

Review Article

High Entropy Alloys, Properties, Applications, And Effect of Alloying Elements

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Abstract

The design of high entropy alloys (HEAs) is a paradigmatic shift in the development and design of novel alloys with novel properties unmatched by conventional alloys. Due to their superior properties, HEAs are promising candidates for use in wide range of new engineering applications. This paper briefly review the metallurgical nature of (HEAs), including novel properties, areas of application; and influence of alloying elements on HEAs. It can be divided into five main sections. The first section focuses on HEAs, identifying and discussing metallurgical nature of HEAs. This section is followed by detailed reviews on novel properties of HEAs. Areas of applications of HEAs discussed in the third section. The fourth section review the influence of alloying elements on the microstructure and mechanical properties of HEAs. Finally, the metallurgical nature of HEAs and its properties, applications, and influence of alloying elements is concluded. Summarizing the findings from literature.

Key Words: High Entropy Alloys, HEAs, Mechanical properties, Novel Applications, Phase transition, Equimolar fraction, Near- equiatomic fraction, Microstructure.

1: Introduction

The advent of high entropy alloys (HEAs), which are composed of more than five principal elements in equiatomic or near-equiatomic fraction is a paradigmatic shift in the development of modern materials with novel properties unmatched by conventional alloys, which based on one and rarely two base elements [1, 2]. Several recent studies focus on HEAs. Many researchers have tried to understand the formation of different phase in HEAs. They also tried to development new methods, theories, and models that can be applied on HEAs. In addition, they tried to understand the thermodynamic origin of phase selection [3-7].

Among studies that have shown the formation of different phase in HEAs is a publication by Sheng et al [8] and Tsao et al [9]. They reported that HEAs predominantly consist of a single – phase solid solution. As shown in table (1) [10], which lists the experimentally phases in HEAs as – cast condition. As evident from table (1), the experimental results shown that HEAs consist of face centered cubic (FCC), body centered cubic (BCC), or face centered cubic (FCC) plus body centered cubic (BCC) structure solid solution. However, a few exceptional cases were noted in some HEAs. For example, minor quantities of intermetallic compound phase with metastable particles was found in some HEAs, such as CrCuFeMoNi [11], CoCuFeNiV [12], CoCrCuFeNi [13], and CoCrCuFeMnNi [14]. Multiple processing techniques, which based on the starting state for the HEA preparation, can be used to produce HEAs, such as mechanical alloying [15], plasma spray method [16], laser cladding process [17], and arc melting technique [18]. Figure (1) shows processing routes of HEAs using arc-melting technique [19].

Table1 The experimentally phases in HEAs as – cast condition [10].

Alloy	Phases reported
AlCoCrCuFeNi	BCC + FCC
AlCoCrCuNi	BCC + FCC
AlCoCrCuNi	BCC + FCC + (B2)
AlCoCrCuNiTi	BCC + Cu + Cr?
AlCoCrFeNi	BCC + B2
AlCoCrFeNi	B2 + L1₂
AlCoCrFeNiTi	BCC + B2
AlCoCuNi	BCC + FCC
AlCrCuFeMnNi	BCC
AlCrCuFeNi	FCC + FCC
AlCrCuFeNiTi	BCC + FCC
AlCrMnNbTi	Laves + unknown
AlCrMnNbV	Laves + unknown
AlCrMoSiTi	B2 + Mo₅Si₃
AlCrMoSiTi	Amorphous
AlCrTiVZr	Compounds
AlMnNbTiV	B2 + laves
AlTiVYZr	Compounds
CoCrCuFeMnNi	FCC
CoCrCuFeNi	FCC
CoCrCuFeNiTi	FCC + Laves
CoCrFeMnNi	FCC
CoCrFeNi	FCC
CoCuFeNiV	FCC
CrCuFeMoNi	FCC
CrMnNbTiV	Laves + unknown
NbMoTaW	BCC
VNbMoTaW	BCC

