IM phases (σ -phase in this alloy). As the temperature drops (to < 300 $^{\circ}$ C here), the Δ S contribution to Δ G is limited, and it is mainly the Δ H that determines the phase stability between the SS phase and IM phase. Therefore, it is not surprising to see the SS phase winning this competition again. A similar trend of phase stability between the SS phase and the IM phase also appears in the Cr₂CuFe₂MnNi alloy. When this alloy is annealed at high temperatures (> 1100 $^{\circ}$ C), only the SS phase exists. However, annealing at intermediate temperatures (in the range of 600 $^{\circ}$ C - 950 $^{\circ}$ C) leads to the co-existence of both the SS and IM phases (ρ -phase) [29]. Clearly, the level of entropy plays a key role in the phase stability of solid solutions in HEAs, particularly at elevated temperatures.

It appears to be the quenched phases that reach equilibrium at temperatures close to the solidus temperature. Currently, in most cases when the HEAs are cast, the alloy temperatures drop sharply from above the liquidus temperature to the ambient temperature. Considering the slow diffusion kinetics in HEAs and the relatively short time scale for solidification, the first-formed solid phases are retained at the room temperature by "quenching" in the Cu mold.

4.4 Summary

The stability of solid solution phases in the high entropy Al_{0.5}CoCrCuFeNi alloy was studied using a series of thermo-mechanical treatments. Although the as-cast alloy had a simple phase constitution of mainly two fcc phases, the cold rolled annealed alloys showed different phase constitutions. Annealing at the intermediate temperature of 700°C led to the co-existence of two fcc phases (disordered and ordered bcc phases), together with an intermetallic σ -phase. At 900°C, the products of annealing were two fcc phases, plus disordered and ordered bcc phases. Interestingly, annealing at 1100°C led to the same phase constitution as in the as-cast alloy, although the relative amount of the Cu-rich fcc phase (and possibly the ordered fcc phase) was higher in the annealed condition. Referring to the calculated equilibrium phase diagram, we found that these annealing conditions induced phases that were actually the equilibrium phases at the relevant annealing temperatures. We suggest that the slow diffusion kinetics in HEAs accounted for the equivalence of annealing to quenching in terms of the phase progression from elevated temperatures to room temperature. We also suggest that the high entropy effect played an important role in determining the phase stability between the solid solution phases and intermetallic compounds in this $Al_{0.5}$ CoCrCuFeNi alloy, and in other HEAs.

Chapter 5: Scientific Principles for Designing HEAs

5.1 Introduction

The generally used alloying elements in HEAs are fcc-type Cu, Al and Ni; bcc-type Fe, Cr, Mo and V; and hcp-type Ti and Co (with a crystal structure at ambient temperature). When these alloying elements are mixed in different combinations, or with same combinations but different amounts of certain elements, fcc, bcc, or mixed fcc and bcc structures may form. For example, cast CoCrCuFeNi (with the same atomic ratio in following references) has the fcc structure, but AlCoCrCuFeNi has the fcc + bcc structure [6]. Altering the amount of Al in the $Al_xCoCrCuFeNi$ system can tune the crystal structure from fcc to fcc + bcc, and to fully bcc [6]. These changes in structure directly affect the alloy's mechanical properties. To again take the Al_xCoCrCuFeNi system as an example, with increasing x, the structure changes from fcc to fcc + bcc, and finally to bcc. The hardness and strength increase with the increasing amount of bcc phases, but the alloys grow brittle [6, 34]. Although the embrittlement mechanism in bcc phases still needs further exploration, it is certainly important to be able to control the formation of bcc phases. Therefore, the target of this project is to discover the physical parameters that control the stability for the fcc and bcc phases in HEAs.

5.2 **Rules for Forming Solid Solution Phases in HEAs**

Wang et al. briefly discussed the reason why adding Al to the Al_xCoCrCu_{1-x}FeNiTi_{0.5} system cause a structural transition from fcc to bcc [71]. These researchers claimed that the alloying of large Al atoms introduces lattice distortion energy, and that the formation of a lower atomic packing efficiency structure, such as bcc, can decrease this distortion energy. This explanation makes sense, but is far from being satisfactory. This theory cannot quantitatively predict when the bcc structure will form as a function of Al additions. Ke et al. claimed that, in the Al_xCo_yCr_zCu_{0.5}Fe_yNi_w system, Ni and Co are fcc stabilizers and Al and Cr are bcc stabilizers: 1.11 Co is equivalent to Ni as an fcc stabilizer, and 2.23 Cr is equivalent to Al as a bcc stabilizer. Furthermore, if the equivalent percentage of Co is greater than 45 at.%, the alloy has an fcc structure, and the alloy has a bcc structure if the equivalent percentage of Cr is greater than 55 at.% [19]. This empirical rule is useful, but it has no scientific merits and is valid only for these specific alloy systems. The establishment of scientific principles to control the crystal structures in HEAs can contribute to the design of HEAs with desirable properties. For example, we can use the less expensive Ni to partially or completely replace the more expensive Co, or we can reduce the amount of Cu, which is known to cause segregation issues because of the mainly positive enthalpy of mixing between Cu and other alloying elements [6].

As a test for the equivalency of Ni and Co as fcc stabilizers, we prepared a series of $Al_xCrCuFeNi_2$ ($0.2 \le x \le 2.5$) alloys to study the effect of Al amount on the phase stability in this alloy system, compared with the well studied $Al_xCoCrCuFeNi$

system. The X-ray diffraction patterns are shown in Fig. 5.2-1. This experiment made it clear that at $x \le 0.7$, the alloys had a single fcc structure, and the bcc phase started to appear at x = 0.8. In the Al_xCoCrCuFeNi system, a fully fcc structure was obtained at $x \le 0.5$ and the bcc phase started to appear at x > 0.8 [6]. The experimental results indicated that Co is not necessarily required in obtaining the solid solution structure in HEAs, which is good for alloy design from an economic perspective. This new alloy system also provided more data for understanding the phase stability in HEAs and the fundamental properties of constituent alloying elements.



Fig. 5.2-1: X-ray diffraction patterns for $Al_xCrCuFeNi_2$ alloys (x = 0.2 ~ 2.5).
Zhang et al. identified relationship between phase stability and atomic size difference, δ , by which $(100\sqrt{\sum_{i=1}^{N} c_i(1 - \frac{r_i}{r})^2}, \bar{r} = \sum_{i=1}^{n} c_i r_i$, where c_i and r_i are atomic percentage and atomic radius of the *i*th component). Theses researchers also devised a formula for the mixing enthalpy ΔH_{mix} , for multi-component alloys, by which the $\Delta H_{mix} = \sum_{i=1, i\neq j}^{n} \Omega_{ij} c_i c_j, \Omega_{ij} = 4\Delta_{mix}^{AB}$, where Δ_{mix}^{AB} is the mixing enthalpy of binary liquid AB alloys [27]. Zhang et al. found that the solid solution tends to form in the region delineated by -15 kJ/mol $\leq \Delta H_{mix} \leq 5$ kJ/mol and $1 \leq \delta \leq 6$. The requirement of atomic size difference for formation of the solid solution structures is not surprising, as it is basically in line with the well established Hume-Rothery rule [61]. The Hume-Rothery rule also gives two further requirements for the formation of solid solutions, namely electro-negativity and electron concentration.

Fang et al. defined the electro-negativity difference in a multi-component alloy system as $\Delta \chi (= \sqrt{\sum_{i=1}^{n} c_i (\chi_i - \bar{\chi})^2}, \bar{\chi} = \sum_{i=1}^{n} c_i \chi_i$, where χ_i is the Pauling electronegativity for the *i*th component) [83]. The effect of electron concentration is a bit more complex. There are basically two definitions of electron concentration: the average number of itinerant electrons per atom (e/a), and the total number of electrons (including the d-electron accommodated in the valence band), which is called the valence electron concentration (VEC) [62, 84]. The e/a or the VEC for a multi-component alloy can be defined as the weighted average from e/a or VEC of the constituent components: $e/a = \sum_{i=1}^{n} c_i (e/a)_i$ or $VEC = \sum_{i=1}^{n} c_i (VEC)_i$, where $(e/a)_i$ and $(VEC)_i$ are the e/a and VEC for the individual elements. The Hume-Rothery rule works with the e/a definition, and e/a has a clear effect on the crystal

structure for the so-called electron compounds, or Hume-Rothery compounds [61]. However, the HEAs comprise mainly transition metals (TMs), and the definition of e/a for TMs is very controversial [62]. Very recently, Mizutani reviewed the various definitions of e/a for TMs and concluded that the e/a for TMs are small positive numbers [62]. Unfortunately, not all e/a for TMs have been determined, and the e/a for each TM element varies in different environments. For convenience, we have used VEC to study the electron concentration effect on the phase stability in HEAs.

