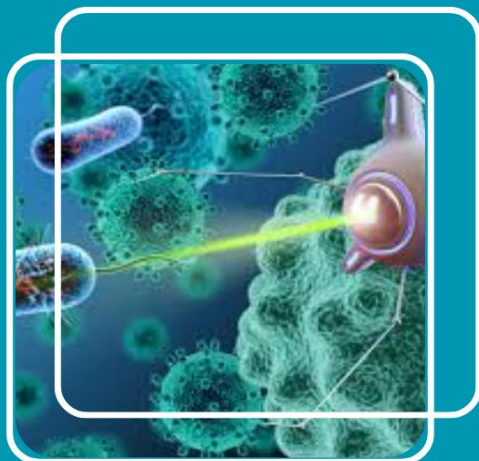


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# Phase Development in High Entropy Alloys as a Result of Interactions Between Constituent Elements

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## Abstract

Many elements may be found in high entropy alloys (HEAs), with five or more main elements in an equiatomic or nearly equiatomic ratio, together with or without minor elements. The name suggests that high mixing entropy is the only factor that determines whether HEAs form solid solution alloys or phases, however other studies have shown that the mutual interaction between elements is a more important factor. Based on the following factors: atomic size difference ( $\delta$ ), mixing entropy ( $\Delta S_{mix}$ ), mixing enthalpy ( $\Delta H_{mix}$ ), valence electron concentration (VEC), and electronegativity difference ( $\Delta\chi$ ), this research proposes guidelines for alloy design in HEAs that aim to generate solid solution phases. Additionally, the impact of an additional parameter  $\Omega$  is covered. The parameter  $\Omega$  is related to the enthalpy of mixing, which is a function of both the time it takes for the components to melt and their average melting point. When these conditions are satisfied, a solid solution phase will develop. Future advancements in HEAs will be greatly motivated by these parametric restrictions.

**Keywords:** High entropy alloys; Atomic size difference solid solution; Crystal structure; Solid solution

## Introduction

An improved metallic substance known as high entropy alloys (HEAs) evolved after bulk metallic glasses (BMGs) were developed. In the late 18th century, Achard proposed the idea of HEAs; in the middle of the 1900s, Yeh and colleagues investigated multicomponent alloys [1,2]. The outstanding features of HEAs, which are often found in single solid solution form, have piqued the interest of the materials world. These qualities include resistance to wear, high hardness, softening at higher temperatures, corrosion, and oxidation. The conventional wisdom of powder metallurgy does not apply to the alloy design approach in HEAs. In contrast to the creation of intermetallic compounds in traditional physical metallurgy processes, the phases formed in HEAs are usually solid solution FCC and/or BCC organized. Consequently, HEAs have received a lot of attention throughout the last decade. Research into HEAs has mostly concentrated on identifying phases, studying microstructures, and determining mechanical and physical characteristics, according to the state of the art [3-8]. The influence of atomic size, valence electrons, and electronegativity of component elements on HEAs was only partially considered, but the results are promising nevertheless [9,10].

Specifically, phase transition in HEAs happens for certain element combinations when the quantities of Al, Cu, Mo, Nb, Si, Ti, and V go over a specific limit. As a result of lattice expansion changing the phase towards a lower  $2\theta$  value, the addition of Ti to AlCoCrFeNiTi<sub>x</sub> transforms the BCC phase to BCC1 (AlNi rich) and BCC2 (Fe-Cr rich) [11]. The same holds true for Al<sub>x</sub>CoCrCuFeNi HEAs; when  $x=0$ , the resulting structure is an FCC, but for  $x=1-1.3$ , the addition of Al transforms the FCC into an FCC+BCC. The FCC+BCC crystal structure may be transformed into a BCC structure by adding more Al ( $x=2.3-3$ ) [12,13]. To examine how adding Al affected the tensile characteristics, He JY et al. synthesized a series of (FeCoNiCrMn)<sub>100-x</sub>Al<sub>x</sub> ( $x=0-20$  at.%) [14]. According to their findings, the brittleness of HEAs is enhanced by the creation of the BCC phase, which causes an increase in tensile strength and a reduction in ductility as a result of the addition of Al. The purpose of this review is to get a better understanding of the physical factors that have a significant impact on the stability of FCC and BCC phases in homogeneous electrolytes.