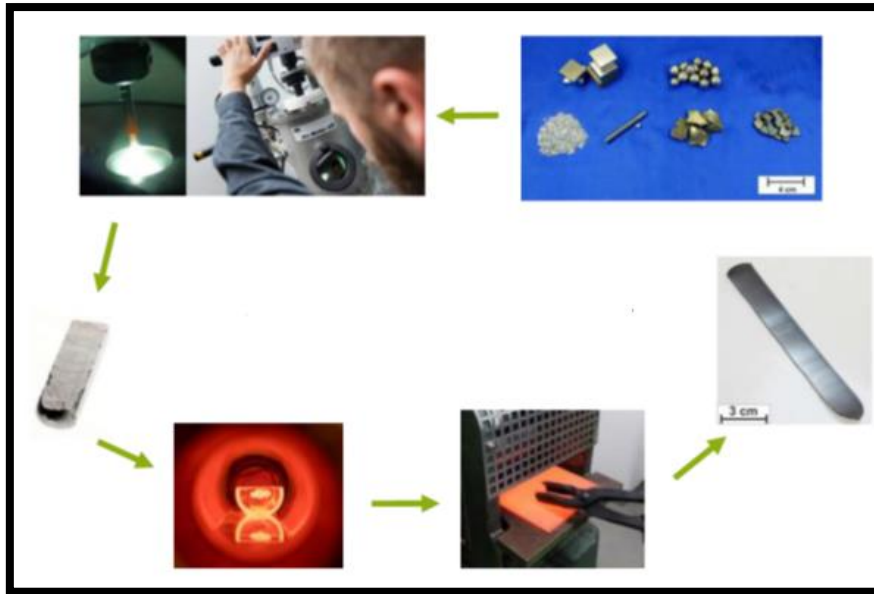


Figure 1 Processing Routes of Heas Using Arc-Melting Technique [19].

2- Properties of High Entropy Alloys (HEAs)

The designed of high entropy alloys were reported that the HEAs have novel properties unmatched conventional alloys. Due to their superior properties, HEAs are promising candidates for use in a wide range of engineering applications.

Previous studies have reported that HEAs have unique mechanical and physical properties exceeding that of most conventional alloys and pure metals. They reported that HEAs have excellent comparable strength to that of metallic glasses and ceramics [20], good thermal stability[21], significant resistance to corrosion [22], excellent wear resistance [23], high hardness and strength [24, 25]. Also, it was reported that HEAs have high compressive strength at room temperature and at high temperatures[26], and have high hardness at high temperature and room temperature[27].

Several research groups have reported that HEAs have excellent tensile properties[28]. Figure (2) shows mechanical properties (yield strength) of HEAs compared with conventional super alloys (Haynes 230 and Inconel 718) [2]. In addition, figure (3) shows strength versus ductility for HEAs compared with conventional alloys [2]. Table (2) lists the properties of HEAs compared with other conventional alloys[2]. As seen in table (2), the HEA (Al₂₀Li₂₀Mg₁₀Sc₂₀Ti₃₀) is about three times stronger than metallic glass (Vit1) and Al alloys (noncrystalline). Also, the (Al₂₀Li₂₀Mg₁₀Sc₂₀Ti₃₀) HEA has excellent specific strength of 0.74 GPa g cm⁻³ with ultralow density of 2.67 g cm⁻³, which is higher than those of Al alloys and Ti alloys and comparable to that of ceramics. In addition to their superior mechanical and physical properties, some HEAs are also reported to possess functional properties[29]. Recent works have reported that, TiCoCrCuFeNi HEA has superparamagnetic properties[7]. In addition, they reported that, Ta₃₄Nb₃₃Hf₈Zr₁₄Ti₁₁ HEA possess superconductivity at T= 7.3 K[30].