5.3 Role of Valence Electron Concentration in fcc or bcc Solid Solution Formation

Following the method used by Zhang et al. [27], the atomic size difference, δ , and the mixing enthalpy, ΔH_{mix} , for the Al_xCoCrCuFeNi [6] and Al_xCrCuFeNi₂ systems are plotted in Fig. 5.3-1. The electro-negativity difference, $\Delta \chi$, and the VEC are also plotted, to show how these factors relate to the Hume-Rothery rule affecting solid solution formation. For convenience, the ΔH_{mix} , $\Delta \chi$ and VEC are all plotted as a function of δ in Fig. 5.3-1, but this does not indicate these parameters are mutually dependent. For comparison, the δ , ΔH_{mix} , $\Delta \chi$ and VEC for three additional systems of HEAs are also plotted in Fig. 5.3-1, namely CoCrCuFeNiTi_x (see Ref. [66]), Al_{0.5}CoCrCuFeNiTi_x (see Ref. [67]) and Al_{0.5}CoCrCuFeNiV_x (see Ref. [22]), in which, compounds are formed in originally fcc-type alloys by increasingly doping the amount of one alloying element (Ti or V). The calculations involved required physicochemical and thermodynamic parameters for the constituent alloying elements, which were drawn from Refs. [45, 47, 63]. Some of these parameters are also listed in Table 5.3-1.



Fig. 5.3-1: Relationship between the mixing enthalpy, ΔH_{mix} (a), the electronegativity, $\Delta \chi$ (b), the valence electron concentration, VEC (c), and the atomic size

difference, δ , for five HEA systems: Al_xCoCrCuFeNi, CoCrCuFeNiTi_x,

Al_{0.5}CoCrCuFeNiV_x, Al_xCrCuFeNi₂ and Al_{0.5}CoCrCuFeTi_x. Note on the legend: fully closed symbols are for solely fcc phases; fully open symbols are for solely bcc phases; top-half closed symbols are for mixes of fcc and bcc phases; left- or righthalf closed symbols are for phases containing at least one compound phase (the leftor right- half simply indicate different types of compounds).

Element	Atom radius (Å)	Pauling Electronegativity	VEC
Al	1.432	1.61	3
В	0.820	2.04	3
С	0.773	2.55	4
Со	1.251	1.88	9
Cr	1.249	1.66	6
Fe	1.241	1.83	8
Mn	1.350	1.55	7
Мо	1.363	2.16	6
Nb	1.429	1.6	5
Ni	1.246	5 1.91	

Table 5.3-1: Physiochemical properties for commonly used elements in HEAs

Element	Atom radius (Å)	Pauling	VEC	
		Electronegativity	VEC	
Та	1.430	1.50	5	
Ti	1.462	1.54	4	
V	1.316	1.63	5	
W	1.367	2.36	6	

As seen from Fig. 5.3-1, using at definition of atomic size difference that mixes enthalpy, valence electron concentration and electro-negativity defined here, ΔH_{mix} is the only effective parameter that can predict the formation of solely solid solutions (hence, no formation of compounds) in HEAs. Solid solutions form when -5 kJ/mol $\leq \Delta H_{mix} \leq 5$ kJ/mol, and compounds tend to form once the ΔH_{mix} is more negative. However, δ , $\Delta \chi$ and VEC all fail to effectively predict the formations of solid solution phases or compounds. Fig. 5.3-1 provides some clues toward obtaining a solely solid solution structure in HEAs based simply on the fundamental properties of constituent elements. This information is certainly useful, but from the measurements shown in Fig. 5.3-1, it is still unclear when the bcc phase formation occurs. A more careful examination of Fig. 5.3-1, however, suggests that bcc phases start to form when the VEC reaches ~ 8.2 (see Fig. 5.3-1 (c)). The other three parameters, ΔH_{mix} , δ and $\Delta \chi$, do not behave with such a clear indicator function. To make the point clearer, the VEC for three HEA systems, Al_xCoCrCuFeNi (see Ref. [6]), Al_xCoCrCu_{0.5}FeNi (see Ref. [19]), and Al_xCoCrCuFeNi₂ (in this project) are plotted in Fig. 5.3-2. In these HEA systems, doping with additional Al causes the phase constitution to shift from a solely fcc to a mixed fcc and bcc phase. Fig. 5.3-2 clearly shows that the VEC can be used to quantitatively predict the phase stability for fcc and bcc phases in HEAs. At VEC \geq 8.2, the solely fcc phase exists. At 6.87 \leq VEC \leq 8.2, the mixed fcc and bcc phases co-exist, and the solely bcc phase exists at VEC < 6.87. We suspect this VEC defined phase stability will work effectively for most cases. To prove this, the VECs for more HEA systems are plotted in Fig. 5.3-3. These systems have fcc, fcc + bcc, or bcc structures containing other alloying elements such as Ti, V, Mn, Nb, Mo, Ta, W, and even metalloid B and C. Data on the VECs of these systems are drawn from Refs. [16, 19, 64, 85, 86]. Although there are still some exceptions, it is clear that the fcc/bcc phase boundary can be delineated by VEC. Concerning the exceptions to this pattern, the VEC-defined fcc/bcc phase boundary seems to work unsatisfactorily for HEA systems containing Mn.



Fig. 5.3-2: Relationship between VEC and the fcc, bcc phase stability for three HEA systems: Al_xCoCrCuFeNi, Al_xCrCuFeNi₂ and Al_xCoCrCu_{0.5}FeNi. Note on the legend: fully closed symbols are for solely fcc phases; fully open symbols are for solely bcc phases; top-half closed symbols are for mixed fcc and bcc phases.



Fig. 5.3-3: Relationship between VEC and the fcc, bcc phase stability for more HEA systems further to Fig. 5.3-2. Note on the legend: fully closed symbols are for solely fcc phases; fully open symbols are for solely bcc phases; top-half closed symbols are for mixed fcc and bcc phases.

5.4 Summary

In summary, the phase stability in HEAs and its relationship to the physicochemical and thermodynamic properties of constituent alloying elements has been systematically studied. The mixing enthalpy determines whether the solid solutions' phases or compounds form within nearly equiatomic multi-component alloy systems. Most importantly, the VEC is found to be the physical parameter that controls the phase stability for fcc or bcc solid solutions. Fcc phases are found to be stable at higher VECs (\geq 8.2), and bcc phases are stable at lower VECs (< 6.87). This project therefore provides valuable input for the understanding of phase stability and the design of ductile crystal structures in HEAs.

Chapter 6: Cobalt-free Al_xCrCuFeNi₂ Alloys

6.1 Introduction

The solid solutions in HEAs are mostly composed of simple fcc- or bcc- types, or a mixture of both. The mechanical properties of HEAs are dominated by the types of their formed solid solutions, although in cases where intermetallic compounds form, the intermetallic compounds might play a more critical role. The fcc-type HEAs usually have good ductility, but their strength is relatively low. The bcc-type HEAs can have much higher strength [32], but their ductility is poor, particularly when under tension. One possible reason is that the ordering of bcc phases causes embrittlement of the material [34, 82]. The difficulty in achieving the seemingly conflicting qualities of strength and ductility in HEAs accounts for the lack of existing reports on room temperature tension data for HEAs, save for a few reports on mainly fcc-type alloys [35, 87-89]. To optimize the mechanical properties of HEAs, it is thus important to effectively control the formation of fcc- or bcc-type solid solutions in HEAs through adjusting the alloy compositions.

In Chapter 5, we showed that the fcc/bcc solid solution formation for as-cast HEAs can be reasonably controlled by tuning the valence electron concentration (VEC). This finding built on the premise that in HEAs, the solid solution phases tend to form preferably. Especially, the elements with higher valence electrons (VE) favor the formation of fcc-type solid solutions. Those elements with lower VE tend to favor the bcc-type solid solution formations. Based on this VEC scheme, we designed a series of $Al_xCrCuFeNi_2$ alloys, by fully replacing the expensive Co element (VE = 9)

with Ni (VE = 10) in the widely studied $Al_xCoCrCuFeNi$ HEAs [6]. We showed that the VEC rule was verified in the newly developed $Al_xCrCuFeNi_2$ alloys, and reported their anomalous solidification microstructures. We believe these microstructures are not seen in other HEAs, and are rarely seen in other conventional non-equiatomic multi-component alloys.