## Analysis

Research on the microstructure and mechanical properties of ascast AlCoCrFeNiV<sub>x</sub>, Al<sub>0.5</sub>CoCrFeCuFeNiV<sub>x</sub>, and CoCrFeMnNiV<sub>x</sub> HEAs with added vanadium has shown that, as the percentage of vanadium increases, the material's hardness decreases and its ductility increases [15,16,17]. Data from the phase analysis of The absence of Al and Cu in the CoCrFeMnNiV<sub>x</sub> phases proves that they are single solution FCC phases. While Al<sub>0.5</sub>CoCrFeCuFeNiV<sub>x</sub> exhibits both FCC and BCC phases ( $x=0.2-1$ ) in contrast to AlCoCrFeNiV<sub>x</sub>, which only yields BCC phases. The change from the FCC to BCC phase in AlCoCrFeNiV<sub>x</sub> occurs because Al has a much larger atomic radius than the other elements in the compound. Similarly, the presence of Al as a BCC stabilizer and Cu's relatively high positive enthalpy compared to other elements [9,18] cause the FCC+BCC phase to form in Al<sub>0.5</sub>CoCrFeCuFeNiV<sub>x</sub>. As a result of Nb's high atomic radius, the BCC phase is produced in AlCoCrFeNb<sub>x</sub>Ni alloys for  $x=0.10-0.412$ , whereas the FCC phase forms in CoCrFeNiNb<sub>x</sub> alloys for  $x=0.103-0.412$  [19,20]. In this case as well, Al stabilizes the BCC. The BCC phase peaks arise at  $x=0.4$ , corresponding to the Si concentration, and their

strength increases as the Si content increases, according to the phase study of Al<sub>0.5</sub>CoCrCuFeNiSix conducted by Xiaotao Liu et al. Because Cu has a positive enthalpy, adding Si to a solid solution of the FCC phase causes the phase to change from FCC to FCC+BCC. The separation of Cu occurs as a consequence of this [21].Zhu et al. conducted extensive research on AlCoCrCuFeNiMox and AlCoCrFeNiMox to study the impact of Mo and Cu. In the first composition, the material shows a combined BCC and FCC structure up to x=0-0.2. After that, only the BCC phase forms (x=0.2-1). In the second composition, the BCC phase is visible for x=0-0.1, and adding Mo (x=0.1-0.5) causes the formation of an unidentified  $\alpha$  phase [22,23]. Elements with spin d-electrons, known as transition materials (TM), have been the focus of much research in HEAs. In order to ensure structural stability in HEAs, it is crucial to examine the properties of d-electrons. The two characteristics that are affected by the d-electrons are the electronegativity and valence electron concentration. The valence electron concentration, or VEC, is the sum of all electrons and d-electrons contained inside the valence band [9,24]. The ability of an atom to attract electrons is known as electronegativity. Humphrey also states that atomic mismatch, often termed atomic size difference, is a highly essential aspect in alloy design. When considering the novel class of HEAs with lattice distortion, atomic mismatch is also an important factor [25]. In order to forecast the stability of phases in solid solutions, we are taking these factors into account in the current investigation.

## Result and Discussion

$\Delta H_{\text{Mix}}$ ,  $\Delta S_{\text{Mix}}$ , VEC,  $\delta$ ,  $\Delta\chi$ , and  $\Omega$  for a series of multicomponent alloys which are in equiatomic or near to equiatomic were statistically analysed and listed in Table 1. The calculations of different parameters were done by Meidema's approach. All the listed alloys were prepared by casting technique and phase analysis was carried out in as cast condition. Table 1 shows the mixing enthalpy calculated by Miedema's approach.