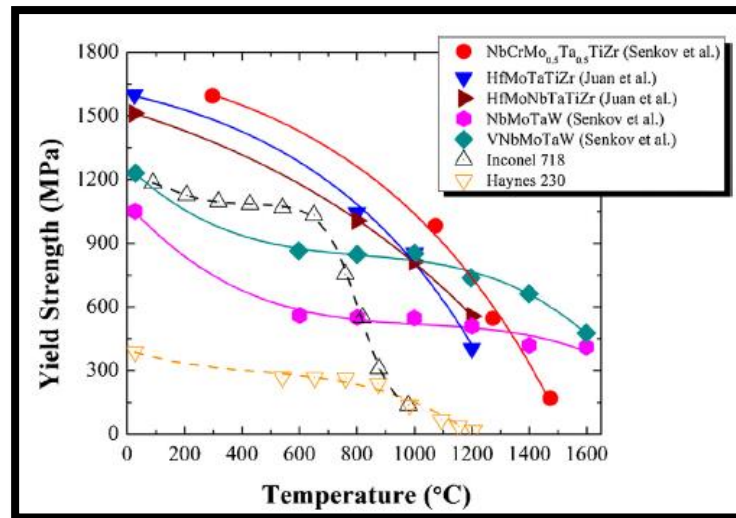


Figure 2 Mechanical properties (yield strength) of HEAs compared with conventional super alloys (Haynes 230 and Inconel 718) [2].

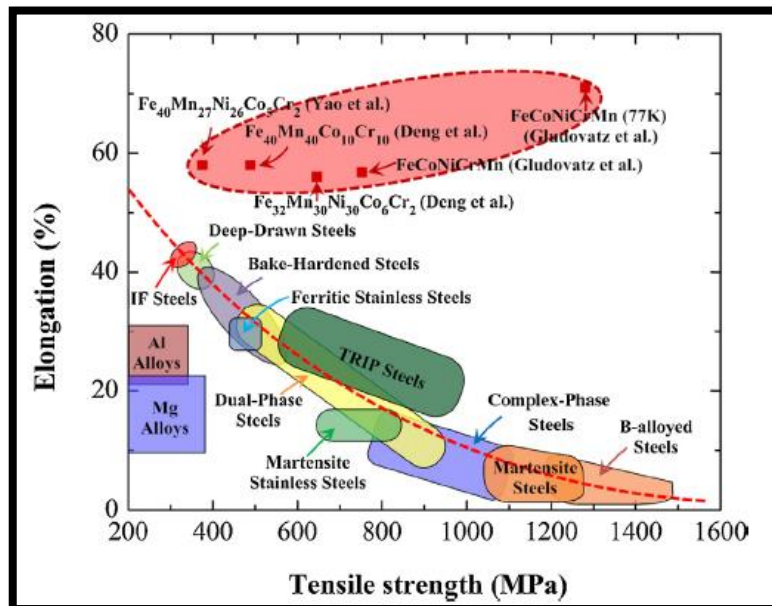


Figure 3 Strength versus ductility for HEAs compared with conventional alloys [2].

Table 2 Properties of HEAs compared with other conventional alloys [2].

Properties	Al ₂₀ Li ₂₀ Mg ₁₀ Sc ₂₀ Ti ₃₀	Low-density refractory HEAs	CrMnFeCoNi (77 K)	Vit1	Al alloys	Ti alloys	Steel alloys
Density (g cm ⁻³)	2.67	6.34-6.67		6.1	2.6-2.9	4.3-5.1	7.8
Hardness (GPa)	5.9	2.99-4.72		5.7	0.20-1.75	0.54-3.80	1.50-4.80
Yield strength, σ_y (GPa)	1.97 ^a	1.00-1.57	0.73	1.9	0.10-0.63	0.18-1.32	0.50-1.60
Specific strength (GPa g ⁻¹ cm ³)	0.74	0.16-0.24		0.32	<0.24	<0.31	<0.21
Fracture toughness (MPa m ^{1/2})			200-300	20-140	23-45	55-115	50-154

3- Applications of High Entropy Alloys (HEAs)

In spite of the fundamental issues of HEAs have not yet been completely resolved, HEAs were reported to have unique properties. These properties and metallurgical nature of HEAs are promising for new path in the development and discoveries of advance materials, which may ultimately led to use in a wide range of new engineering applications.