The phase stability, particularly the phase stability of solid solutions, is a critical issue for HEAs. It has been shown in Chapter 4 that the solid solution phases obtained in the as-cast HEAs are actually the first forming solid phases upon cooling from the molten liquids. The preferred formation of solid phase over intermetallic compounds in these HEAs results from the large entropic contribution to Gibbs free energy at high-temperatures [90]. Furthermore, these high temperature stable solid solutions can be preserved in cooling to room temperature, in a manner similar to the freezing of an amorphous phase from the molten liquid [36]. The probable mechanism for preserving these solid phases is the diffusion kinetics, which in HEAs is very sluggish [4]. This sluggishness prevents the transformations towards equilibrium phases from happening within the timescale of the cooling process. If we bearing in mind the metastable nature of solid solutions in the cast HEAs, it is natural to ask a series of questions. What then, are the equilibrium phases? How thermally stable are these metastable solid solutions? Conceivably, when the temperature decreases and hence the entropic contribution to the Gibbs free energy becomes less significant, the solid solutions might not be energetically stable. Intermetallic compounds are thus highly likely to form at intermediate temperatures. However, the formation of such compounds could be kinetically hindered,

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considering the sluggish diffusion kinetics in HEAs. Revealing the phase stability in HEAs thus becomes a challenging topic, which forms another focus of this project.

The target alloy we used for studying phase stability, $Al_{0.5}CrCuFeNi_2$, is one of a series of alloys from the newly developed $Al_xCrCuFeNi_2$ system. Our methodology was to combine experiments and thermodynamic calculations. Experimentally, the as-cast $Al_{0.5}CrCuFeNi_2$ alloys were cold rolled and then annealed extensively at intermediate and high temperatures (700°C to 1100°C). This process allowed us to see how the metastable solid solutions in the as-cast condition evolved with thermomechanical treatments. The cold work was required to provide the driving energy for the phase transformation that occurs during the recrystallization process. The thermodynamic calculation played more than a complementary role here, as the kinetic difficulty in reaching the equilibrium phases in HEAs makes it hard to tell whether the equilibrium conditions have been reached experimentally. The predicted equilibrium phases from the thermodynamic calculations were purely based on energetic considerations, and hence were not affected by kinetic factors. This combination of the experimental approach with thermodynamic calculations provided a unique and a comprehensive understanding of the phase stability in HEAs.

Another focus of this project was the alloy's tensile properties, on which available reports have been rare [35, 87-89, 91, 92]. The tensile properties of the $Al_{0.5}CrCuFeNi_2$ alloys were carefully measured and statistically analyzed. We believe this research to be the first systematic investigation of the tensile properties

of HEAs. We also studied the correlation of tensile properties to indentation behavior which revealed the asymmetry of tension-compression to plasticity in HEAs.

6.2 As-cast Alloys

6.2.1 Phase Analysis

The XRD patterns for the Al_xCrCuFeNi₂ alloys are given in Fig. 6.2.1-1 (a). At $x \le 1$ 0.7, only fcc-type solid solutions were detected. Bcc solid solutions started to be detected at x = 0.8 and the amount of fcc solid solutions decreased with increasing Al. The ordering of the bcc solid solutions was seen to accompany their formation. The ordered bcc phases were already detected at x = 0.9, as seen from the superlattice diffraction peaks. At x = 1.8, fcc solid solutions could not be detected, suggesting either that they no longer existed, or their amount was tiny. We also noted that the peak shapes for the (1 1 0) bcc peaks were all asymmetric for alloys, with $x \ge 1.5$, which indicated the possible superimposition of a different set of bcctype peaks. For clarity, the peak shapes for the (1 1 0) bcc peaks are further highlighted in Fig. 6.2.1-1 (b). The asymmetry of these peaks was robustly judged by the peak fitting procedure, in that if a peak could not be fitted well using one set of Pearson VII shaped peaks [93], and instead good fitting could be reached using two sets of Person VII peaks, then we regarded that peak as asymmetrical. In the Al_xCrCuFeNi₂ alloys, the transition of the solid solution types from fcc to mixed fccand bcc-types, and finally to bcc-types (ordered and disordered) followed the VEC rule that we proposed previously.



Fig. 6.2.1-1: (a) XRD patterns for the as-cast Al_xCrCuFeNi₂ alloys; (b) enlarged view of (a) at $2\theta = 48^{\circ} - 55^{\circ}$

6.2.2 Microstructure Characterization

The representative microstructures for the $Al_xCrCuFeNi_2$ alloys are shown in Fig. 6.2.2-1. For the solely fcc structured alloys, such as $Al_{0.5}CrCuFeNi_2$ as seen in Fig. 6.2.2-1(a), the microstructure showed a typical dendritic structure. The chemical analysis showed that Fe and Cr were more common in the dendritic regions, and Cu was mildly enriched in the inter-dendritic regions (see Table 6.2.2-1). Only one set of fcc peaks was detected by XRD, although the microstructure indicated the existence of two phases. This finding suggested that both the dendritic and inter-dendritic phases had the fcc structure with close lattice parameters. The dendritic structures remained in $Al_{0.9}CrCuFeNi_2$, although at this condition a bcc phase had already formed.

An enlarged view of the inter-dendritic region in $Al_{0.9}CrCuFeNi_2$, as seen in Fig. 6.2.2-2(a), showed a (short) rod form structure. These rods have an average length of about 200 nm, dispersed in the matrix of the inter-dendritic regions. In $Al_{1.2}CrCuFeNi_2$, the dendritic structure completely disappeared, and the microstructure illustrated in Fig. 6.2.2-2(b) showed a universal rod form. No other characteristic microstructural features were observed. This finding suggested that $Al_{1.2}CrCuFeNi_2$ is very close to a eutectic composition, or that composition is within the eutectic coupled zone under the non-equilibrium solidification condition [61]. Most rods were of a similar size to those in the inter-dendritic region in $Al_{0.9}CrCuFeNi_2$, with an average length of ~ 180 nm. Some longer rods with a

length of ~ 450 nm were also seen, as indicated by the dotted ellipse in Fig. 6.2.2-2(b). The microstructures in $Al_{2.0}CrCuFeNi_2$, $Al_{2.2}CrCuFeNi_2$ and $Al_{2.5}CrCuFeNi_2$ were mainly composed of densely distributed colonies, with sunflower or chrysanthemum-like morphologies, i.e., petal-like microstructures radiating from the disk florets and seed-like precipitates densely dispersed inside the disk florets. This morphological analogy was particularly evident in $Al_{2.2}CrCuFeNi_2$, which is therefore highlighted in Fig. 6.2.2-2(c) – (e). Some ribbon-like structures were also observed between the colonies in these alloys, except in $Al_{2.5}CrCuFeNi_2$. The seed-like precipitates were also rarely seen in $Al_{2.5}CrCuFeNi_2$.

The sunflower-like solidification microstructures were never observed in other HEAs, and to our knowledge, were rarely seen in conventional multi-component alloys. We believe that a microstructure most comparable to the structure seen here appears in an as-cast pseudo-binary NiAl(Ti)-Cr(Mo) eutectic alloy (with the nominal composition of Ni-32Al-28Cr-3Mo-4Ti, at.%) [94], in which the eutectic phases presented a sunflower-like morphology. However, the microstructure in the NiAl(Ti)-Cr(Mo) alloy was much coarser than that found in Al_xCrCuFeNi₂ alloys (x = 1.5 - 2.5) in terms of the size of the petals and seed particles, and the spacing between the petals. More specifically, the length of the petals in the NiAl(Ti)-Cr(Mo) alloy was about 50 µm, and the petals reached ~ 10 µm in Al_{2.5}CrCuFeNi₂. The size of the seed-like precipitates was ~ 1 µm in the NiAl(Ti)-Cr(Mo) alloy, and it was ~ 200 nm in the Al_xCrCuFeNi₂ alloys.



Fig. 6.2.2-1: Microstructures for the as-cast $Al_xCrCuFeNi_2$ alloys. x = (a) 0.5; (b) 0.9; (c) 1.2; (d) 2.0; (e) 2.2; (f) 2.5.

Table 6.2.2-1: Elemental analysis for three representative Al_xCrCuFeNi₂ alloys.