Element	Al	Si	Ti	V	Cr	Fe	Co	Ni	Cu	Nb	Mo
Al		-19	-30	-16	-10	-11	-19	-22	-1	-18	-5
Si			-66	-48	-37	-35	-38	-40	-19	-56	-35
Ti				-2	-7	-17	-28	-35	-9	2	-4
V					-2	-7	-14	-18	5	-1	0
Cr						-1	-4	-7	12	-7	0
Fe							-1	-2	13	-16	-2
Co								0	6	-25	-5
Ni									4	-30	-7
Cu										3	19
Nb											-6

**Table 1:** Mixing enthalpy (kJ/mol) calculated by miedema's approach [30]

According to the Hume-Rothery (H-R) rule, the atomic size difference is a potent parameter in controlling or determining the solubility of alloys. H-R rule for binary alloys, the atomic size difference is defined by  $|r_A - r_B|/r_B$  where  $r_A$  and  $r_B$  are atomic radii of solute and solvent respectively. For simplicity, Zhang, *et al.* studied the collective behavior of constituent elements and gives the relation for atomic mismatch ( $\delta$ ), mixing enthalpy ( $\Delta H_{\text{Mix}}$ ), and mixing entropy ( $\Delta S_{\text{Mix}}$ ) on the solid solution phases of multicomponent alloy, which are:

$$\sqrt{\sum_{i=1}^n C_i \left(1 - \frac{r_i}{r}\right)^2} \quad \delta = 100 \quad (1)$$

Where  $r = \sum_{i=1}^n C_i r_i$ , n is the number of alloying elements,  $C_i$  and  $r_i$  are the atomic percentage and atomic radius of the  $i^{\text{th}}$  element respectively.

$$\Delta H_{mix} = \sum_{i=1, i \neq j}^n \Omega_{ij} C_i C_j \quad (2)$$

Where  $\Omega_{ij} = 4\Delta_{mix}^{AB} \Delta_{mix}^{AB}$  is the mixing enthalpy of binary liquid AB alloys and

$$\Delta S_{mix} = -R \sum_{i=1}^n C_i \ln C_i \quad (3)$$

Where R is the gas constant (8.314 J/mol. K) [26,27].

Fang, *et al.* studied the relationship between the phase stability and electronegative difference in a multicomponent alloy system, which is given as

$$\Delta\chi = \sqrt{\sum_{i=1}^n C_i (\chi_i - \bar{\chi})^2} \quad (4)$$

Where  $\bar{\chi} = \sum_{i=1}^n C_i \chi_i$  is the Pauling Electronegativity for the  $i^{\text{th}}$  element [28].

Gue and Thaddeus introduced the effect of valence electron concentration (VEC), which is the number of total electrons accommodated in valence band, given by

$$VEC = \sum_{i=1}^n C_i (VEC)_i \quad (5)$$

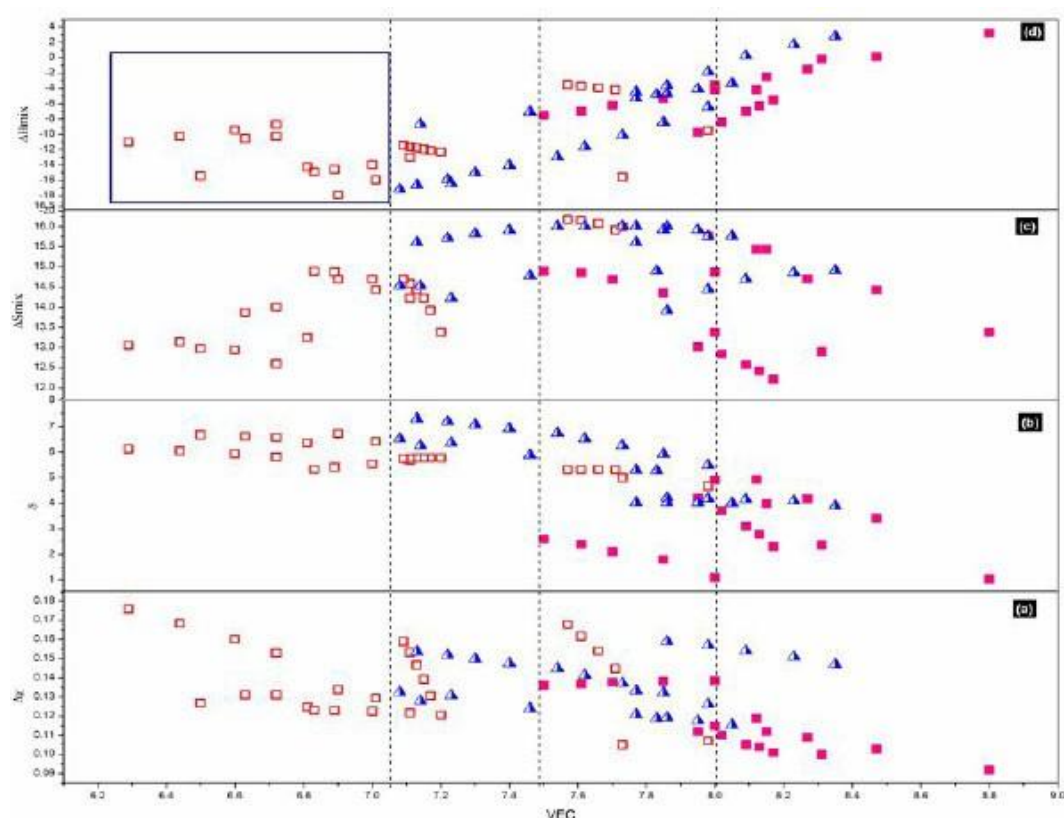
Where  $(VEC)_i$  is the VEC for the  $i^{\text{th}}$  element [24,29].

