

**Processing, Microstructures, and Mechanical Behavior
of High-Entropy Alloys**

**A Thesis Presented for the
Master of Science Degree**

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Abstract

Recently, high-entropy alloys (HEAs) have attracted increasing attentions because of their unique compositions, microstructures, and adjustable properties. In this work, microstructure and phase composition of the AlCoCrFeNi high-entropy alloy (HEA) were studied in as-cast and heat-treated conditions. Using a combination of Electron Backscatter Diffraction (EBSD), X-ray energy spectroscopy analysis, and synchrotron X-ray diffraction techniques, two nonequilibrium phases were identified in the as-cast condition: *BCC_A2* and *B2*. Long-term heat treatment transformed these nonequilibrium phases into four equilibrium phases: *FCC_A1*, *BCC_A2*, *B2*, and σ [sigma] phase. The electron microscopic results were consistent with thermodynamic simulations of the equilibrium and nonequilibrium conditions.

Tensile properties of AlCoCrFeNi high entropy alloy (HEA) in two conditions, (i) as-cast and (ii) heat-treated, were also reported. The heat treatment consisted of hot isostatic pressing at 1,373 K, 207 MPa for 1 hours followed by annealing at 1,423 K for 50 hours. A noticeable increase in the tensile ductility occurred after heat treatment. During deformation at 973 K, elongation of the heat-treated alloy was 11 %, while the as-cast alloy showed elongation of only ~ 0.9 %. The ultimate tensile strength was almost unaffected by heat treatment, and it was 407 ± 5 MPa at 973 K. The properties of the alloy were correlated to its as-cast and heat-treated microstructures. The fracture mechanisms were discussed in detail by analyzing the features on and below the fracture surface. The formation of *FCC_A1* phase, less casting pores, and residual stresses removed, may contribute to the significant improvement of tensile behavior.

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1. Literature Review

1.1. Introduction

Recently, high-entropy alloys (HEAs) have attracted increasing attentions because of their unique compositions, microstructures, and adjustable properties [1-17]. They are loosely defined as solid solution alloys that contain more than five principal elements in equal or near equal atomic percent (at. %). Normally, the atomic fraction of each component is greater than 5 at%. The multicomponent equimolar alloys should locate at the center of a multicomponent phase diagram, and their configuration entropy of mixing reaches its maximum ($R \ln N$; R is the gas constant and N the number of component in the system) for a solution phase. These alloys are defined as HEAs by Yeh et al. [2], and named by Cantor et al. [1, 18] as multicomponent alloys. Both refer to the same concept. There are also some other names, such as multi-principal-elements alloys, equimolar alloys, equiatomic ratio alloys, substitutional alloys, and multicomponent alloys, and so on.

Cantor et al. [1, 18] pointed out that a conventional alloy development strategy leads to an enormous amount of knowledge about alloys based on one or two components, but little or no knowledge about alloys containing several main components in near-equal proportions. Theoretical and experimental works on the occurrence, structure, and properties of crystalline phases have been restricted to alloys based on one or two main components. Thus, the information and understanding are highly developed on alloys close to the corners and edges of a multicomponent phase diagram, with much less

knowledge about alloys located at the center of the phase diagram. This imbalance is significant for ternary alloys, but becomes rapidly much more pronounced as the number of components increases. For most quaternary and other higher-order systems, information about alloys at the center of the phase diagram is virtually nonexistent except those HEA systems that have been reported recently.

The yield strength of the body-centered cubic (BCC) HEAs can be rather high [19], usually comparable to BMGs [19]. Moreover, the high strength can be kept up to 973 K or higher for some HEAs based on 3d transition metals [4]. In contrast, BMGs can only keep their high strength below their glass-transition temperature. The configuration entropy, S , of random mixing of N elements are defined by the following equation:

$$\Delta S = -R \sum_{i=1}^N x_i \ln x_i \quad [1]$$

where R is the Gas constant, x_i is the mole fraction of an element i in the alloy and

$\sum_{i=1}^N x_i = 1$. The entropy of mixing of N elements approaches the maximum value S_m

$$\Delta S_m = R \ln N \quad [2]$$

when the elements are mixed at equimolar concentrations, and, according to Equation [2], S_m increases rapidly with an increase in the number of the alloying elements. Experimenting with different compositions, people found out that, when N is equal or larger than 5, and the concentrations of each of the alloying elements are between 5 and 35 atomic percent (at. %), the high mixing entropy can considerably decrease the Gibbs

free energy and stabilize solid-solution-like phases with relatively simple crystal structures, over competing intermetallic phases [1, 2, 6, 20, 21].

The high-entropy effects, or multicomponent effects, are intended to stabilize the high-entropy phases, such as solid-solution phases and amorphous phases rather than ordered intermetallic phases with lower entropy. For the alloy system, the Gibbs free mixing energy can be expressed as follows:

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \quad [3]$$

Here, the ΔG_{mix} is the Gibbs free mixing energy, ΔH_{mix} is the mixing enthalpy, and ΔS_{mix} is the mixing entropy, and T is the absolute temperature. From Equation [3], if ΔH_{mix} remains constant, increasing mixing entropy will reduce Gibbs free energy, stabilizing the alloy system. The phenomenon will be more obvious at elevated temperatures, owing to higher T , lowering ΔG_{mix} . Thus, owing to the solid solution strengthening mechanism (the randomly arranged solute atoms inhibit dislocation motion), the yield strength of the HEAs can be rather high, usually comparable to the bulk metallic glasses (BMGs). BMGs can only keep their high strength below the glass-transition temperatures or even only at room temperature, but the high strength of HEAs can be kept up to 973 K or even higher [4].

High entropy of mixing stabilizes disordered solid solutions. However, the entropy term decreases linearly with a decrease in temperature. Ordered intermetallic phases have considerably smaller enthalpy of formation than the random solid solutions. With a decrease in temperature, diffusion and thus kinetics of phase transformations slows down.

For use in elevated temperature applications, the microstructure of HEAs must be stable, because any phase transformations occurring during use could deteriorate properties, initiate creep or failure. At the same time, suppressed kinetics may lead to precipitation of very fine, nanometer-sized particles and considerably improve properties of these alloys at ambient temperatures. Therefore, as candidate materials for high-temperature structural applications, studying of phase and microstructure stability in HEAs is particularly beneficial.

1.2. Mechanical Behavior

Superior structural alloys remain in a high demand for some extreme environmental engineering, particularly in the nuclear, turbine, and aerospace industries. HEAs are reported with high hardness and high compressive strength both at room temperature and elevated temperatures owing to their particular microstructures [2, 21-27]. HEAs also have shown great integrated tensile properties, including both high ultimate tensile strength and reasonable ductility [28-30]. Overall, it has been reported that the FCC-structured HEAs exhibit low strength and high plasticity, and BCC-structured HEAs show high strength and low plasticity. Thus, the structure types are the dominant factor for controlling the strength or hardness of HEAs. In this chapter, we will review some of the HEAs papers concern mechanical properties: what has been reported, why so, and hence, design and development to the next level.

1.2.1. Mechanical Behavior at Room Temperature

For room-temperature mechanical properties of HEAs, the yield strength can be varied from 300 MPa for the FCC-structured alloys to about 3,000 MPa for the BCC-structured alloys [3, 19]. The values of Vickers hardness range from 100 to 900. The structure types are one of the dominant factors for controlling the mechanical behavior of HEAs at room temperature. Here, we would like to discuss two other effects on mechanical behavior.

1.2.1.1. Alloying Effect

Like other conventional alloys, small amounts of alloying elements can also be added to HEAs to increase or reduce the strength, plasticity, hardness, etc. The addition of one alloying element to improve one property may have unintended effects on other properties. For example, in order to investigate the differences of effects of various alloying elements on mechanical properties of AlCoCrFeNi alloy, the effects of C, Mo, Nb, Si, Ti elements on AlCoCrFeNi alloy have been investigated systematically [19, 31-33].

Ma et al. [33] studied the Nb alloying effect, finding that the microstructures and properties of the AlCoCrFeNb_xNi HEAs became two phases in the prepared AlCoCrFeNb_xNi HEAs: one is body-centered-cubic (BCC) solid solution phase [Figure 1(a)]; the other is the Laves phase of (CoCr)Nb type. The microstructures of the alloy series vary from hypoeutectic to hypereutectic, and the compressive yield strength and Vickers hardness have an approximately linear increase with increasing Nb content, as shown in Figure 1(b) [33].