		Element (at. %)				
Alloys	Region	Al	Cr	Cu	Fe	Ni
Al _{0.5} CrCuFeNi ₂	Nominal	9.0	18.2	18.2	18.2	36.4

		Element (at. %)				
Alloys	Region	Al	Cr	Cu	Fe	Ni
(WDS)	Dendrite	8.8	20.9	12.8	21.2	36.5
	Inter-dendrite	12.2	14.9	26.3	13.9	32.7
	Nominal	15.1	17.0	17.0	17.0	33.9
Al _{0.9} CrCuFeNi ₂	Dendrite	13.0	20.7	11.8	21.1	33.4
(WDS)	Inter-dendrite: matrix	11.2	20.9	14.2	20.1	33.5
	Inter-dendrite: rod	26.0	13.0	18.4	10.0	32.6
	Nominal	28.5	14.3	14.3	14.3	28.6
	Petal	3.6	53.7	1.3	38.2	3.3
	Inter-petal	35.1	1.4	15.4	7.0	41.1
Al _{2.0} CrCuFeNi ₂ (TEM-EDS)	Floret: matrix	35.6	1.3	16.5	6.3	40.3
	Floret: seed	15.3	32.6	6.3	29.7	16.1
	Ribbon	22.7	20.0	11.4	18.5	27.4
	Inter-colony	19.0	3.9	25.3	9.3	42.6



Fig. 6.2.2-2: (a) Enlarged view of the inter-dendritic microstructure in
Al_{0.9}CrCuFeNi₂; (b) enlarged view of the eutectic microstructure in Al_{1.2}CrCuFeNi₂.
The dash-pointed ellipses indicate traces of the lamellar structure; (c) flower-like
microstructures in Al_{2.2}CrCuFeNi₂; (d) sunflower-like microstructure in region A of
(c); (e) chrysanthemum-like microstructure in region B of (c)

If we combine the phase identification and microstructural information (particularly for the eutectic-like microstructure seen in Al_{1.2}CrCuFeNi₂) with the recently achieved understanding that the phases found in the as-cast alloys are indeed the first formed phases upon cooling from the liquid state [95], then the solidification behavior in the Al_xCrCuFeNi₂ alloys can be envisaged as follows. In Al_{0.5}CrCuFeNi₂, the Fe- and Cr-rich fcc phase formed the dendrite, and the Cu-rich fcc phase solidified later in the inter-dendritic region. Al_{0.9}CrCuFeNi₂ is a hypoeutectic alloy. Its primary phase was the fcc phase in forming the dendrite, and its inter-dendritic phases were fcc/bcc eutectic. The matrix in the inter-dendritic region had a composition of rods with roughly a (Ni, Cu)₅₀(Al, Cr, Fe)₅₀ form, similar to that seen in a B2-structured NiAl-like intermetallic phase [96]. The weak visibility of the superlattice diffraction peaks in the XRD pattern was presumably due to the small presence of the B2 phase, with its weak diffraction intensities [50]. The almost completely eutectic structure seen in Al1.2CrCuFeNi2 suggested either that this was a eutectic composition, or that composition fell into the eutectic coupled zone under a non-equilibrium solidification condition.

Based on the relative volumes of the fcc and B2 phases, and on the B2 phase in $Al_{0.9}CrCuFeNi_2$ having the rod form, it is reasonable to infer that the rods in $Al_{1.2}CrCuFeNi_2$ were in the B2 phase, and that the matrix remained in the fcc phase. Generally, the microstructure in metallic-metallic eutectic alloys presents either a lamellar or a rod form, depending on the interfacial energy [97]. When the two phases have close volume percentages (30% – 50%), a lamellar microstructure is preferred. A rod form is preferred when the volume percentage of one phase is less

than 30%, and particularly if this is the phase that forms the rods. It was therefore surprising to see the B2 phase forming the rods in this Al_{1.2}CrCuFeNi₂ alloy, as its volume percentage was certainly far above 30%, judging from both the XRD and the microstructural observations. The mechanism behind this anomaly could very possibly resemble the effect of the tertiary element in the lamella-to-rod transition in simple metallic alloys [98]. When the partition coefficients for a tertiary element in the two phases vary significantly, that element's gathering at the front of the liquidsolid interface of one phase tends to inhibit that phase's further growth, while the other phase grows relatively faster. Due to the bridging growth mechanism [99], the lagging phase is gradually isolated by the faster growing phase, and finally develops a rod form. Analogously, we believe that the formation of the rod-form B2 phase in Al_{1.2}CrCuFeNi₂ was resulted from its inhibited growth. However, the mechanism in this case could instead involve the difficulty in synergetic diffusion of the elements in the multi-component ordered B2 phase, and simultaneously the relatively faster growth of the less ordered fcc phase. Traces of the lamellar structure could still be observed though, as indicated by the ellipse in Fig. 6.2.2-2(b). Considering the importance of eutectic alloys in high temperature applications and the fine microstructure seen in Al_{1.2}CrCuFeNi₂, this alloy is potentially of engineering interest, and will be further investigated elsewhere.

 $Al_{2.0}CrCuFeNi_2$ and $Al_{2.2}CrCuFeNi_2$ can both be regarded as hyper-eutectic alloys. Their formation of sunflower-like microstructures can be envisaged as follows. The disk floret is the primary phase, and the eutectic structure then grows onto this floret in a radiating manner as the alloy cools further. This scenario is known to occur for the hyper-eutectic Al-35 wt.% Cu alloy, in which the eutectic radiates from the primary CuAl₂ phase [100], and this can well account for the almost perfectly sunflower-like microstructures for Al_{2.2}CrCuFeNi₂, as seen in Figs. 6.2.2-1(e), 6.2.2-2(c) and 6.2.2-2(d), except for the seed-like particles seen inside the disk floret. From XRD analysis, it is known that the main phases in this alloy are two bcc-type phases.

Referring to the elemental analysis results given in Table 6.2.2-1, it is reasonable to infer that a B2 phase formed primarily as the disk floret. This B2 phase then grew alternatively with an A2 (disordered bcc) phase on the disk floret, forming the radiating eutectic structure. The petals were the A2 phase, and they were rich in Cr and Fe, but significantly depleted in Al, Cu and Ni. The matrix of the disk floret and the inter-petal regions had almost the same compositions, which can be written in the form of (Ni, Fe)₅₀(Al, Cr, Cu)₅₀ [96], which supports our assumption that these formations were of the same B2 phase. The chemical composition of the seed particles was rich in Cr and Fe. Judging from their morphology and distribution, these seed particles could very possibly be products of the spinodal decomposition of the B2 phase at a lower temperature, upon further cooling of the alloy, and these particles have the A2 structure. The spinodal decomposition of a bcc phase into two compositionally different bcc phases is commonly seen in HEAs [6]. Generally, however, the products are modulated plates, although in some cases spherical particles are also observed, which minimize the elastic strain energy [101]. The cubic and spherical particles seen here could also originate from the need to minimize the strain energy. If the size of the primary phase is small, or the shape

deviates from the spheroid (ideal isotropic growth), a chrysanthemum-like or a distorted sunflower-like microstructure is expected, as seen in Figs. 6.2.2-2(e) and 6.2.2-1(d). The composition of inter-colony regions can be written in the form of (Ni, Fe)₅₀(Al, Cr, Cu)₅₀ and these regions have the B2 structure, although their compositions (mainly Al and Cu) differ slightly with the B2 phases in the matrix of the floret and the inter-petal regions. The ribbon-like features may also have the B2 structure, as they seemed to form at a higher temperature and they were not seen in Al_{2.5}CrCuFeNi₂. In Al_{2.5}CrCuFeNi₂ there was very little B2 phase, and hence the disk florets and seed particles were not seen.

6.2.3 Mechanical Behavior

The hardness of the Al_xCrCuFeNi₂ alloys increased with the increasing amount of alloyed Al (Fig. 6.2.3-1), in accordance with the previous findings that the bcc phase had a higher hardness/strength than the fcc phase [32]. More specifically, the hardness increased almost linearly from HV 161 at Al_{0.2}CrCuFeNi₂, where only an fcc phase was detected, to HV 393 at Al_{1.0}CrCuFeNi₂, where the main phase was still fcc, but bcc phases had already formed. There was a sharp increase in hardness to HV 520 at Al_{1.2}CrCuFeNi₂, and at this composition the bcc phases were dominant. As shown in the Microstructure Characterization section, Al_{1.2}CrCuFeNi₂ is almost fully eutectic. With a further increase in the volume percentage of the bcc phases and their simultaneous ordering, the hardness increased slowly and reached HV 596 at Al_{2.5}CrCuFeNi₂.