It was reported that HEAs could be used in transportation industry and energy sectors[31]. Their lightweight and high strength make HEAs potential candidates where these properties are in great demand [31]. Furthermore, recent works have reported that HEAs have successfully been employed in high – temperature applications, for examples, nuclear industries, rocket nozzles, high-pressure vessels, and gas turbines [32]. They reported that HEAs have refractory elements such as tantalum, niobium, and molybdenum possess high strength above 1200°C make HEAs potential candidates for high – temperature applications[33]. In addition they reported that HEAs containing low – density refractory elements could be used in the aerospace industry [33]. Their light – weight tolerant to high temperature make HEAs potential candidates where these properties are in demand[33]. Also, it was reported that HEAs have special functional and physical properties make HEAs potential candidates for electronic applications[30]. Recent works have reported that the special cryogenic properties of HEAs would make them useful for cryogenic applications, for examples, pipe work, rocket casings, and liquid O₂ liquid equipment or liquid N₂ equipment [32]. Also, they reported that HEAs can be used as wear – resistant coatings[34], heat resistant coatings[34], and biomedical coatings[35]. Furthermore, it was reported that light – weight HEAs can be used as casings for mobile facilities, transportation industry and battery anode materials[1].

4- Effect of Alloying Elements on the Microstructure and Mechanical Properties of High Entropy Alloys (HEAs)

Several recent studies focus on the effect of alloying elements on the microstructure and mechanical properties of high entropy alloys (HEAs). Many researchers have tried to understand the role of alloying elements addition on stabilized or destabilized the microstructure of HEAs. Change or transforms from one face or structure to new phase or structure, for example, the HEA systems change from face centered cubic (FCC) to body centered cubic (BCC) or to FCC + BCC, or to BCC + hexagonal close packed (HCP) when increase of alloying element content. In addition, they tried to understand the role of alloying elements additions on the mechanical properties of HEAs. For examples, the influence of alloying elements on yield stress, fracture strength, hardness, plastic strain, fracture strength, tensile elongation, ductility and compressive strength of HEAs. Some of recent studies on the effect of alloying elements on the microstructure and mechanical properties of high entropy alloys are discussed in this section.

The effect of titanium addition on the AlCoCrFeNi HEA was reported by Zhou et al.[36]. The results of their study revealed that the alloy has excellent compressive mechanical properties at room temperatures as you can see from figure 4. In addition, they reported that the AlCoCrFeNiTi_x when x = 0, 0.5, 1, 1.5 is composed of the solid solution with body centered cubic (BCC) structure. They also found that the alloy with 0.5 titanium has excellent mechanical properties, including yield stress, plastic strain and fracture strength.

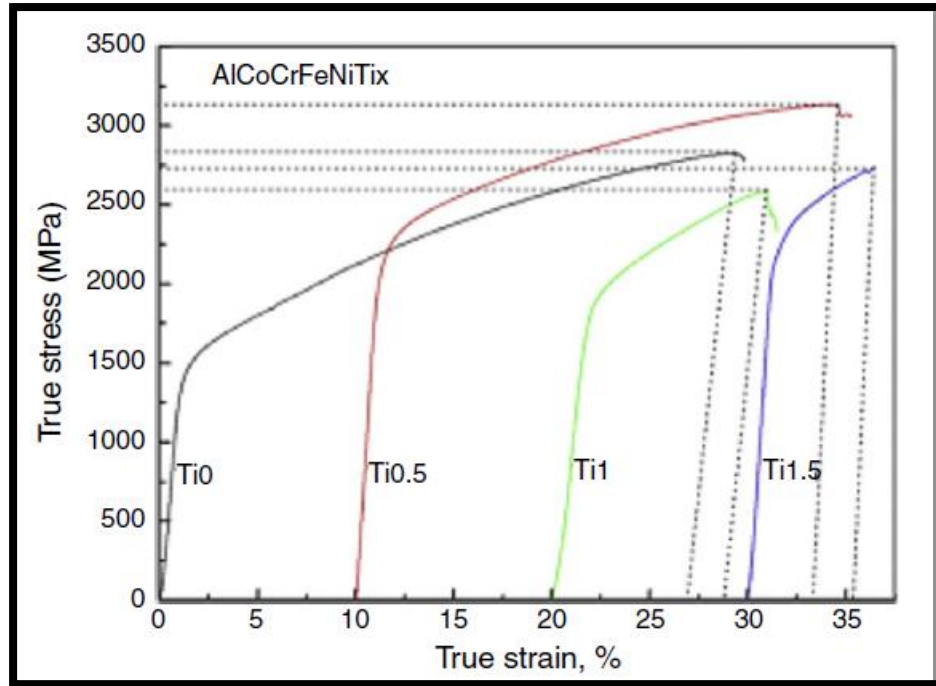


Figure 4 Compressive true stress - strain curves of AlCoCrFeNiTi_x HEA [36].