Zhou et al. investigated the Ti alloying effect on AlCoCrFeNiTi_x, designed by using the strategy of equiatomic ratio and high entropy of mixing. The alloy system is composed mainly of body centered cubic solid solution and possesses excellent room-temperature compressive mechanical properties, as shown in Figure 2. Particularly for AlCoCrFeNiTi_{0.5} alloy, the yield stress, fracture strength, and plastic strain are as high as 2.26 GPa, 3.14 GPa, and 23.3%, respectively, which are superior to most of the high-strength alloys such as bulk metallic glasses [19, 34].

1.2.1.2. Cooling-Rate Effect

The high cooling rates are effective for reducing the inter-dendrite composition segregation and making the microstructure more uniform, and the ductility can be improved while the yield strength has no significant change.

Wang et al. [24] studied the cooling rates effects on the microstructure and mechanical behaviors of a high entropy alloy of AlCoCrFeNi by preparing as-cast rod samples with different diameters. Smaller diameter rod samples have higher cooling rate when using the same equipments. He found that the cast diameter samples has the same phase of BCC solid solution while higher cooling rates lead to more uniform microstructures with reduced inter-dendrite composition segregation, as shown in Figure 3a-d [24]. With decreasing casting diameter, which means increasing cooling rate, both the strength and the plasticity are increased slightly, as shown in Figure 3e.

1.2.2. Mechanical Behavior at Elevated Temperatures

The high-temperature properties of the HEAs were also extensively studied. Like, conventional alloys, the microstructures and mechanical properties can be modified and tuned to reach the optimum. Figure 4 shows that the yield strength decreases with increasing the testing temperature. It is seen that the low Al-content alloy exhibits low yield strength, but it decreases slowly with increasing temperature. Figure 5 shows the change in mechanical properties of the Al_{0.5}CoCrCuFeNi HEA of the rolled sample as the temperature increased. Figure 6 presents that the mechanical properties of the Al_{0.5}CoCrCuFeNi HEA of annealed samples as a function of the testing temperature.

After annealing, the strength and hardness decrease while the elongation increases and the strength decreases slowly with increasing the temperature, which means that heat-treatment will highly influence on the mechanical properties, especially at elevated temperatures. We'd like to discuss the heat-treatment effect on high temperature properties of HEAs, including one kind of high performance HEAs at elevated temperatures, called refractory HEAs.

1.2.2.1. Heat-Treatment Effects

Figure 7 shows the microstructure of the AlCrCuNiFeCo HEA in (a) as-cast and (b) hot-forged conditions [28]. Considerable refinement of the cast microstructure was observed after extensive multistep forging at 1,223 K. Figure 8 presents the typical stress-strain curves of the as-cast (a) and hot-forged (b) samples deformed at different temperatures with an initial strain rate of 10^{-3} s^{-1} [28]. We find that, after forging, the alloy is considerably softer and much more deformable than the as-cast alloy. Figure 9 exhibits the photographs of tensile samples after deformation at 1,273 K: (a) a nondeformed sample; (b) an as-cast sample (tensile ductility, $d = 77\%$); and (c) a forged sample ($d = 864\%$) at a strain rate of 10^{-3} s^{-1} . The forged sample demonstrates highly homogeneous flow, great resistance to neck formation, and extraordinarily high elongation of 864 %. Figure 10 presents the corresponding SEM images of the fracture surfaces of samples after tensile-testing deformation at room temperature: (a and b) as-cast and (c and d) hot-forged conditions [28]. At low magnification, the as-cast alloy sample has a coarse-faceted appearance (Figure 10a), whereas the forged sample has fine granular appearance (Figure 10c). This observation is consistent with the much smaller grain/particle size of

the forged condition than the as-cast condition. High magnification images confirm brittle, quasi-cleavage, fracture of the as-cast alloy, with such characteristic features as flat facets, angular faceted steps, river-pattern markings, cleavage feathers, and tongues (Figure 10b). At the same time, high magnification images of the forged sample confirm a mixed type of brittle and ductile fracture (Figure 10d). The brittle type fracture is reflected by the presence of flat facets with characteristic river-pattern markings inside large dimples, while the ductile type fracture is reflected in numerous dimples of different diameters surrounding the flat facets. It is likely that, during tensile deformation of the forged sample, cracks are formed at the interfaces of the BCC and FCC particles by brittle fracture, and then the crack opening into voids occurs by plastic deformation of nearest, more ductile regions [28].

1.2.2.2. Refractory HEAs

Currently, Ni-based superalloys already have the great combination of elevated temperature properties, including creep resistance, corrosion resistance, and damage tolerance, but operating temperatures are reaching the theoretical limits of these materials. The high entropy alloying (HEA) approach was used to develop new refractory alloys, which contain several principal alloying elements at near equiatomic concentrations, using new metallic materials with higher melting points, such as refractory molybdenum (Mo) and niobium (Nb) alloys [4, 6, 21-23].

Senkov et al. [4] reported the yield strength of NbMoTaW and VNbMoTaW alloys at high temperatures, as shown in Figure 11. From Figure 11, we can see that the V addition

is beneficial for increasing the strength, but not suitable for the heat-softening resistance. Figure 12 exhibits the specific yield-strength change with increasing the temperature for the TaNbHfZrTi, TaNbMoW, TaNbVMoW, and CrCoCuFeNiAl_{0.5} cast alloys [22]. It can be seen that the high specific yield strength of the CrCoCuFeNiAl_{0.5} HEAs can be sustained over to 1,100 K, and the TaNbMoW HEA can sustain its high specific strength to 1800 K. Figure 13 shows the backscatter images of the NbMoTaW and VNbMoTaW HEAs after the deformation of 1,673 K.

Lower density and better room temperature ductility are required if we seek for applications in the aerospace engineering. By replacing V, Ta, and W in the NbMoTaW and VNbMoTaW alloys with lighter Cr, Mo, and Zr, respectively, the density of the new refractory NbCrMo_{0.5}Ta_{0.5}TiZr HEAs alloy was reduced to 8.2 g/cm³. In addition, the new alloy showed improved room temperature ductility, relative to the NbMoTaW and VNbMoTaW alloys. Figure 14 exhibits the engineering stress-strain compression curves of the NbCrMo_{0.5}Ta_{0.5}TiZr alloy samples after HIP at 296 K, 1,073 K, 1,273 K, and 1,473 K [23]. During deformation at 296 K, the yield strength was 1,595 MPa and continuous strengthening occurred until the alloy fractured by localized shear at peak strength of 2,046 MPa accumulating about a 5% strain. During testing at T = 1,073 K, yield strength decreased to 983 MPa, the peak strength of 1,100 MPa was achieved at a strain of 4.2%, and the sample fractured by shear at a strain of about 6%, after a decrease in strength to 1,050 MPa. An increase in the testing temperature to 1,273 K resulted in a considerable softening of the alloy after a short stage of strain hardening. At this temperature, yield strength ($\sigma_{0.2}$) = 546 MPa, compressive strength (σ_p) = 630 MPa, and the minimum

strength achieved during strain softening was 393 MPa after a plastic strain of about 22%. At this temperature, the sample did not fracture. An increase in the temperature to 1,473 K, led to a further decrease in the flow stress of the alloy, and $\sigma_{0.2}$ was 170 MPa. The peak stress of 190 MPa was reached shortly after yielding, followed by weak softening and a steady state flow at the minimum strength ($\sigma_{\min}$) = 135 MPa. No sample fracture occurred at this temperature.

Figure 15 presents the SEM secondary-electron images of the fracture surface of a NbCrMo_{0.5}Ta_{0.5}TiZr alloy samples after compression deformation at room temperature [23]. It shows a combination of plastic and brittle deformation mechanism. The formation of dimples is convincing evidence of ductile deformation, while the pieces of teared microstructure are the sign of quasi-cleavage fracture of the FCC (Laves) phase, as well as along the interfaces.

In all, refractory HEAs is a entirely novel concept and relatively new area. Compared to compositions with 3d elements, refractory HEAs (4d elements) show exceptionally promising mechanical properties, especially at elevated temperatures. More fields including new compositions and fracture mechanism need to be explored.