Fig. 6.2.3-1: Hardness for the as-cast $Al_xCrCuFeNi_2$ alloys. The dotted lines are drawn to guide the eyes.

6.3 Effects of Thermo-mechanical Treatment

6.3.1 Phase Analysis

The XRD patterns for as-cast, cold rolled, and 1-day and 5-day annealed $Al_{0.5}CrCuFeNi_2$ alloys at 700°C to 1100°C are shown in Fig. 6.3.1-1. In both the ascast and cold rolled alloys, there appeared to be only one fcc phase. In alloys annealed at 700°C, both the bcc and ordered fcc phases formed, and the amount of ordered fcc phase increased with extended annealing time. The intensities of the ordered fcc phase became weak in 900°C and 1100°C annealed alloys. The bcc phase was still observed in 900°C annealed alloys, but this phase disappeared in 1100°C annealed alloys. The lattice constants for the fcc and ordered fcc phases were calculated to be ~ 3.59 Å, and the ordering reaction made almost no change to the lattice parameter. The lattice constant for the bcc phase was ~ 2.88 Å.



Fig. 6.3.1-1: XRD patterns for as-cast (a), cold rolled (b), and for alloys annealed for 1-day and 5-day, at 700 $^{\circ}$ C (c) and (d), at 900 $^{\circ}$ C (e) and (f) and at 1100 $^{\circ}$ C (g) and (h),

respectively.

6.3.2 Microstructure Characterization

Fig. 6.3.2-1 shows the microstructures for as-cast, cold rolled and annealed $Al_{0.5}CrCuFeNi_2$ alloys. Dendritic structures were observed in the as-cast and cold rolled alloys. The EDS analysis (given in Table 6.3.2-1) showed that the dendritic

region and inter-dendritic region had very similar chemical compositions, although Cr was seen to be slightly enriched in the inter-dendritic region and Al was slightly depleted. We note here that the Cu segregation in Co-free $Al_{0.5}CrCuFeNi_2$ was much less significant than that in $Al_{0.5}CoCrCuFeNi$ [6], possibly because of the increase in Ni, and hence the extended solutions of Cu in Ni [102]. Another reason for Cu segregation could be the mixing enthalpy in Cu-Ni (+4 kJ/mol), which was less positive than in Cu-Co (+6 kJ/mol) [47]. The XRD results (see Fig. 6.3.1-1) showed that both dendritic and inter-dendritic regions had an fcc structure, and the lattice constants were very close.



Fig. 6.3.2-1: Secondary electron images for $Al_{0.5}CrCuFeNi_2$ alloys (a) as-cast, (b) cold rolled. Other sections show alloys annealed for 1-day (1D) and 5-day (5D) at different temperatures: sections (c) and (d) at 700°C, sections (e) and (f) at 900°C, and sections (g) and (h) at 1100°C. The circles in (e) and (f) highlight the needle-like

features.

Table 6.3.2-1: EDS analyses for as-cast (AC), and 5-day (5D) annealed

Material		Element (at. %)				
	Region	Al	Cr	Cu	Fe	Ni
	Nominal	9.0	18.2	18.2	18.2	36.4
AC	Dendrite	7.9	21.0	11.6	21.6	37.9
	Inter-dendrite	1.9	27.4	13.7	20.7	36.2
700℃/5D	Dendrite	7.1	22.5	10.9	23.3	36.2
	Inter-dendrite	4.1	34.1	13.3	18.1	30.4
900℃/5D	Grain	6.0	19.6	13.2	22.8	38.5
	Particle	3.2	62.8	4.3	17.7	12.0
1100°C/5D	Grain	6.3	23.6	12.4	21.5	36.2

The dendritic morphology remained in alloys annealed at 700°C, indicating that at this temperature ($T/T_m = 0.56$, with T_m measured to be 1242°C by DSC) the recrystallization was not yet complete. As seen in Table 6.3.2-1, the compositions of the dendritic region were similar to those in as-cast alloys, which suggested that dendritic regions had the fcc structure. The XRD result (Fig. 6.3.1-1), indicated that

the inter-dendritic regions had a mixed fcc and bcc structure. As a result, the compositions for the inter-dendritic regions in Table 6.3.2-1 should be interpreted as the averaged compositions of the fcc and bcc phases. A closer look at the dendritic region revealed interesting features: flourishing needle-like microstructures appeared to be decomposed from the dendrites, as shown in Figs. 6.3.2-2 and 6.3.2-3. A typical TEM image for these needles is shown in Fig. 6.3.2-3, with the corresponding selected area diffraction pattern given in the inset. The needles typically had a width of ~ 60 nm, and a length of ~ 1 μ m. TEM analysis revealed that these needle-like microstructures had the L1₂-type ordered fcc structure, as evidenced by their indexed superlattice diffraction spots. The microstructural observation was in agreement with the XRD result (see Fig. 6.3.1-1).



Fig. 6.3.2-2: (a) Needle-like microstructures in the 700° C/1-day annealed Al_{0.5}CrCuFeNi₂ alloy; (b) an enlarged view of needle-like microstructures.



Fig. 6.3.2-3: A typical TEM image of needle-like microstructures in the 700° C/1-day annealed Al_{0.5}CrCuFeNi₂ alloy, with the selected-area diffraction pattern shown in the inset. Indexed diffraction spots comprise both allowed and forbidden (or superlattice) reflections for the fcc structure.

Poly-grained microstructures were observed in alloys annealed at 900°C and 1100°C, which indicated that the recrystallization had completed above 900°C (T/T_m > 0.72). A comparison of the compositional information and the XRD result (see Fig. 6.3.1-1), suggests that the poly-grains in the 900°C annealed alloys had an fcc structure, and the inter- or intra-granular particles had a bcc structure. The composition of the fcc and bcc phases seen here (Table 6.3.2-1) also reasonably satisfied the VEC rule, in that fcc phases had a larger VEC (> 8.2), and bcc phases had a smaller VEC (< 6.87). The compositions of the fcc-structured poly-grains were quite similar to the fcc

structured dendrites seen in the as-cast and 700° C annealed alloys. The bcc structured particles were significantly enriched in Cr, but depleted in Al, Cu and Ni. A small amount of needle-like ordered fcc phases could still be observed in the 900 °C annealed specimens, as pointed out by the circles in Fig. 6.3.2-1 (e) and (f). This observation was also in agreement with the XRD result (Fig. 6.3.1-1).

The extension of annealing time from 1 day to 5 days did not cause significant grain growth, as the poly-grain size increased from ~ 7.5μ m to ~ 12.6μ m, and the particle size increased slightly from ~ 1.4μ m to ~ 2.0μ m. No apparent secondary particles were observed in 1100° C annealed alloys, and this echoed the XRD result (Fig. 6.3.1-1), in that there was no bcc phase formation in these alloys. The small amount of ordered fcc phases that was detected by XRD could not be observed microstructurally in the 1100° C annealed alloys. The grain boundaries in 1100° C/5-day annealed alloy were difficult to be revealed by etching, and we believe that the seemingly secondary phases inside the grains were etching artifacts. The average grain size increased slightly from ~ 30μ m to ~ 36μ m when the annealing time was extended from 1 day to 5 days, but the size of the larger grains increased more significantly, typically from ~ 45μ m to ~ 80μ m.

6.3.3 Mechanical Behavior

Fig. 6.3.3-1 shows the hardness variation for as-cast, cold rolled and annealed $Al_{0.5}CrCuFeNi_2$ alloys. The hardness of the as-cast alloy was HV 218, and this

increased to HV 382 after being cold rolled from 3mm down to 1.7mm in thickness. Annealing at 700°C for one day increased the hardness to HV 419. This hardening could originate from the newly formed bcc phase and from the $L1_2$ structured phase. The extension of annealing time to 5 days at this temperature caused a slight decrease in hardness to HV 410, probably due to the recovering process that released the strain energy. Unlike the results for the cold rolled alloy, one day of annealing at 900°C caused almost no change, as the hardness shifted only from HV 382 to HV 380. In this case, the hardening due to the newly formed bcc phases and a small amount of L1₂ structured phases was balanced by the hardness reduction due to the fully released strain energy during the recrystallization process. Even when the annealing time was extended to 5 days, the hardness remained nearly constant (moving to HV 383). Annealing at the higher temperature of 1100°C caused the hardness to drop to HV 305 and then HV 306 after annealing for 1 day and 5 days, respectively. Apparently, the hardness reduction due to the recrystallization could not compensate for the hardening due to the new phase formation. The fact that the hardness could remain almost constant after extensively annealing the alloys at such a high temperature $(T/T_m = 0.88)$ was indeed impressive. This anti-softening character at elevated temperatures offers great potentials for HEAs to be used in high temperature environments.