In addition of these three critical parameters, another one more parameter,  $\Omega$  is used to predict the phase formation behavior of HEAs, given as

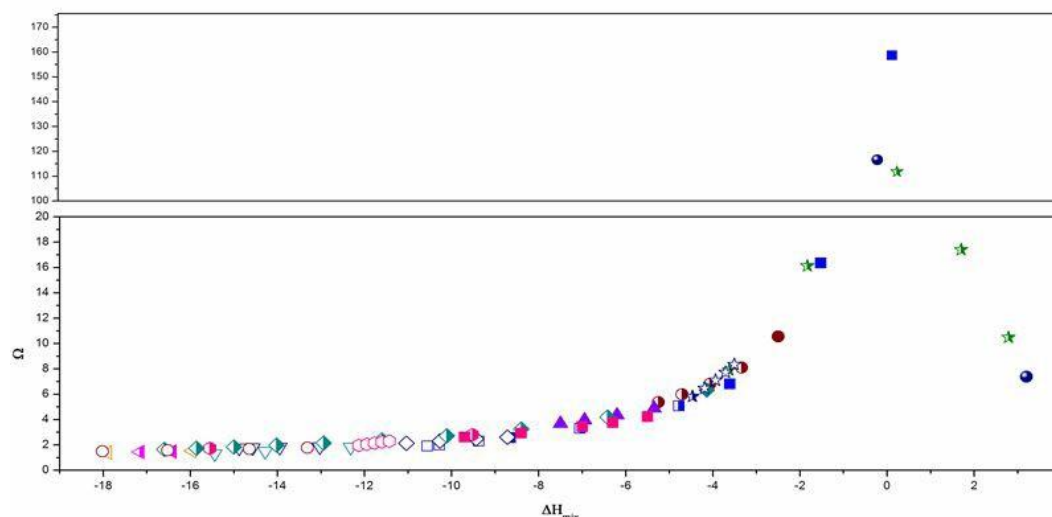
$$\Omega = \frac{T_m \Delta S_{mix}}{|\Delta H_{mix}|} \quad (6)$$

Where  $T_m$  is the melting temperature of n-elements alloy and calculated as  $T_m = \sum_{i=1}^n C_i (T_m)_i$  here,  $(T_m)_i$  is the melting point temperature of the  $i^{\text{th}}$  element [21].