1.2.3. Mechanical Behavior at Cryogenic Temperatures

It is well acknowledged that the low-temperature mechanical properties are particularly beneficial for actual applications of metallic alloys. The mechanical behaviors of HEAs at cryogenic temperatures are yet to be investigated in detail. It is also known that FCC metals do not exhibit a ductile-brittle transition temperature (DBTT), so should we expect

the same for FCC HEAs? Meanwhile, because DBTT is known for BCC metals, has anybody done work on deformation of BCC HEAs at low T? The aim of this chapter is to review the compressive characteristics of both BCC and FCC HEAs at cryogenic temperatures.

Qiao et al. studied the compressive characteristics of a single-phase BCC HEA with the composition of AlCoCrFeNi at 77 K [35]. For the AlCoCrFeNi HEA, there is no obvious ductile to brittle transition even the temperature is lowered to 77 K. Comparing with the compression properties at different temperatures, it is concluded that the yielding strengths and fracture strengths of the AlCoCrFeNi HEA increase by 29.7 % and 19.9 %, respectively, when the temperatures decrease from 298 to 77 K, as shown in Figure 16. However, the fracture strains change gently, while the fracture modes at 298 and 77 K are intergranular and transgranular, respectively, as shown in Figure 17 [35]. That is to say, the DBTT of AlCoCrFeNi BCC HEA is lower than 77 K.

High-entropy alloy $\text{Al}_{0.5}\text{CoCrCuFeNi}$ has been deformed by compression and the peculiarities of the plastic deformation have been studied by Laktionova et al. [36] in a temperature range from 300 K to 4.2 K. The alloy has been found to provide a high strength and plasticity greater than 30 % in this temperature range: the yield stress amounts to 450 MPa for 300 K and 750 MPa for 4.2 K, as shown in Figure 18. At temperatures below 15 K, the smooth behavior of the stress-strain curves changes to the serrated one. Thus, FCC HEAs do not exhibit DBTT, like FCC metals.

1.2.4. Fatigue Behavior

Many potential applications for HEAs, such as aircraft engine components, frequently encounter cyclic loading. If we seek for the application in the aerospace industry or other field, besides monotonic loading, the fatigue behavior and lifetime prediction are one of the most influential factors, which are necessary to be studied and explored, yet seldom reported. The limited publication published so far is concerning the fatigue behavior of $\text{Al}_{0.5}\text{CoCrCuFeNi}$ HEAs, discussed as below.

Hemphill et al. [16] studied fatigue behavior of the $\text{Al}_{0.5}\text{CoCrCuFeNi}$ HEA and compared the results to many conventional alloys, such as steels, titanium alloys, and advanced BMGs. Figure 19a shows that a typical stress range versus the number of cycles to failure (S-N) curves comparing fatigue ratios [fatigue ratio = fatigue endurance limit / ultimate tensile strength (UTS)] of the $\text{Al}_{0.5}\text{CoCrCuFeNi}$ HEA to other conventional alloys, and BMGs [16]. The lower bound of the fatigue ratios of HEAs compares favorably to those of steels, titanium, and nickel alloys, and outperforms zirconium alloys as well as some of the Zr-based BMGs. Moreover, for some materials, such as ultra-high strength steels and wrought aluminum alloys, their high tensile strengths result in lower fatigue ratios due to their brittle nature. The strong group (which is defined as samples in the group contain fewer fabrication defects and can reveal the intrinsic fatigue behavior of the HEA) of HEAs tends to outperform these materials by displaying a greater fatigue ratio than materials with comparable tensile strengths due to the reduced number of defects. The upper bound of the fatigue limit of HEAs is significantly higher than that of other conventional alloys and BMGs, showing that HEAs have the potential to outperform

these materials in structural applications with improved fabrication and processing. These results are highly encouraging for excellent fatigue resistance in HEAs and with possible long fatigue life, even at stresses approaching the ultimate stress. Because of the lack of the literature on the fatigue behavior of HEAs, the focus of the continuing research should be placed on the data points that show an unexpectedly long fatigue life. If the necessary information on the fatigue resistance can be found and a prediction model for fatigue specimens can be developed, HEAs have a promising future in numerous applications for components in fatigue environments.

Figure 19a illustrates the fatigue-endurance limits for the $\text{Al}_{0.5}\text{CoCrCuFeNi}$ HEA as a function of UTS. One reason for the high fatigue strength of HEAs is the high tensile strength of these materials. It can be clearly seen that as the UTS increases the fatigue endurance limit also increases in a linear fashion, approximately equal to 0.5 for most materials [16]. HEAs follow a similar pattern and even exceed this ratio, with an upper bound of 0.703. To better compare the fatigue performance of HEAs with other materials with respect to their UTS, the fatigue ratios are used, as shown in Figure 19b.

1.2.5. Wear Behavior

HEAs show exceptional potential for use in tools, molds and structural components, so wear is a crucial phenomenon in such kind of applications. Tests on the wear behavior of HEAs have been conducted under abrasive conditions and adhesive conditions.

Chuang et al. [37] reported that the wear resistances of the $\text{Co}_{1.5}\text{CrFeNi}_{1.5}\text{Ti}$ and $\text{Al}_{0.2}\text{Co}_{1.5}\text{CrFeNi}_{1.5}\text{Ti}$ alloys are better than that of conventional wear-resistant steels with

similar hardness, as shown in Figure 20. The excellent antioxidation property and resistance to thermal softening in these HEAs are proposed to be the main reasons for the outstanding wear resistance.

Alloying can also affect on the wear behavior of HEAs. Wu et al. [38] studied adhesive wear behavior of $\text{Al}_x\text{CoCrCuFeNi}$ high-entropy alloys as a function of aluminum content. He found that, for higher Al content, the worn surface is smooth and yields fine debris with high oxygen content, which gives a large improvement in wear resistance, as shown in Figure 21. The reason of this improvement is attributed to its high hardness, which not only resists plastic deformation and delamination, but also brings about the oxidative wear in which oxide film could assist the wear resistance[38].