Fig. 6.3.3-1: The Vickers hardness for as-cast (AC), cold rolled (CR), and 1 day (1D) and 5 days (5D) annealed alloys, at different temperatures.

The indentation impressions of as-cast and 5-day annealed alloys are shown in Fig. 6.3.3-2. Interestingly, slip lines around the impressions could only be observed in the alloys that contained no bcc phase, i.e., the as-cast and 1100° C annealed alloys. For 700°C and 900°C annealed alloys, no slip lines could be spotted. Chang et al. suggested that the occurrence of slip lines around the indentation impression could be used to roughly gauge the plasticity of HEAs, and those showing slip lines should have good plasticity [103]. Considering that the formation of the bcc phase in HEAs tends to embrittle the material [6], the observed slip line phenomena seemed to support Chang's argument. However, the tension results indicated that the slip lines could at most be considered as indicators of malleability (at compression), rather than ductility (at tension).



Fig. 6.3.3-2: Optical micrographs of the indentation impressions of Al_{0.5}CrCuFeNi₂. Sample conditions are (a) as-cast, (b) 700°C/5-day annealed, (c) 900°C/5-day annealed, and (d) 1100°C/5-day annealed.

Room temperature tensile behavior is rarely reported for HEAs, mainly because of the seemingly contradictory high strength and high tensile ductility of HEAs at room temperature. Fcc-structured HEAs usually have some tensile ductility, but their strengths are low. However, HEAs containing the bcc phase can have high strength, but poor tensile ductility, if the premise is correct that the bcc phases significantly strengthen the material. As a result, the reported mechanical behavior of HEAs mainly comes from compression tests, but only a limited number of reports for tension test results are available [35, 87-89, 91, 92]. Surprisingly, the few available

reports on tensile properties provided no information on the scattering of tensile strength or elongation. The reproducibility and reliability of such data are certainly critical, especially if we consider the possibility of many casting defects in the ascast HEAs and the sensitivity of tensile properties to these defects. To deal with this issue, we carefully measured the tensile properties of both solely fcc-structured and bcc phase-containing HEAs, and both as-cast and thermo-mechanically treated alloys. The scattering of the tension data was evaluated with care.

Representative engineering stress-strain curves for as-cast and 1-day annealed $Al_{0.5}$ CrCuFeNi₂ alloys are presented in Fig. 6.3.3-3, with the statistical results of the tensile strength and elongation given in Fig. 6.3.3-4 and Table 6.3.3-1. The main results of this test were in accordance with the previous observations on the mechanical behavior of HEAs. As-cast alloys with disordered fcc structures had, on average, a yield stress (σ_v) of 363 (± 59) MPa, a fracture stress (σ_u) of 500 (± 18) MPa and an elongation (ε_p) of 16.1% (± 6.7%). The fractured surfaces showed a dimple-like morphology that is typical of ductile deformation behavior. The scatterings on the yield strength and fracture strength were reasonable, but the variation in tensile elongation was large. Alloys annealed at 700 $^\circ\!C$ had a σ_y of 630 (± 270) MPa, a σ_u of 922 (± 247) MPa and an ϵ_p of 4.2% (± 1.4%). The fractured surfaces exhibited many cracks, and this significantly brittle fracture behavior could possibly explain the anomalously low tensile strength of these 700°C annealed alloys. Their strengths were lower than those of 900°C annealed alloys, and this went against the trend in hardness variation for these alloys (see Fig. 6.3.3-1 and Table 6.3.3-1). The best σ_v and σ_u obtained for 700°C annealed alloys were 1085 and 1326

MPa, respectively, and these values are believed to more truly reflect their intrinsic properties. The cracks might have been initiated from the remaining casting defects or the L1₂ structured phases, whose formation may have caused the material to fail before reaching its intrinsic strength. Alloys annealed at 900°C had a σ_y of 704 (± 186) MPa and a σ_u of 1088 (± 17) MPa. The scattering on σ_u was small, but it was relatively large for σ_y . However, the scattering on σ_y was much smaller than that for the 700°C annealed alloys. The fractured surface exhibited mixed dimple-like and micro-cracking features. The average tensile strain, or ε_p , of tested specimens was 5.6% (± 3.4%), which was close to the widely accepted threshold tensile ductility of 5% (marked in Fig. 6.3.3-4 (b)). Alloys annealed at 1100°C typically showed a brittle inter-granular fracture behavior, resulting in a σ_y of 360 (± 96) MPa, a σ_u of 639 (± 5) MPa, and a limited ε_p of 3.4% (± 0.6%). The scatterings on both the tensile strength and elongation were relatively small.


Fig. 6.3.3-3: Tension stress-strain curves for as-cast and 1-day (1D) annealed $Al_{0.5}CrCuFeNi_2$ alloys at 700°C, 900°C and 1100°C. The insets show their fracture surface morphologies.



Fig. 6.3.3-4: A comparison of tensile strengths for as-cast and 1-day annealed $Al_{0.5}CrCuFeNi_2$ alloys at 700°C, 900°C and 1100°C. The 5% tensile strain, commonly accepted as the threshold strain differentiating ductile or brittle behavior, is marked for reference.

Table 6.3.3-1: Yield strength, ultimate tensile strength and elongation of as-cast (AC) and 1-day (1D) annealed Al_{0.5}CrCuFeNi₂ alloys at 700°C, 900°C and 1100

	Hardness (H, MPa)	Yield strength (σ_y , MPa)	Η/σy	Ultimate tensile strength (σ_u, MPa)	Η/σu	Elongation $(\varepsilon_p, \%)$
AC	~ 2138	363 ± 59	5.3 ~ 6.7	500 ± 18	4.2 ~ 4.4	16.1 ± 6.7
700 °C/ 1D	~ 4105	630 ± 270	3.8 ~ 10.6	922 ± 247	3.1 ~ 6.1	4.2 ± 1.4
900 °C/ 1D	~ 3727	704 ± 186	4.5 ~ 6.5	1088 ± 17	3.4 ~ 3.5	5.6 ± 3.4
1100 °C/ 1D	~ 2986	360 ± 96	6.4 ~ 10.5	639 ± 5	4.6 ~ 4.7	3.4 ± 0.6

The measured tensile properties had some agreements with the behavior of the slip lines as seen in Fig. 6.3.3-2 in that apparent slip lines were observed in ductile alloys, i.e., as-cast alloys, but not in brittle or quasi-brittle alloys, i.e., 700° C and 900° C

annealed alloys. However, there was an apparent discrepancy. Alloys annealed at 1100°C exhibited distinctive slip lines around the indentation impressions, but they were tensile brittle. This result suggested that the slip lines could not serve as an indicator of ductility (at tension), and at most these lines could be related to the malleability (at compression). This explanation needs further experimental verification. However, the experimental results already observed here and elsewhere suggested that a tension-compression asymmetry exists in the plasticity of HEAs. For example, in Ref. [77] it was reported that the as-cast AlCoCrCuFeNi alloy had a large compressive plasticity, but this alloy was known to be tension brittle [87]. The listed hardness to strength (σ_y or σ_u) ratios in Table 6.3.3-1 obviously deviate from the Tabor's relation (H $\approx 3\sigma$, $\sigma = \sigma_y$ or σ_u) in the positive direction [104, 105]. According to a recent statistical analysis of the relation between hardness and strength [105], this positive deviation is ubiquitous for brittle metallic glasses or ceramic materials.

6.4 Thermodynamics Calculations

6.4.1 Metastability of the Solid Solution Phases

The Thermo-Calc program, based on the CALPHAD method, has been widely used to evaluate the phase constitution in complex multi-component alloy systems [80]. However, its application to multi-component alloys with equiatomic or close-toequiatomic compositions has been sporadic so far [106-108]. In this work, the Thermo-Calc program was used to obtain an estimation of the equilibrium phases at various temperatures for the Al_{0.5}CoCrCuNi₂ alloy. The calculations were based on the TTNI8 database, which was developed for Ni-based alloys. Calculations based on this database were proven effective in Chapter 4 for analysis of a high entropy $Al_{0.5}$ CoCrCuFeNi alloy.