To forecast the stability of FCC and BCC solid solutions, however, this empirical connection criteria is valid for certain combinations of the component constituents. This paper's goal is to examine the physical characteristics that may be used to predict the stability of FCC and BCC phases in HEAs. The authors Tong et al. examined how the inclusion of aluminum changed the mechanical characteristics and microstructure of an  $\text{Al}_x\text{CoCrCuFeNi}$  multi-component alloy. The alloys exhibited a basic FCC structure when  $x < 0.5$ , according to their observations. At  $x = 0.8$ , we found FCC and BCC phases that were intermingled. Spinodal breakdown resulted in the formation of a single BCC structure for Al concentrations  $x > 1.0$ -2.8. The result was a rise in hardness value and structural transfer from FCC to FCC+BCC to BCC. The strong binding interactions between Al atoms and other metallic atoms, the solid solution hardening, and the relatively large size of Al atoms all contribute to this phenomenon [12]. The hardness value of  $\text{Al}_{0.5}\text{CoCrCuFeNiTi}_x$  grew as the titanium concentration did, according to Chen et al. Although the wear resistance did not significantly improve up to 0.6 Ti content, it increased fast from 0.6 to 1.0 Ti content and reached its maximum at  $x = 1.0$  [9]. Light transition metal (Cr, Mn, Fe, Co, Ni, Cu) based HEAs have a greater mixing enthalpy in the FCC phase, as shown in Figure 1. However, when big size elements like as Al, Ti, V, and Nb are included, the enthalpy lowers. Figure 1 demonstrates that the mixing enthalpy ranges from -9.7 to 3.2 for the FCC phase for the majority of the materials investigated in this work. The stability of a single BCC phase is compromised and the majority of FCC phases are produced in the area when the VEC ranges are more than or equal to 7.95. In contrast, all three combinations—FCC, BCC, and FCC+BCC—have been seen for VEC values between 7.2 and 7.95, however the BCC phase exhibits great stability for VEC values less than or equal to 7.2. The range of atomic mismatch ( $\delta$ ) for the FCC phase is  $1.03 \leq \delta \leq 3.7$ , for the BCC phase it is  $5.33 \leq \delta \leq 7.01$ , and for the FCC and FCC+BCC phases it is  $3.7 \leq \delta \leq 7.01$ . It can be seen that the value of  $\delta$  grows as the quantity of element in composition increases, while the enthalpy drops for the same compositions, in connection to the mixing enthalpy ( $\Delta H_{\text{mix}}$ ) and atomic mismatch ( $\delta$ ). According to Figure 1, the FCC phase was not stable when the electronegativity ( $\Delta\chi$ ) value was more than or equal to 0.138, while both the FCC and FCC+BCC phases were stable when the electronegativity ( $\Delta\chi$ ) value was less than or equal to 0.11. The inverse proportionality of  $\Delta H_{\text{mix}}$  and  $\Omega$ , as expressed mathematically, is confirmed by Figure 2.



**Figure 1:** Variation of different parameters with Valence Electron Concentration (VEC). Note on the Legend: Fully Closed Symbols for Sole FCC, Fully Open Symbols for Sole BCC Phase; Right-Half Closed Symbols for Mixes FCC and BCC Phases



**Figure 2:** Variation of  $\Omega$  with respect to mixing enthalpy ( $\Delta H_{mix}$ ) for variety of high entropy alloys

The critical value  $\Omega=1$  is proposed to form the solid solution. If  $\Omega>1$ , the solid solution formation will be more and if  $\Omega\leq 1$  intermetallic compound formation and also segregation will exceed that of solid solution to form [13,31]. The analysis done in this work of  $\Omega$  also satisfies the condition given above. However, the exactness of these criterion requires more experimental analysis to make sure. Figure 2 shows the variation of different parameters with respect to valence electron concentration. This clearly indicates that, the beyond the 7.25 value of VEC, mixing enthalpy goes on increase. But, changes in cases of mixing entropy, atomic size mismatch and electronegativity variation in values with VEC value does not follows any specific pattern.

## Conclusion

Multiple scholars have investigated the geometric influence and thermodynamic approach to phase selection analysis for as-cast high entropy alloys. In multi-component systems that are either equiatomic or non-equiatomic, the high mixing entropy is not the sole criterion for predicting the solid solution phases of BCC, BCC, and FCC+BCC. For the purpose of predicting phases in HEAs, this article summarizes several empirical conditions. Factors such as atomic size mismatch, valence electron concentration, mixing enthalpy, and controlling the development of the FCC and BCC phases relies heavily on electronegativity. The FCC phases are stable for  $VEC > 7.95$ , whereas the BCC phase is very stable for  $VEC < 7.2$ . Each of the three possible combinations—FCC, BCC, and FCC+BCC—has been seen with VEC values ranging from 7.2 to 7.95. Atomic size mismatch is another crucial characteristic; in this case, the FCC phase remains stable for  $\delta < 3.7$ , whereas the BCC phase is formed for  $\delta > 5.33$ . This work also discusses the effect of electronegativity and notes that the FCC phase was not stable for  $\Delta\chi > 0.138$ , while the FCC and FCC+BCC phases are stable for  $\Delta\chi \leq 11.5$ . For multi-component HEAs, an additional parameter  $\Omega$  is computed, which suggests that  $\Omega$  should be greater than or equal to 1 in order for the solid solution phase to be stable.