Among the studies, that shown the influence of aluminum and copper on the microstructure and mechanical properties of HEAs is a publication by Fan et al. [37]. In the study, the authors investigated the effect of aluminum and copper on microstructure and mechanical properties of the FeCrNiCo HEAs. They reported that the microstructure of the (FeCrNiCo)Al_xCu_x transforms from face centered cubic (FCC) structure to face centered cubic (FCC) + body centered cubic (BCC) structure, and then , to only body centered cubic (BCC) structure with additions of aluminum from 0.5 to 1. Also, their results showed that the additions of aluminum to (FeCrNiCo)Al_xCu_x HEAs improve the mechanical properties of the alloy. For examples, hardness and Young's modulus of the alloys. Furthermore, they reported that when aluminum was $x=1$, the additions of copper greatly decreased the fracture strength of the (FeCrNiCo)Al_xCu_x HEAs.

Li et al.[38], then published more results of the study the influence of aluminum on the microstructure and mechanical properties of HEAs. Their report published results of effect of aluminum additions on the FeCoNiCrCu0.5Al_x where $x=0.5$ to 1.5 have been investigated. The results showed that as aluminum level increased from 0.5 to 1.5, the microstructure of the FeCoNiCrCu0.5Al_x HEAs changed from face centered cubic (FCC) phase to body centered cubic (BCC). In addition, they reported independently on the microstructure, the FeCoNiCrCu0.5Al_x as cast condition showed higher hardness and higher corrosion resistance.

Among studies that have shown the influence of vanadium addition on the microstructure and mechanical properties of AlCoCrFeNi HEA is a publication by Dong et al.[39]. In this study the authors investigated the effect of vanadium alloying on AlCoCrFeNiV_x ($x=0, 0.2, 0.5, 0.8, 1$). Their results showed that high compressive strength of 3297.8 MPa and high plastic strain of 26.8% can be obtained in AlCoCrFeNiV0.2 alloy as can observed in figure 5. They also reported that with increase vanadium content the Vickers hardness greatly increased from 534 to 648.8 HV. In addition, they found that as vanadium element level increased from $x=0$ to $x=3$, the microstructure of the Al0.5CoCrFeNiV_x changed from face centered cubic (FCC) phase to face centered cubic (FCC) + sigma (σ) phases, then to body centered cubic (BCC) structure.