One unique characteristic of HEAs is their formation of simple solid solutions within highly concentrated multi-component alloys. Naturally, one can question the stability of these solid solutions, especially in the as-cast condition. Are these solid solutions equilibrium phases? There are possibly two ways to clarify this matter: 1) experimentally, by using thermo-mechanical treatments to see whether any phase transformation is occurring, and 2) theoretically, by calculating the equilibrium phase diagram based on thermodynamic considerations, for example by using the CALPHAD method [80]. However, caution is needed for both of these methods. For the thermo-mechanical treatments, it is hard to determine whether the equilibrium condition has been reached, particularly if we consider the reportedly slow diffusion kinetics of HEAs [1, 4, 109]. However, the reliability and accuracy of thermodynamic calculations depends greatly on the availability of databases that have been proven to work effectively, and such database are lacking for HEAs. There are already a few reports on calculating the equilibrium phase diagrams for HEAs [106, 108], and we expect that the thermodynamic calculations will play an increasingly important role in understanding the phase stability of HEAs. In a previous investigation (in Chapter 4), we used the Thermo-Calc software to calculate the equilibrium phases for an Al_{0.5}CoCrCuFeNi high entropy alloy at different temperatures, and compared the theoretical predictions with experimentally detected This experiment led to phases after thermo-mechanical treatments. an

unprecedented understanding of the stability of solid solution phases in HEAs. Basically, it was proposed that the solid solution phases in as-cast alloys are actually the first formed solid phases in the process of solidification. These solid solutions are energetically stable at high temperatures due to their significant entropic contribution to the Gibbs free energy [90], which is a unique characteristic of HEAs. Furthermore, these high temperature-stable solid solutions are frozen when reduced to room temperature, as enabled by the slow diffusion kinetics of HEAs. In other words, the time for cooling is simply too short compared with the timescale required to complete the phase transformations. Similarly, for annealed alloys, equilibrium phases at the annealing temperatures are also frozen to the room temperature, even when the specimens are cooled inside the furnace rather than water quenched. Following the same methodology, we examined the above proposed scenario using the Co-free Al_{0.5}CrCuFeNi₂ alloy.

The calculated equilibrium phases at different temperatures for $Al_{0.5}CrCuFeNi_2$ are shown in Fig. 6.4.1-1. We note that the predicted melting point is ~ 1246°C, which is almost exactly equal to the experimentally measured value (1242°C). This certainly gives some confidence concerning the validity of the thermodynamic calculations. By comparing the predictions with experimental results, and assuming that equilibrium phases have been reached after thermo-mechanical treatments, it can be concluded that the above proposed scenario for HEAs was reconfirmed in this experiment. According to Fig. 6.4.1-1, the first formed solid phases are two disordered fcc phases. Experimentally, as-cast alloys comprised two disordered fcc phases, which had close lattice parameters. The calculated equilibrium phases at 1100° C also involved two disordered fcc phases, but the experimentally observed phases in 1100° C annealed alloys were one disordered and one ordered fcc phase. This discrepancy in ordering between the thermodynamic calculations and experiments was also found for the previously studied Al_{0.5}CoCrCuFeNi alloy. This finding suggests the need for an updated materials database specially designed for HEAs. At 900°C, the calculated equilibrium phases are two disordered fcc phases and one ordered bcc (B2) phase, but experiments on 900°C annealed alloys showed a composition of one disordered fcc phase, one ordered fcc phase and one disordered bcc phase. Once again, the agreement between predictions and experimental results was good, except for the discrepancy in ordering. When the temperature decreased from 900 $^{\circ}$ C to 700 $^{\circ}$ C, other equilibrium phases existing at 900°C remained but two new phases formed: one ordered fcc phase (γ' phase with the L1₂ structure) and one σ -phase. Experimentally, 700 °C annealed alloys had a simpler phase constitution: one disordered fcc phase, one ordered fcc phase and one disordered bcc phase, i.e., the same as phase found in the 900 $^{\circ}$ C annealed alloys. Apart from the ordering issue, an additional discrepancy was the existence of the σ -phase. Further investigation of the σ -phase is covered in Section 6.4.2.



Fig. 6.4.1-1: Equilibrium calculation results of the phase fraction (mass) as a function of temperature for the $Al_{0.5}CrCuFeNi_2$ alloy. Three annealing temperature points used in this project are marked for reference. Symbols in the plot: $A1^1$ and $A1^2$ for two compositionally different disordered fcc phases, B2 for the ordered bcc phase, γ' for the ordered fcc phase, σ for the σ -phase, and L for the liquid phase.

6.4.2 The σ -phase

The σ -phase is an important class of topologically close-packed (TCP) phases. This phase has a tetragonal crystal structure and is known to be hard and brittle. The σ -phase can have the compositions of CrFe, CoCr or CoFeNi. The compositional ranges are large, and are not limited to the stoichiometric compounds [110]. The formation of this phase often tends to lower the ductility and toughness of the

material. The σ -phase was predicted to exist in the low to intermediate temperature range (~ 300°C to 850°C) in the Al_{0.5}CoCrCuFeNi alloy, and was experimentally detected in 700°C annealed alloys. The σ -phase was also experimentally observed in HEA systems such as Al_{0.3}CrFe_{1.5}MnNi_{0.5} [111], AlCoCrFeMo_{0.5}Ni_x [112], CoCrFeNiTi_x [113], AlCoCr_xFeMo_{0.5}Ni [114], Al_{0.3}CoCrFeNiMo_{0.1} [115], AlCo_xCrFeMo_{0.5}Ni [68] and Al_{0.5}CoCrCuFeNiV_x [22]. For the target alloy used in this project, Al_{0.5}CrCuFeNi₂, thermodynamic calculations suggested that the σ -phase can form in the low temperature region up to ~ 850°C (Fig. 6.4.1-1). However, this phase was not experimentally observed in 700°C annealed alloys, either by the XRD (Fig. 6.3.1-1) or by microstructural observation (Fig. 6.3.2-1).

The failure to observe the σ -phase could originate from insufficient driving energy or insufficient annealing time. For the Al_{0.5}CoCrCuFeNi alloy, a direct annealing of the cast alloy at 700°C for one day, without the precursory cold rolling process, did not produce any σ -phase. To exclude the driving energy factor as much as possible, we conducted two more experiments. First, we cold rolled the alloy to 1.7 mm (a 43.3% reduction in thickness) and annealed the sample for the extensive time of 20 days at 700°C. Second, we further cold rolled the alloy to 1 mm (a 66.7% reduction in thickness) and annealed it for 5 days at 700°C. The XRD results for the two newly treated alloys are given in Fig. 6.4.2-1, and no σ -phase was detected in either case. It is safe, therefore, to conclude that the σ -phase does not exist in 700°C annealed alloys.



Fig. 6.4.2-1: (color online) XRD patterns for the cold-rolled to 1.7 mm and then 700 $^{\circ}C/20$ -day (20D) annealed Al_{0.5}CrCuFeNi₂ alloy, and the cold-rolled to 1 mm and 700 $^{\circ}C/5$ -day (5D) annealed alloy. Results for the cold-rolled to 1.7 mm then 700 $^{\circ}C/7$

1-day (1D) and 5-day (5D) annealed alloys are also included for comparison.

The discrepancy on the σ -phase most probably originated from using a non-ideal database for thermodynamic calculations. The accuracy of Thermo-Calc calculations relies on a high quality thermodynamic database, developed by critical assessments and systematical evaluations of various experimental data and theoretical information. As mentioned previously, our calculations were based on a database that was specially designed for Ni-based alloys and not for HEAs. Although a general agreement between thermodynamic calculations and experimental results was achieved, the occurrence of some discrepancies, such as

those regarding to the ordering of phases, is understandable. The prediction of the temperature window for the σ -phase could also be inaccurate.

6.5 Summary

By using the valence electron concentration rule that we proposed previously, a series of Co-free Al_xCrCuFeNi₂ high entropy alloys were developed, fully replacing the expensive Co element with Ni in the widely studied Al_xCoCrCuFeNi alloys. The hardness of these alloys increased with the increasing amount of the alloyed Al. Interestingly, the solidification microstructure, or more specifically, the eutectic microstructures in these alloys showed some anomalies that were not seen in other high entropy alloys, or even in conventional multi-component alloys. Submicron rod-like microstructures existed in the fcc/B2 eutectic alloy, although the volume percentage of the rod-like B2 phase was high. Sunflower-like microstructures existed in the hyper-eutectic alloys, with the primary B2 phase composed of disk florets, with eutectic A2-type petals and B2-type inter-petal phases radiating from the disk florets. Also fine spinodal decomposed A2 phase took the appearance of seed particles.