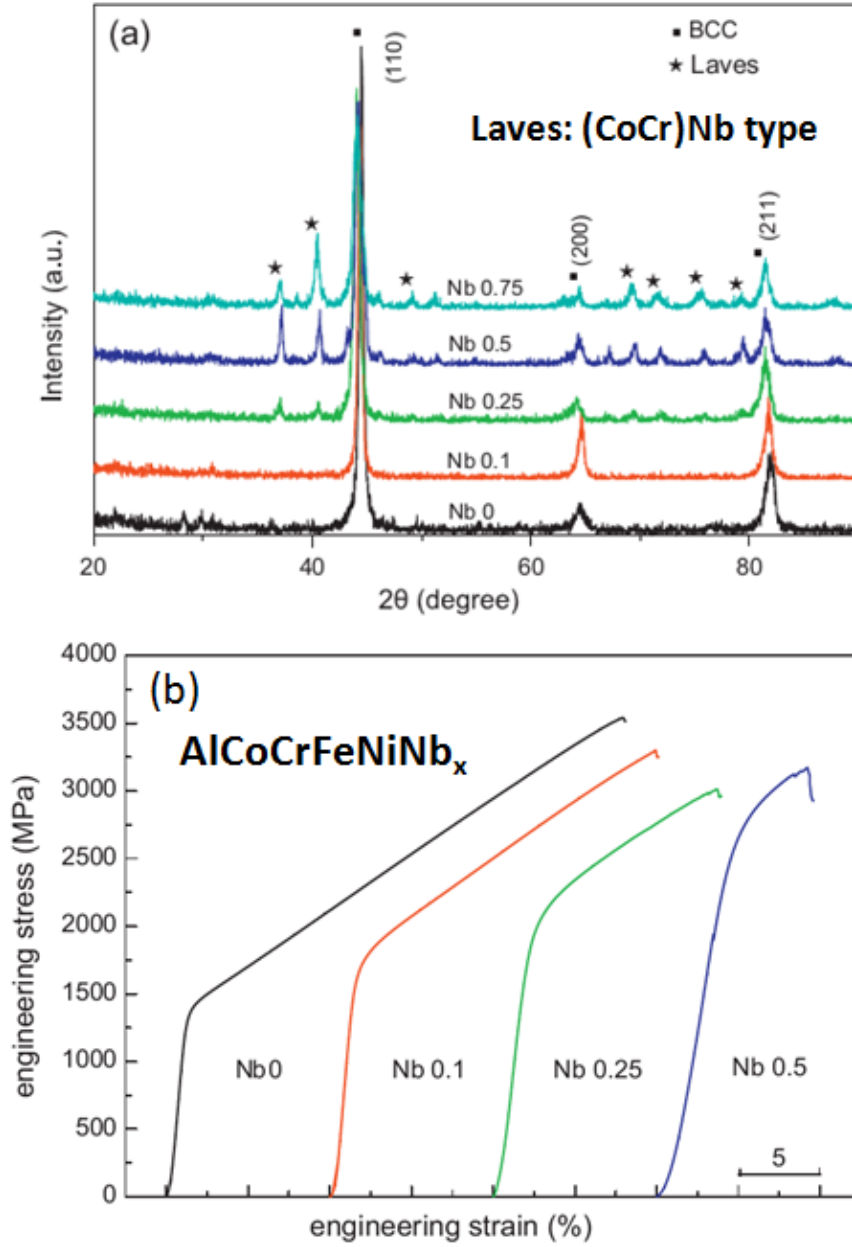


Figure 1. (a) The addition of Nb elements ($x = 0, 0.1, 0.25, 0.5$, and 0.75) into this HEA changes the original phase constitution, which yields the formation of ordered Laves phase besides solid solution phase. (b) The compressive stress-strain curves of the AlCoCrFeNiNb_x cylindrical samples with a diameter of 5 mm ($x = 0, 0.1, 0.25$, and 0.5). Literature results from [33]

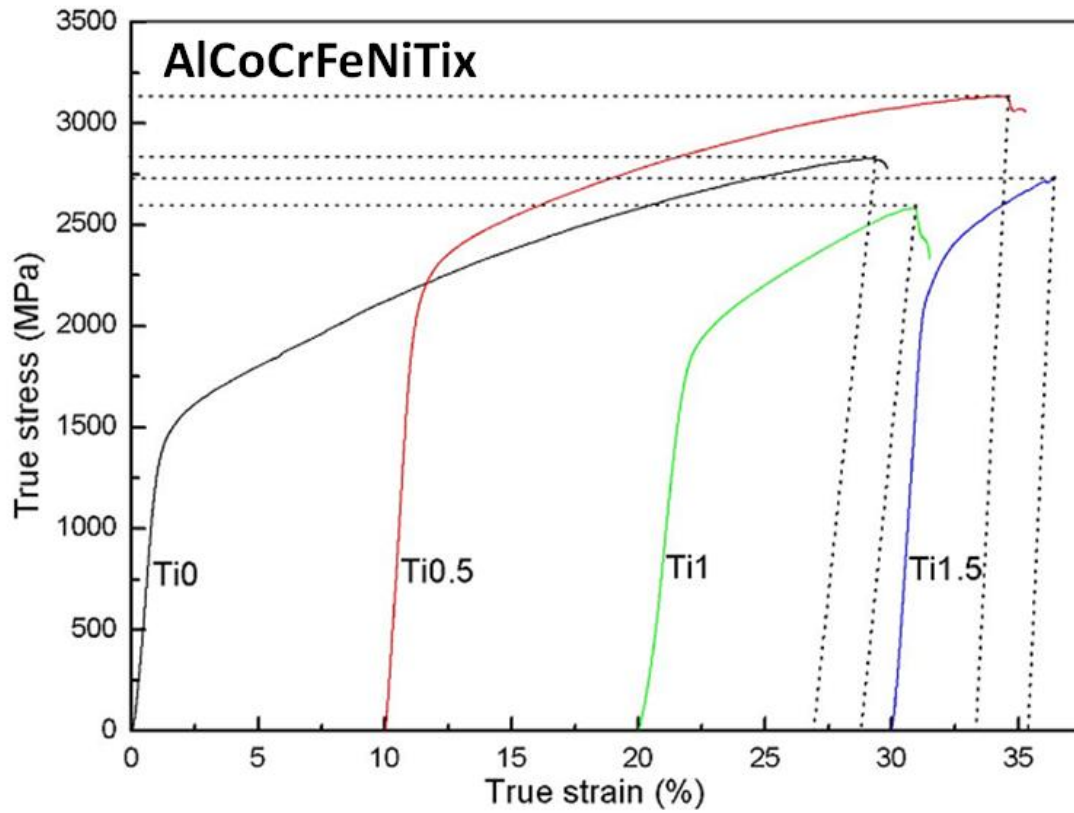


Figure 2. Compressive true stress-strain curves of AlCoCrFeNiTix alloy cylindrical samples with a diameter of 5 mm. Literature results from [19]

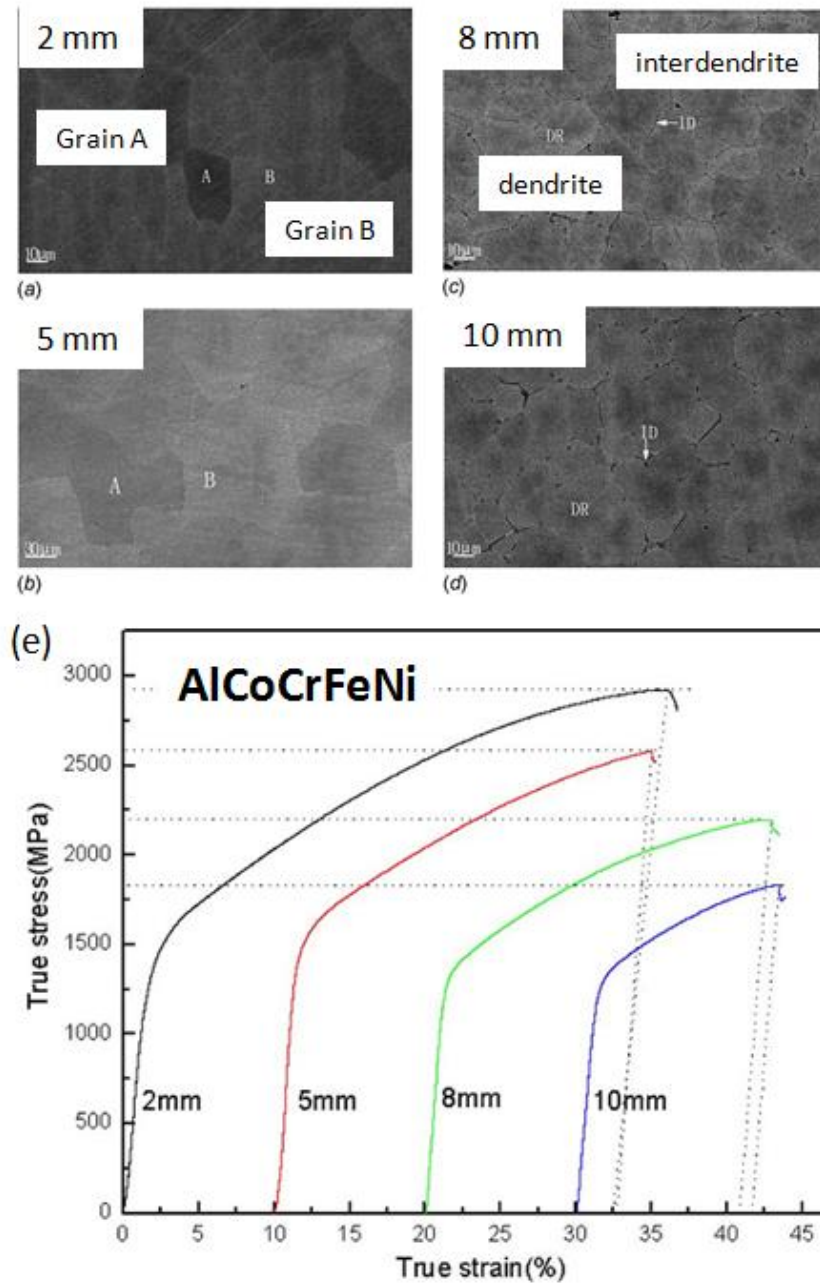


Figure 3. As the cooling rate increasing, the percentage of interdendritic phase is reduced (a-d), but both the strength and the plasticity are enhanced significantly (e). Compressive true stress-true strain curves for the AlCoCrFeNi alloy cylindrical samples with different diameters. Literature results from [24]