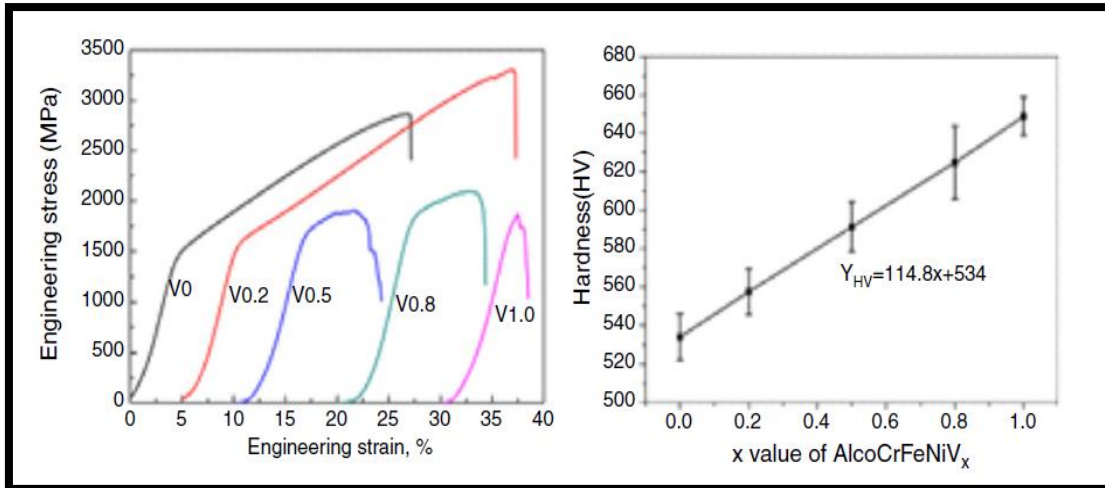


Figure 5 Compressive engineering stress - strain and hardness curves of AlCoCrFeNiV_x HEA [39].

Liu et al. [40], investigated the effects of Niobium addition on the microstructure and mechanical properties of CoCrFeNi HEA. Their study presented results of the CoCrFeNiNb_x with five component. They reported that as Niobium element increased the microstructure of CoCrFeNiNb_x HEAs transforms from face centered cubic (FCC) to face centered cubic (FCC) + hexagonal close packed (HCP) structure (see figure 6). They also found that the yield strength and fracture strength increase as the Niobium content increase. For example, they reported that the fracture strength of CoCrFeNiNb₀ is 413 MPa, but significantly increased for CoCrFeNiNb_{0.412} to 1004 MPa. Also, the yield strengths of alloy CoCrFeNiNb₀ HEA is 147 MPa, but greatly enhanced for CoCrFeNiNb_{0.412} to 637 MPa. In contrast, they reported that as Niobium element level increased from 0 to 0.412, the tensile elongation significantly decreased from 49.1 % to 1.3 %.