The phase stability and tensile properties of an $Al_{0.5}CrCuFeNi_2$ high entropy alloy were systematically studied. Revealing the phase stability of the solid solution phases is a critical issue for HEAs, but a thorough understanding of these phases has been complicated by the slow diffusion kinetics of HEAs, which makes the phase transformation towards the equilibrium phases difficult to complete. Our investigation of phase stability combined both thermo-mechanical experiments and thermodynamic calculations, providing a more innovative and comprehensive understanding of this important topic. Prior to this project, tensile properties have rarely been reported for HEAs, and no statistical study of these tension properties has been done previously. In this project, however, the tensile properties of the Al_{0.5}CrCuFeNi₂ alloy were systematically studied, and their correlations to indentation behavior were also investigated. The main conclusions from this project are summarized below.

- (1) The metastable nature of the solid solution phases in HEAs was confirmed. Due to the slow diffusion kinetics in HEAs, high temperature-stable phases could be easily retained in cooling to room temperature, as the timescale required to complete the phase transformations was much longer than that of the cooling process. The experimental observations were in a basic agreement with the thermodynamic calculation predictions.
- (2) The phase constitutions in the as-cast and 1100°C annealed alloys were both composed of fcc structured solid solutions, with the only differences being in the level of ordering. The bcc phase formed in 700°C and 900°C annealed alloys. In 700°C annealed alloys, the σ-phase was absent, but needle-like L1₂ structured phases were prominent. In 900°C annealed alloys, fine L1₂ structured phases also existed, taking a needle-like form.
- (3) The Al_{0.5}CrCuFeNi₂ alloy exhibited impressive microstructural (grain growth) and mechanical stabilities (hardness) against high temperatures up to 1100° C (T/T_m = 0.88).

(4) Only as-cast alloys with disordered fcc structures and a dendritic morphology showed sufficient tensile plasticity. The 700°C annealed alloys with the highest hardness exhibited abnormally low tensile strength, even though they possessed the highest hardness, possibly due to the initiation of cracks from remaining casting defects, or the effects of needle-like L1₂ structured phases. A large variability in tensile properties was recorded. The HEAs exhibited tension-compression asymmetry on plasticity, and their relationship between hardness and strength deviated significantly from that predicted by Tabor's rule.

Chapter 7: Conclusions and Future Work

7.1 Conclusions

This project conducted a systematic study of the phase stability of HEAs in response to thermo-mechanical treatments and alloying element effects. The scientific principle for distinguishing the stability of fcc and bcc solid solutions was established by introducing a physical parameter of VEC. Based on the experimental and thermodynamic calculation results, and on our theoretical analysis, we can draw the following conclusions.

(1) Phase stability of Al_{0.5}CoCrCuFeNi:

The stability of the solid solution phases in the high entropy $Al_{0.5}CoCrCuFeNi$ alloy was studied using a series of thermo-mechanical treatments. Although the as-cast alloy showed a simple phase constitution of mainly two fcc phases, the cold rolled annealed alloys showed different phase constitutions. Annealing at the intermediate temperature of 700°C led to the co-existence of two fcc phases, disordered and ordered bcc phases, and an intermetallic σ -phase. At 900°C, the annealing products were two fcc phases, plus disordered and ordered bcc phases. Interestingly, annealing at 1100°C led to the same phase constitution as that seen in the as-cast alloy, although the relative amount of the Cu-rich fcc phase (and possibly the ordered fcc phase) was higher in the annealed condition. By referring to the calculated equilibrium phase diagram, it was found that these annealing induced phases were actually the equilibrium phases at the relevant annealing temperatures. The slow diffusion kinetics in HEAs was suggested to account

for the equivalent quenched-in of these phases from elevated temperatures to the room temperature. The high entropy effect was believed to play an important role in determining the phase stability between the solid solution phases and intermetallic compounds in this Al_{0.5}CoCrCuFeNi alloy, as well as other HEAs.

(2) The effect of VEC on stability of fcc or bcc phase in HEAs:

The phase stability in HEAs and its relationship to the physicochemical and thermodynamic properties of constituent alloying elements were systematically studied. The mixing enthalpy determined whether solid solution phases or intermetallic compounds formed in the nearly equiatomic multi-component alloy systems. Most importantly, the VEC was found to be the physical parameter to control the phase stability for fcc or bcc solid solutions. Fcc phases were found to be stable at higher VECs (≥ 8.2), but bcc phases were stable at lower VECs (< 6.87). This project has therefore provided valuable input for understanding phase stability and for designing ductile crystal structures in HEAs.

(3) Phase stability and unique solidification morphology in a Co-free Al_xCrCuFeNi₂ system:

By using the VEC rule that was proposed previously, a series of Co-free $Al_xCrCuFeNi_2$ high entropy alloys were developed, fully replacing the expensive Co element with Ni in the widely studied $Al_xCoCrCuFeNi$ alloys. The hardness of these alloys increased with the increasing amount of the alloyed Al. Interestingly, the solidification microstructure, or more specifically, the eutectic microstructures in these alloys showed some anomalies that were not seen in other high entropy alloys, or even in

conventional multi-component alloys. Submicron rod-like microstructures existed in the fcc/B2 eutectic alloy, although the volume percentage of the rod-like B2 phase remained high. Sunflower-like microstructures existed in the hyper-eutectic alloys, with the primary B2 phase constituting disk florets, with eutectic A2-type petals and B2-type inter-petal phases radiating from the disk florets. Also fine spinodal decomposed A2 phase took the appearance of seed particles.

(4) Phase stability and mechanical behavior of Al_{0.5}CrCuFeNi₂:

The phase stability and tensile properties of an Al_{0.5}CrCuFeNi₂ high entropy alloy were systematically studied. The investigation of the phase stability in this project combined both thermo-mechanical experiments and thermodynamic calculations. providing a more innovative and comprehensive understanding of this important topic. To date, tensile properties have rarely been reported for HEAs, and no statistical study of their tension properties has been done previously. However, the tensile properties of the Al_{0.5}CrCuFeNi₂ alloy were systematically studied in this project, and their correlations with indentation behavior were also investigated. The main conclusions concerning the phase stability and mechanical properties of Al_{0.5}CrCuFeNi₂ are summarized below.

(i) The metastable nature of the solid solution phases in HEAs was confirmed. Due to the slow diffusion kinetics, high temperature stable phases could be easily preserved to room temperature, as the timescale required to complete the phase transformations was much longer than that of the cooling process. The experimental observations were in reasonable agreement with the thermodynamic calculation predictions.

- (ii) The phase constitutions in the as-cast and the 1100°C annealed alloys were both composed of fcc structured solid solutions, with the only difference being in the level of ordering. Bcc phase formed in 700°C and 900°C annealed alloys. In 700°C annealed alloys, the σ -phase was absent, but needle-like L1₂ structured phases were prominent. In 900°C annealed alloys, fine L1₂ structured phases also existed, taking a needle-like form.
- (iii) The Al_{0.5}CrCuFeNi₂ alloy exhibited impressive microstructural (grain growth) and mechanical stabilities (hardness) against high temperatures up to 1100° C (T/T_m = 0.88).
- (iv) Only as-cast alloys with disordered fcc structures and a dendritic morphology showed sufficient tensile plasticity. The 700°C annealed alloys with the highest hardness exhibited an abnormally low tensile strength, even though they possessed the highest hardness, possibly due to the initiation of cracks from the remaining casting defects or the effect of the needle-like L1₂ structured phases. A large variability of measured tensile properties was recorded. HEAs exhibited tension-compression asymmetry on plasticity, and their relationship between hardness and strength deviated significantly from that predicted by Tabor's rule.

7.2 Suggestions for Future Work

One advantage of HEAs for potential structural application is their high strength and hardness. However, at present, the achievement of high strength and hardness in HEAs is done at the sacrifice of ductility. The ductile HEAs are composed of purely fcc-type solid solutions, and their strength is relatively low. The formation of bcc-type solid solutions (which accompany the ordered bcc phases) and of inter-metallic compound phases can improve the strength significantly, but they also tend to embrittle the alloys. This issue has to be solved to pave the way for the structural application of HEAs. The strength and ductility of HEAs can be fine-tuned by modifying the phase constitutions or the microstructures. For example, phase formation can be influenced by tuning the relative composition of the disordered and ordered fcc phases, or by introducing gradient structures in fcc-type HEAs through the surface mechanical attrition treatments (SMAT). By such design methods, new HEAs with both high strength and high ductility may be developed.

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