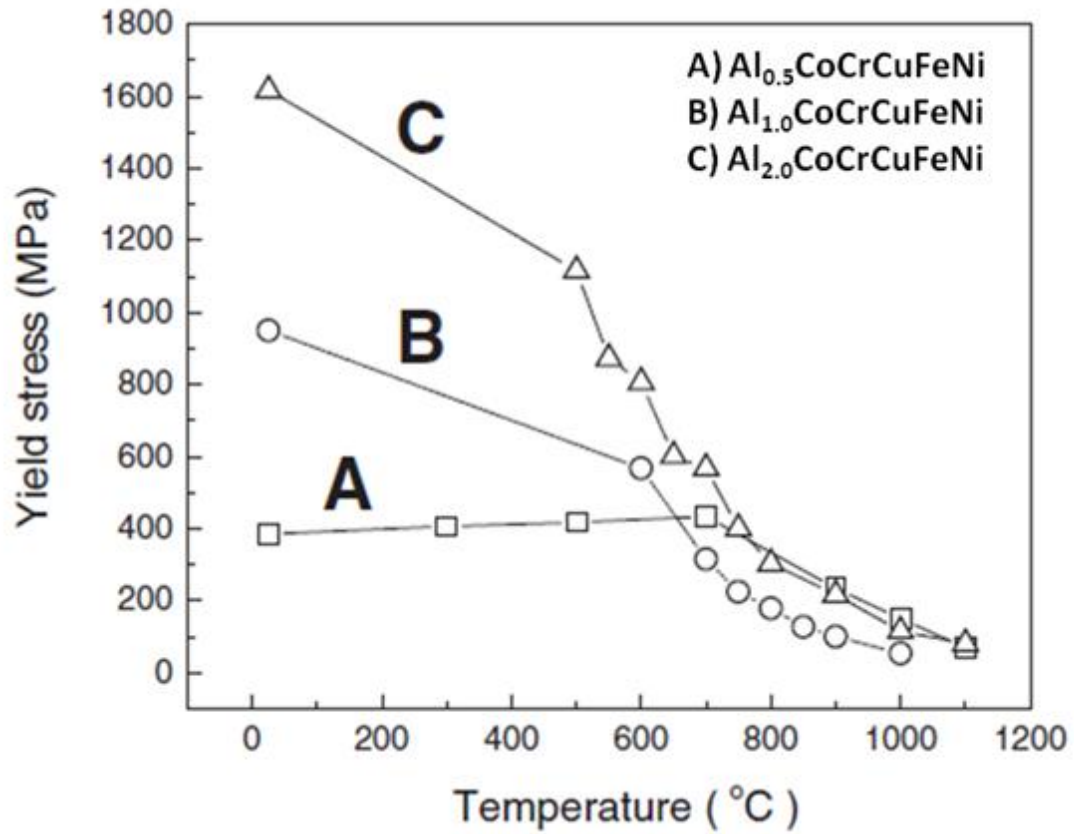


Figure 4. Compressive yield strength of $\text{Al}_x\text{CoCrCuFeNi}$ alloy system tested at different temperatures: A) $\text{Al}_{0.5}\text{CoCrCuFeNi}$, B) $\text{Al}_{1.0}\text{CoCrCuFeNi}$, and C) $\text{Al}_{2.0}\text{CoCrCuFeNi}$ alloys. Literature results from [2]

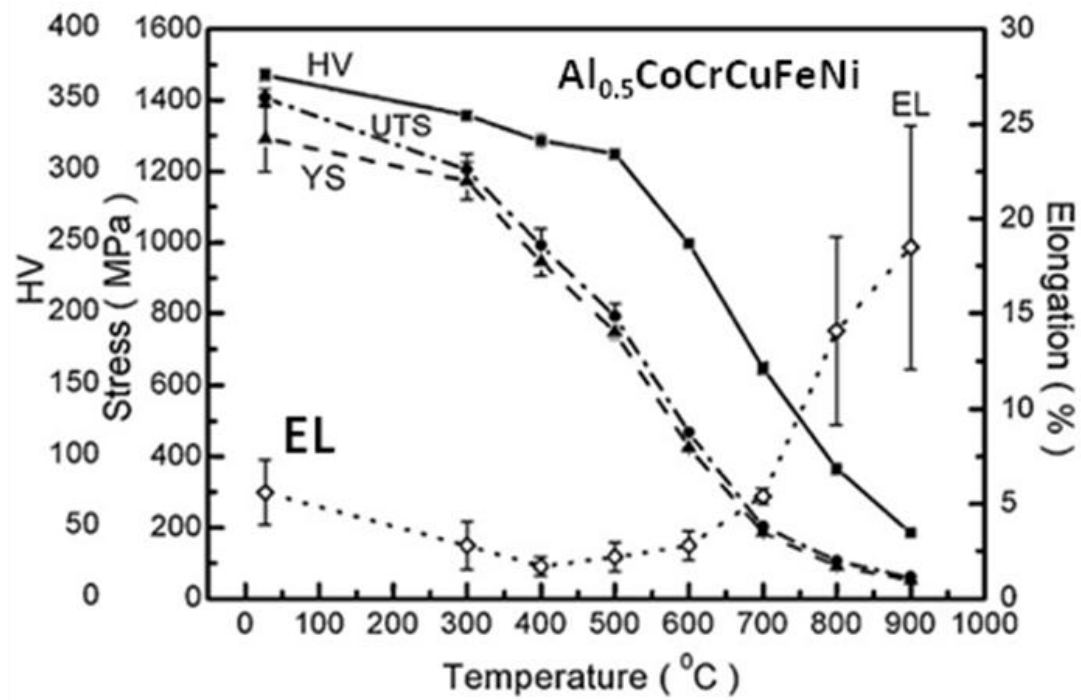


Figure 5. Hardness, strength and elongation as a function of temperature for as-rolled samples. Literature results from [30]

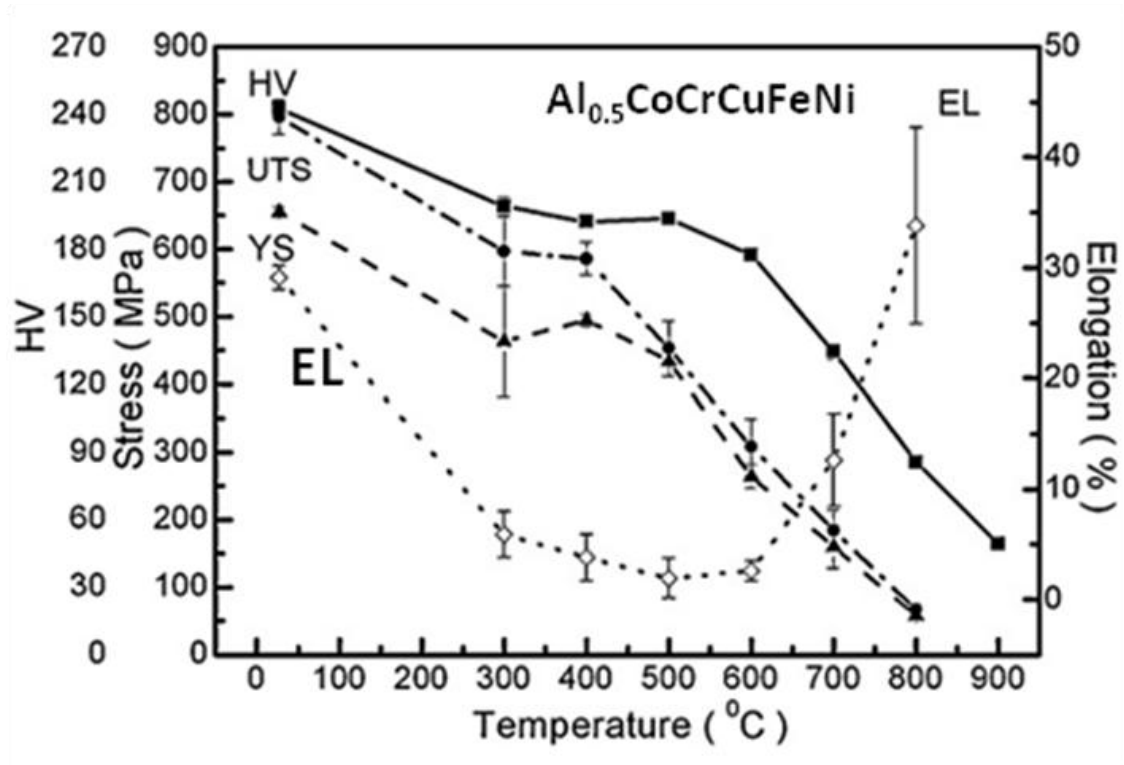


Figure 6. Hardness, strength and elongation as a function of temperature for as annealed samples. Literature results from [30]