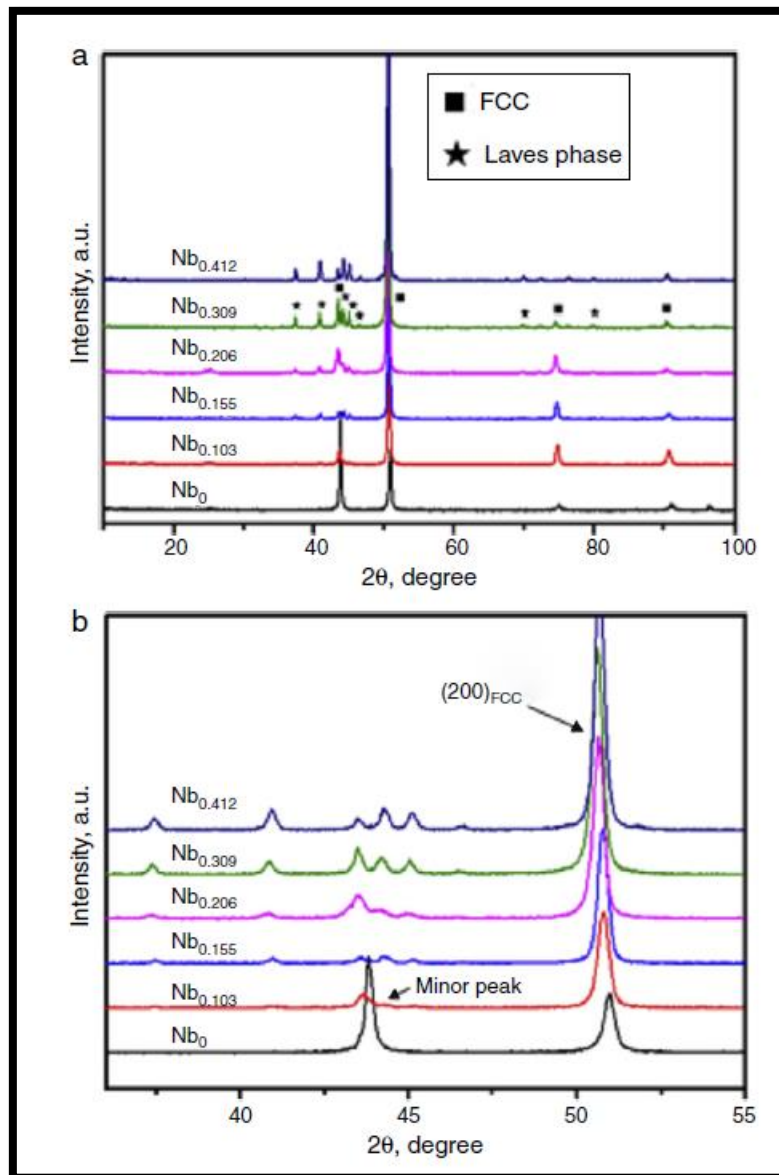


Figure 6 XRD patterns of as - cast CoCrFeNiNbx HEA [40].

Among the studies that have shown the effect of molybdenum alloying on the microstructure and mechanical properties of AlCrFeNi HEA is a publication by Dong et al.[41]. In the study the authors investigated the effect of molybdenum addition on AlCrFeNiMox $x = 0, 0.2, 0.5, 0.8, 1$ HEAs. They reported that the microstructure of alloy system transforms from two body centered cubic (BCC) phase to one body centered cubic (BCC) phase + sigma (σ) phase (FeCrMo). Their study showed that the yield strength increased from 1406.2 to 1748.6 MPa as molybdenum element level increased from $x = 0$ to $x = 0.5$. They also reported that the AlCrFeNiMo0.2 HEAS showed higher fracture strength and plastic strain of 3222 MPa and 0.287 respectively. Their study also showed that fracture strength significantly decreased from 3222 MPa to 1512.5 MPa when molybdenum level increased from 0.2 to 0.8 (see figure 7). They found that the plastic strain 0.287 decreased to 0 when molybdenum in the level $x = 0.8$ (see figure). In contrast, they reported that the Vickers hardness increased from 472.4 to 911.5 HV as molybdenum concentration increase from 0.2 to 0.8.