## References

1. First, Murty BS, Yeh JW, and Ranganathan S (2014) High-Entropy Alloys: An Overview of Their Origins and Development. Hyperentropy alloys 1–12. Rajanathan S. (2003) said 2. Mixed delights: beverages infused with several metals. Research in Science 85: 1404-6.3. The microstructure and wear behavior of high-entropy alloys  $Al_xCo_{1.5}CrFeNi_{1.5}Ti_y$  were studied by Chuang MH, Tsai MH, Wang WR, Lin SJ, and Yeh JW in 2011. The abstract is published in Acta Mater 59: 6308-17. 4. Alloys with Multiple Components and High Entropy (Cantor B. 2014). Thermodynamics 16: 4749–68. 5. Microstructure and Properties of  $Al_{0.5}CoCrCuFeNiTi_x$  ( $x=0-2.0$ ) High-Entropy Alloys, by Chen MR, Lin SJ, Yeh JW, Chen SK, Huang YS, and colleagues (2006). Thesis published in Mater Trans 47(2017): 1395–1401. 6. Senkov ON, Scott JM, Senkova SV, Miracle DB, Woodward CF (2011) Characteristics and microstructure of a high-entropy TaNbHfZrTi alloy at room temperature. Citation: J. Alloys Compd 509: 6043-48. In 2011, Hsu CY, Juan CC, Wang WR, Sheu TS, and Yeh JW published an article on high-entropy alloys  $AlCoCrFeMo_{0.5}Ni$  and its exceptional hot hardness and softening resistance. Mathematical and Scientific Reviews A 528: 3581–85. 8.  $AlCoCrFeNiTi_x$  solid solution alloys with outstanding room temperature mechanical characteristics were described by Zhou YJ, Zhang Y, Wang YL, and Chen GL in 2007. "Appl Phys Lett" 90: 181904. The effect of valence electron concentration on the stability of the fcc or bcc phase in high entropy alloys was studied by Guo S, Chun Ng, Jian Lu, and Liu CT in 2011. J. Appl. Phys. 109: 103505. 10. The influence of electro-negativity on the stability of topologically close-packed phases in high entropy alloys was studied by Dong Y, Lu Y, Jiang L, Wang T, and Li T in 2014. Publication: Intermetallics 52: 105–109. Yu Y, Wang J, Li J, Kou H, and Liu W. (2015) characterized BCC phases in high entropy alloys of  $AlCoCrFeNiTi_x$ . 18. Materials Letters 138: 78–80. 12. A study conducted by Tong et al. (2005) examined the