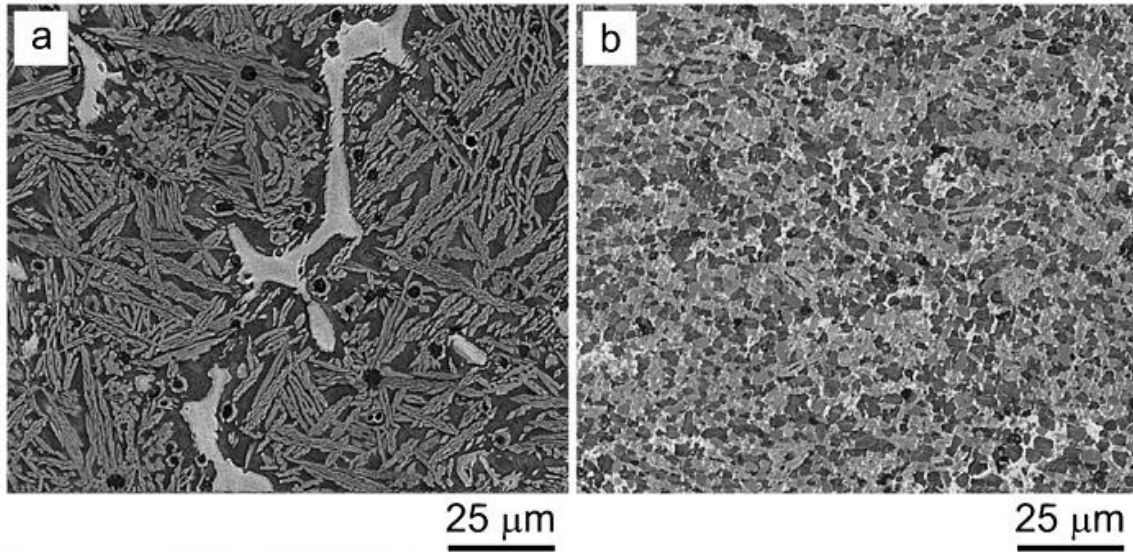


Figure 7. Microstructure of the AlCrCuNiFeCo HEA in (a) as-cast and (b) hot-forged conditions. Literature results from [28]

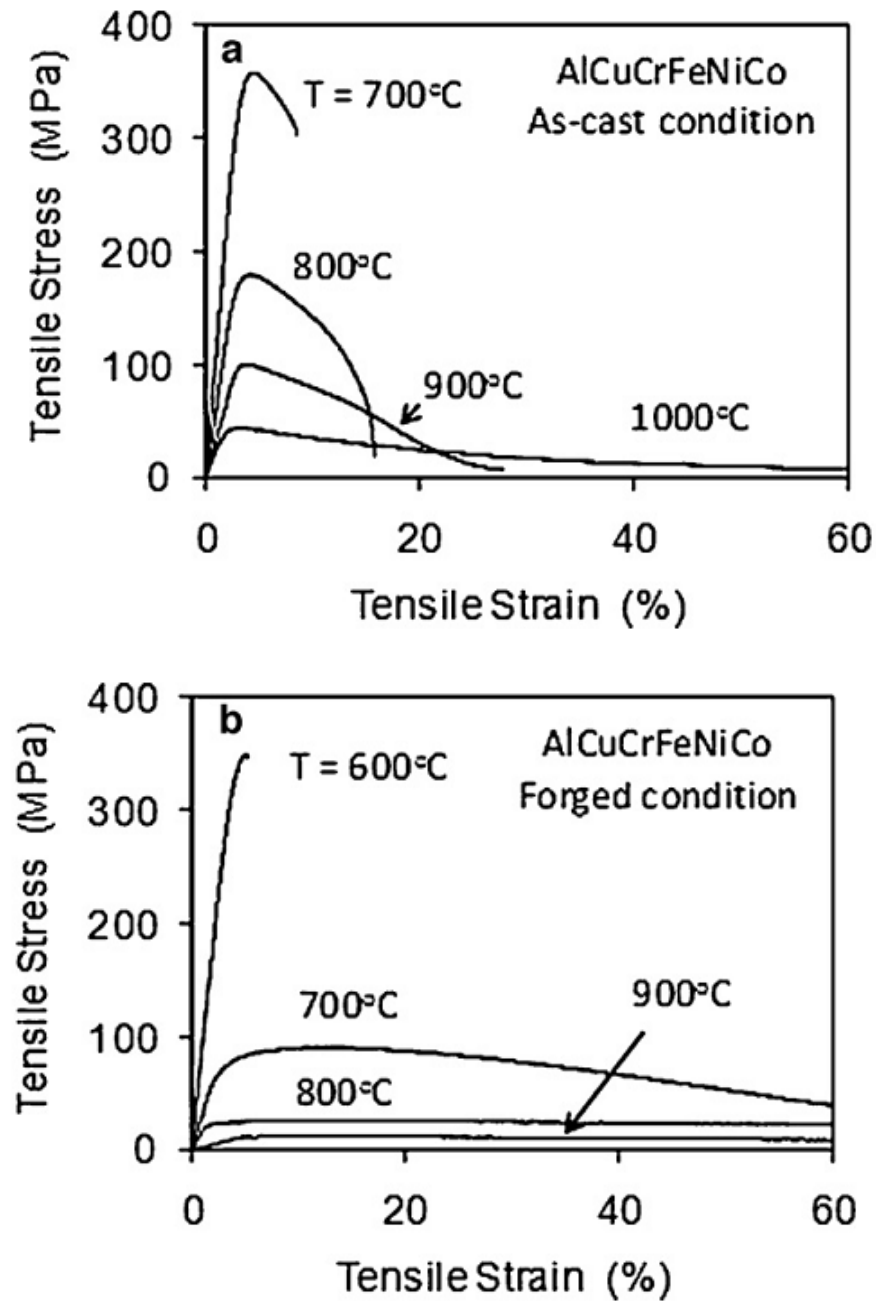


Figure 8. Typical stress-strain curves of AlCoCrCuFeNi (a) the as-cast and (b) hot forged samples deformed at different temperatures and the initial strain rate of 10^{-3} s^{-1} . Literature results from [28]

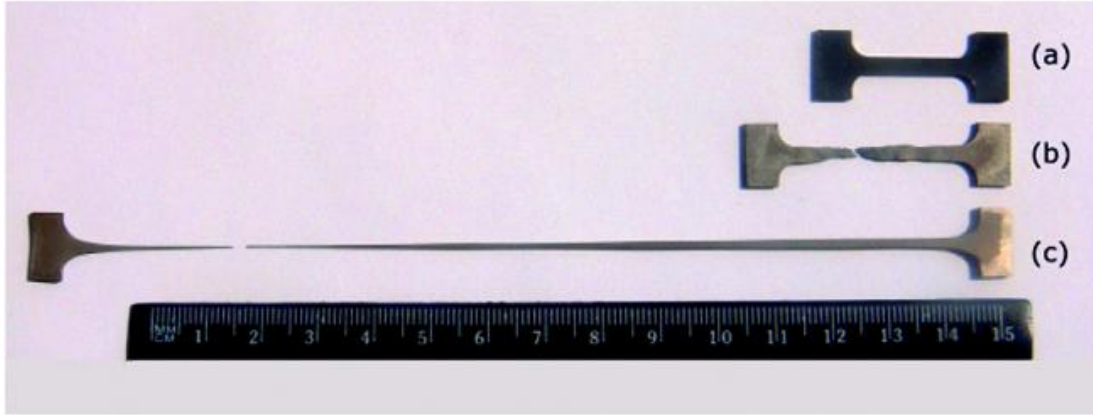


Figure 9. Photographs of AlCoCrCuFeNi tensile samples after deformation at 1,273 K: (a) a nondeformed sample; (b) as-cast sample ($\epsilon = 77\%$); and (c) forged sample ($\epsilon = 864\%$). $\dot{\epsilon} = 10^{-3} \text{ s}^{-1}$. Literature results from [28]