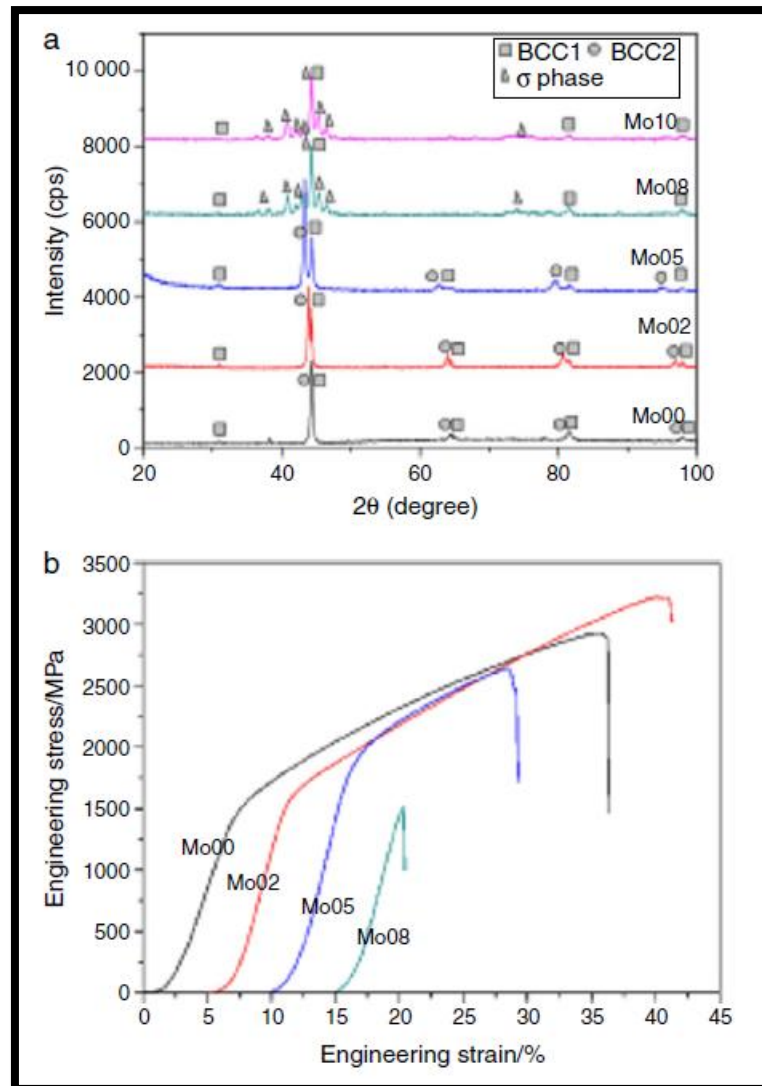


Figure 7 XRD and stress - strain patterns of the AlCrFeNiMox HEA [41].

Among the studies that have shown the influence of alloying elements on the microstructure and mechanical properties of HEAs is a publication by Liu et al.[42]. In the study, the authors investigated the effect of silicon addition on Al_{0.5}CoCrNiSix high entropy alloy. They found that the microstructure of Al_{0.5}CoCrNiSix HEAs changed from a closed – packed face centered cubic phase to loose – packed body centered cubic phase when silicon content increases. In addition, they reported that the compressive strength of the Al_{0.5}CoCrNiSix increased when the silicon concentration increases. They also reported that as silicon content increases the ductility significantly decreased.

Liu et al.[43], studied the effect of tin addition on the microstructure and mechanical properties of FeMnNiCuCo HEA. Their study presented results of the effect of tin alloying on of FeMnNiCuCoSn_x HEAs where $x = 0, 0.03, 0.05, 0.08, 0.1, \text{ and } 0.2$. They reported that as tin element level of $0.03 < x < 0.05$, the FeMnNiCuCoSn_x HEAs showed higher plasticity and higher tensile strength. They also reported that high strength of 476.9 MPa and high elongation strain of 16.9% can be obtain when tin content is $0.03 < x < 0.05$. Their study showed that the Vickers hardness increased with increase of tin element content.

5- Conclusions

The following conclusions have been made from this review:

- 1- HEAs have novel properties unmatched by conventional alloys.
- 2- The attractive properties of HEAs are promising for a wide range of new engineering applications.

- 3- Multiple processing techniques can be used to produce HEAs, such as mechanical alloying, plasma spray method, laser cladding process, and arc melting technique.
- 4- Alloying elements play a significant role in the microstructure and mechanical properties of HEAs.

Conflicts of Interest

The author declares that they have no conflicts of interest.

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مقالة مراجعة:

الشبائك العالية الانتروبي، خصائصها، تطبيقاتها، و تأثير عناصر السبك

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الخلاصة:

يعد تصميم الشبائك عالية الانتروبي تحولا نموذجيا في تطوير وتصميم شبائك جديد لا مثيل لها في الشبائك التقليدية . نظرا لخاصتها المتفوقة تعد الشبائك عالية الانتروبي مرشحة واعدة للاستخدام في مجموعة واسعة من التطبيقات الهندسية الجديدة. تستعرض هذه المقالة بايجاز الطبع المعدني للشبائك عالية الانتروبي، بما في ذلك خصائصها الجديدة، مجالات التطبيق، تأثير عناصر السبك في الشبائك العالية الانتروبي. المقالة تقسم الى خمسة اقسام رئيسية. يركز القسم الأول على الشبائك العالية الانتروبي بصورة عامه. يتبع هذا الجزء من المقالة سرد تفصيلي حول الخصائص الجديدة للشبائك عالية الانتروبي. تطبيقات الشبائك العالية الانتروبي نوقشت بالتفصيل في الجزء الثالث من المقالة. يستعرض القسم الرابع من المقالة تأثير عناصر السبك في البنية المجهرية والخواص الميكانيكية للشبائك عالية الانتروبي. أخيرا ظظو تم انهاء المقالة بملخص للبحوث المنشورة واخر التطورات في الشبائك العالية الانتروبي.

الكلمات الدالة: شبائك عالية الانتروبي، الخصائص الميكانيكية، تطبيقات جديدة، التحولات الطورية، متساوية الذرات، شبه متساوية الذرات، البنية المجهرية.