microstructure of a high-entropy alloy system including Al<sub>x</sub>CoCrCuFeNi and its multiprincipal constituents. Metall Surface Science Letters 36: 881–893. 13. Mechanical characteristics of an Al<sub>0.5</sub>CoCrCuFeNi wrought alloy as a function of temperature (Tsai CW, Tsai MH, Yeh JW, Yang CC, 2010). Page 160–5 of the Journal of Alloys and Composites, volume 490. 14. In 2014, He et al. investigated how the inclusion of aluminum affected the tensile characteristics and structural development of a high-entropy alloy system consisting of FeCoNiCrMn. Published in Acta Mater 62: 105–13. 15. The impact of vanadium addition on the microstructure and characteristics of AlCoCrFeNi high entropy alloy was studied by Dong Y, Zhou K, Lu Y, Gao X, Wang T, and colleagues in 2014. Page 67–72 of Mater Des 57. In 2015, Stepanov et al. investigated how the V content affected the mechanical characteristics and microstructure of high entropy alloys composed of CrFeMnNiV<sub>x</sub>. Published in the Journal of Alloys and Composites, volume 628, pages 170-85. 17. Adding vanadium to an Al<sub>0.5</sub>CoCrCuFeNi high-entropy alloy changes its microstructure, hardness, and wear resistance (Chen MR, Lin SJ, Yeh JW, Chuang MH, Chen SK, et al., 2006). Metall Research in Mater. Sci. 37: 1363–1369. 18. In a solution of 3.5% sodium chloride, Hsu YJ, Chiang WC, and Wu JK (2005) studied the corrosion behavior of high-entropy FeCoNiCrCu<sub>x</sub> alloys. Published in Mater Chem Phys 92: 112–117. 19. The impact of nickel addition on the microstructure and characteristics of an AlCoCrFeNi high-entropy alloy was studied by Ma SG and Zhang Y in 2012. Chapter 20 of Mater Sci Eng A 532: 480-6. Cheng JB, Liang XB, and Xu BS (2014) CoCrCuFeNi high-entropy alloy coatings: how adding Nb affects their structure and mechanical behaviors. Volume 240, Issues 184–90, Surf Coatings Tech; 21. Concerning the microstructures, phase assemblages, and characteristics of high-entropy alloys Al<sub>0.5</sub>CoCrCuFeNiSix, Liu X, Lei W, Ma L, Liu J, Liu J, et al. (2015). Journal of Alloys and Composites, volume 630, pages 151-62. Section 22. Research on the microstructure and compressive characteristics of multicomponent AlCoCrFeNiMox alloys was published in 2010 by Zhu et al. The article is published in Mater Sci Eng A 527: 6975-9. 24. The microstructure and compressive characteristics of multicomponent AlCoCrCuFeNiMox alloys were studied by Zhu JM, Zhang HF, Fu HM, Wang AM, Li H, and colleagues in 2010. The link is cited as J Alloys Compd 497: 52-6. 24. Discourse on Several Aspects of Phase Diagrams and Phase Transformations (Massalski TB, 2010). (Mater Trans 51: 583–596) 25. In 2015, Wang, Qiu, Yang, and Liu investigated the impact of atomic size and lattice distortion in high-entropy alloys that had just been created and included numerous primary elements. Article published in Intermetallics, volume 64, pages 63–9. Table of contents. In their 2012 paper, Yang and Zhang anticipated a solid-solution stability in multi-component alloys with a high entropy. Mater Published in the Journal of Chemical Physics, volume 132, pages 233-238, 27. Analysis of high-entropy alloy microstructures and their characteristics by Zhang Y, Zuo TT, Tang Z, Gao MC, Dahmen KA, and colleagues (2014). Advances in Materials Science 61: 1-93. 28. Researchers Fang, Xiao, Xia L, Li, and Dong (2003) Connection between bond characteristics and the lengths of supercooled liquid areas in bulk metallic glasses based on magnesium. J Chapter 29 of Non Cryst Solids 321: 120–5. Amorphous or solid-solution phase formation in high-entropy alloys: a study by Guo and Liu (2011). Journal of the American Society for the Advancement of Science, Volume 21, Issue 4, pages 433-56, p. 30. Wear behavior of AlCoCrFexMo<sub>0.5</sub>Ni high-entropy alloys as a function of iron concentration (Hsu CY, Sheu TS, Yeh JW, Chen SK, 2010). Section 268: 653–659. 31. The impact of alloying elements on the microstructure and characteristics of high-entropy alloys including several primary elements was studied by Li C, Li JC, Zhao M, and Jiang Q in 2009. Journal of Alloys and Composites, 475, 752–758. 32. Wang W, Zhu ZX, Lu YP, Wu PH, Liu N, Yang W, et al. (2015) How multicomponent CoCrCu<sub>x</sub>FeMoNi high-entropy alloys solidify and their microstructure. (Mater Sci Eng A 642, 142–143, 33). Co addition to Ti<sub>0.5</sub>CrFeNiAlCo high entropy alloy changes its crystal structure and mechanical characteristics, according to Wang FJ and Zhang Y (2008). Scientific American 496: 214-6.

The microstructure and mechanical properties of CoCrFeNi high-entropy alloys as a result of Nb additions were studied in a 2015 study by Liu WH, He JY, Huang HL, Wang H, Lu ZP, and colleagues. Publication: Intermetallics, Volume 60, Pages 1–8.