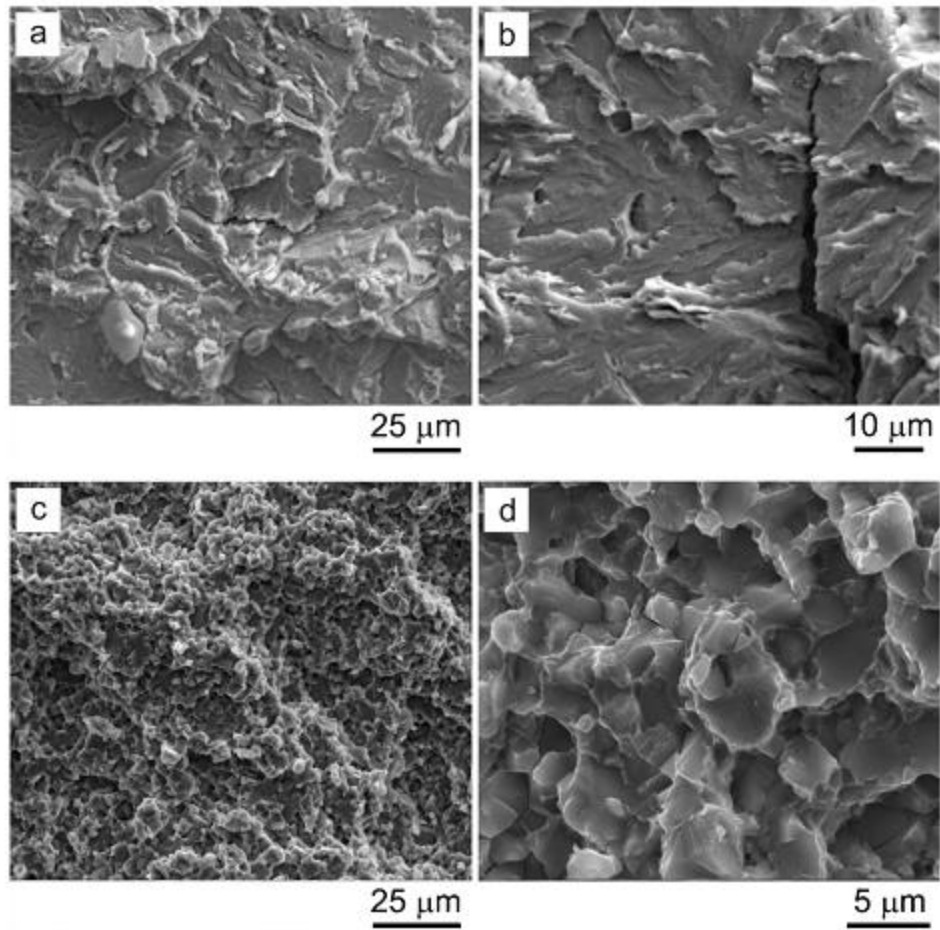


Figure 10. SEM images of the AlCoCrCuFeNi fracture surfaces of tensile samples after tensile testing deformation at room temperature. a and b: as-cast; c and d: hot forged conditions. Literature results from [28]

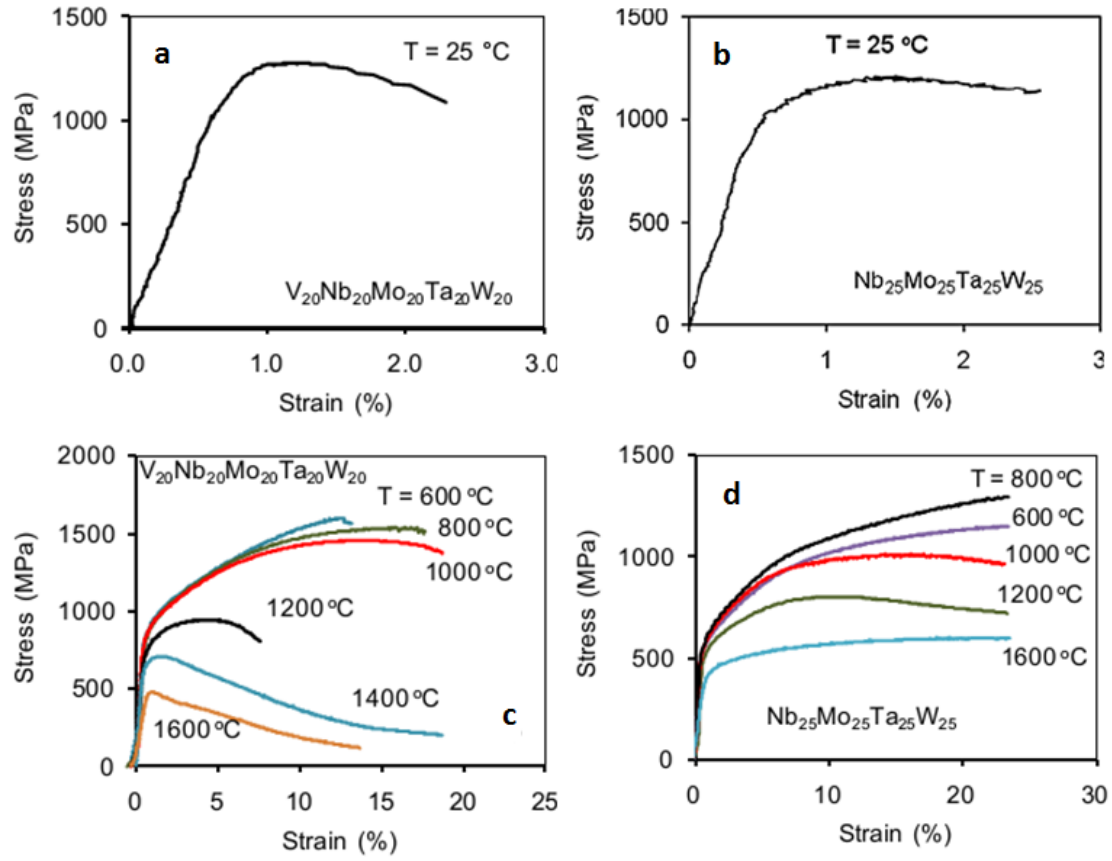


Figure 11. Compressive engineering stress-strain curves of NbMoTaW and VNbMoTaW HEAs at room temperature and high temperatures. Literature results from [4]

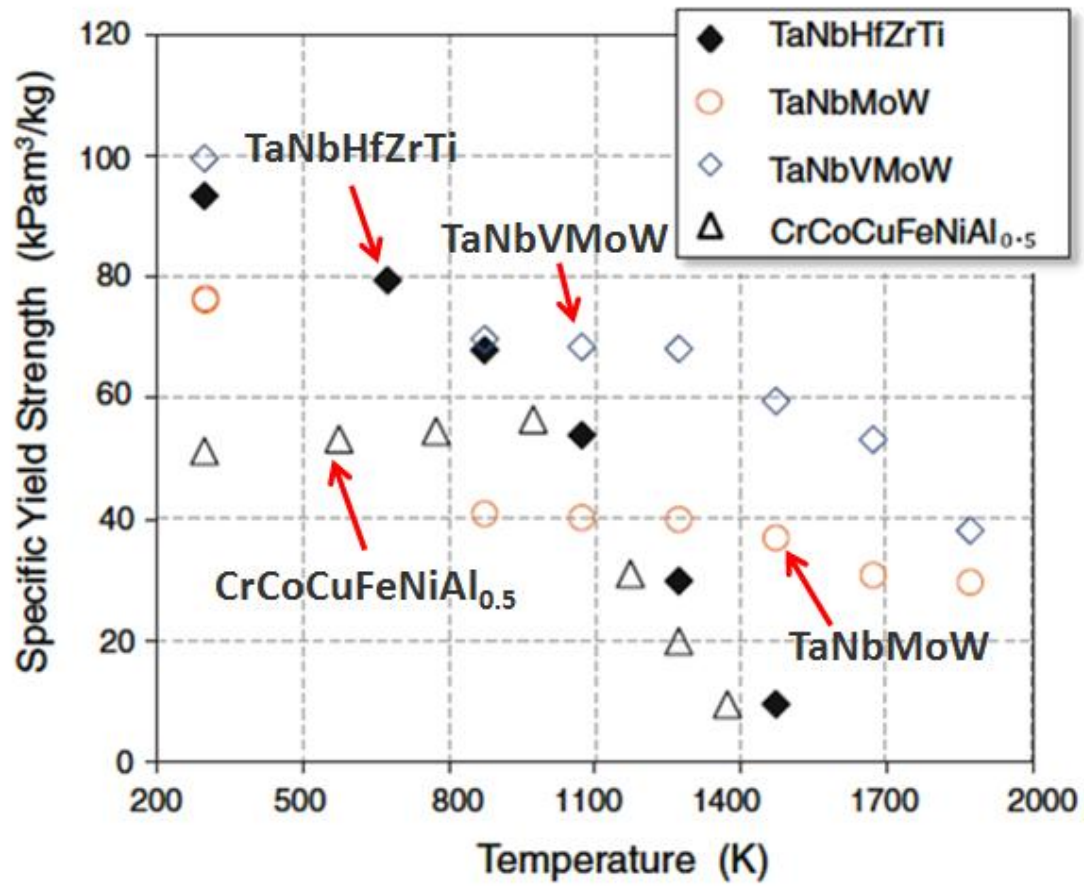


Figure 12. The temperature dependence of the specific yield-strength of the TaNbHfZrTi alloy in comparison with that for TaNbMoW, TaNbVMoW, and CrCoCuFeNiAl_{0.5} cast alloys. Literature results from [22]

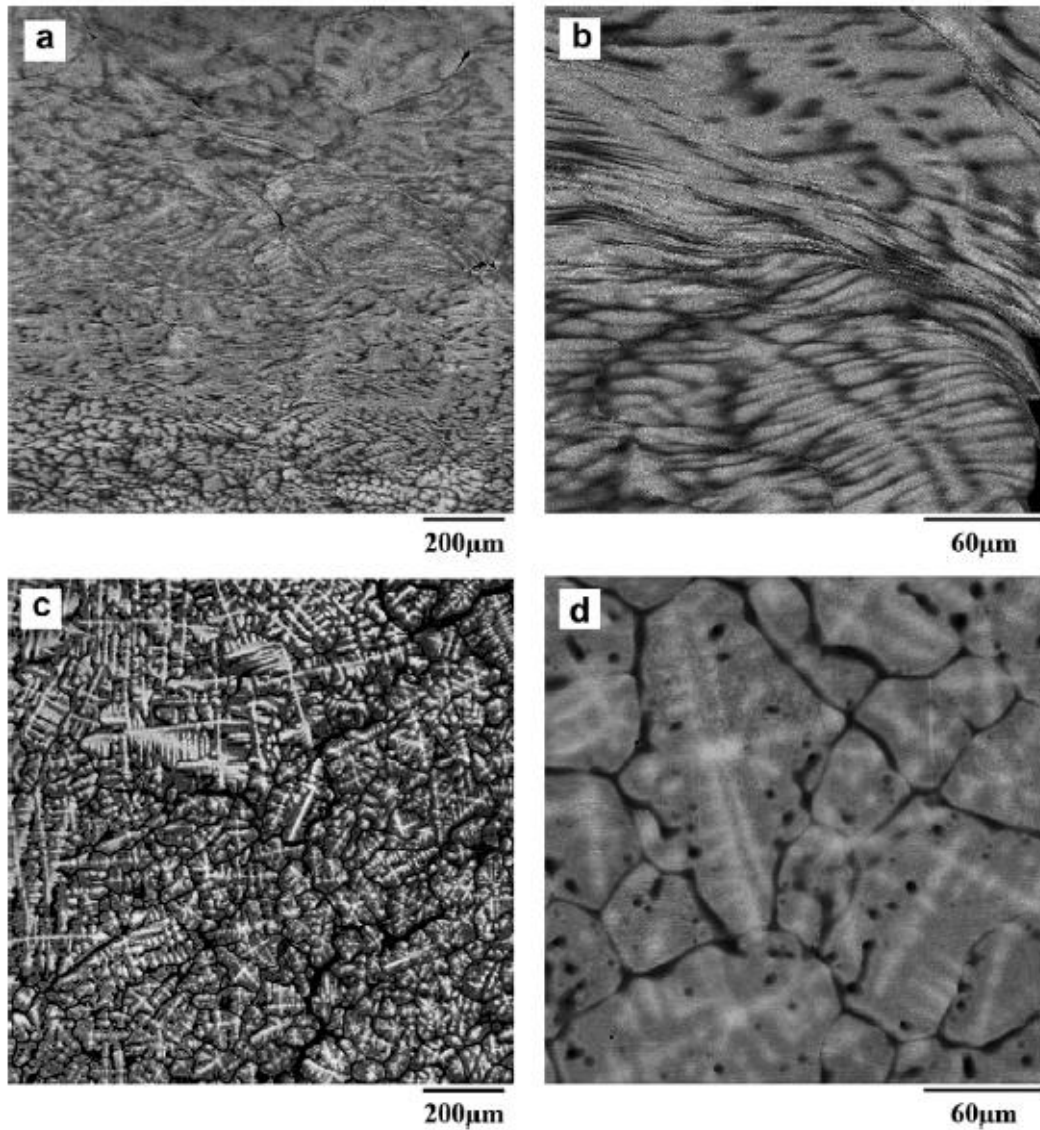


Figure 13. SEM backscatter images of the (a, b) Nb₂₅Mo₂₅Ta₂₅W₂₅ and (c, d) V₂₀Nb₂₀Mo₂₀Ta₂₀W₂₀ alloys after compressive deformation at 1673 K. Depicted crosssection are parallel to the loading direction (vertical) and located halfway between the surface and center of the samples. Literature results from [4]

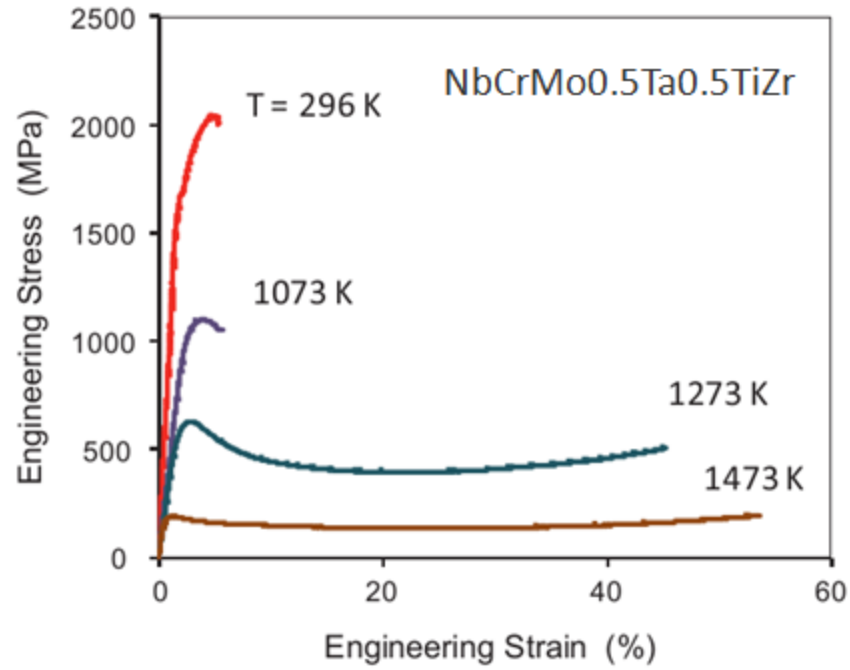


Figure 14. The engineering stress-strain compression curves of the NbCrMo_{0.5}Ta_{0.5}TiZr alloy samples after HIP at 296 K, 1,073 K, 1,273 K, and 1,473 K. Literature results from [23]

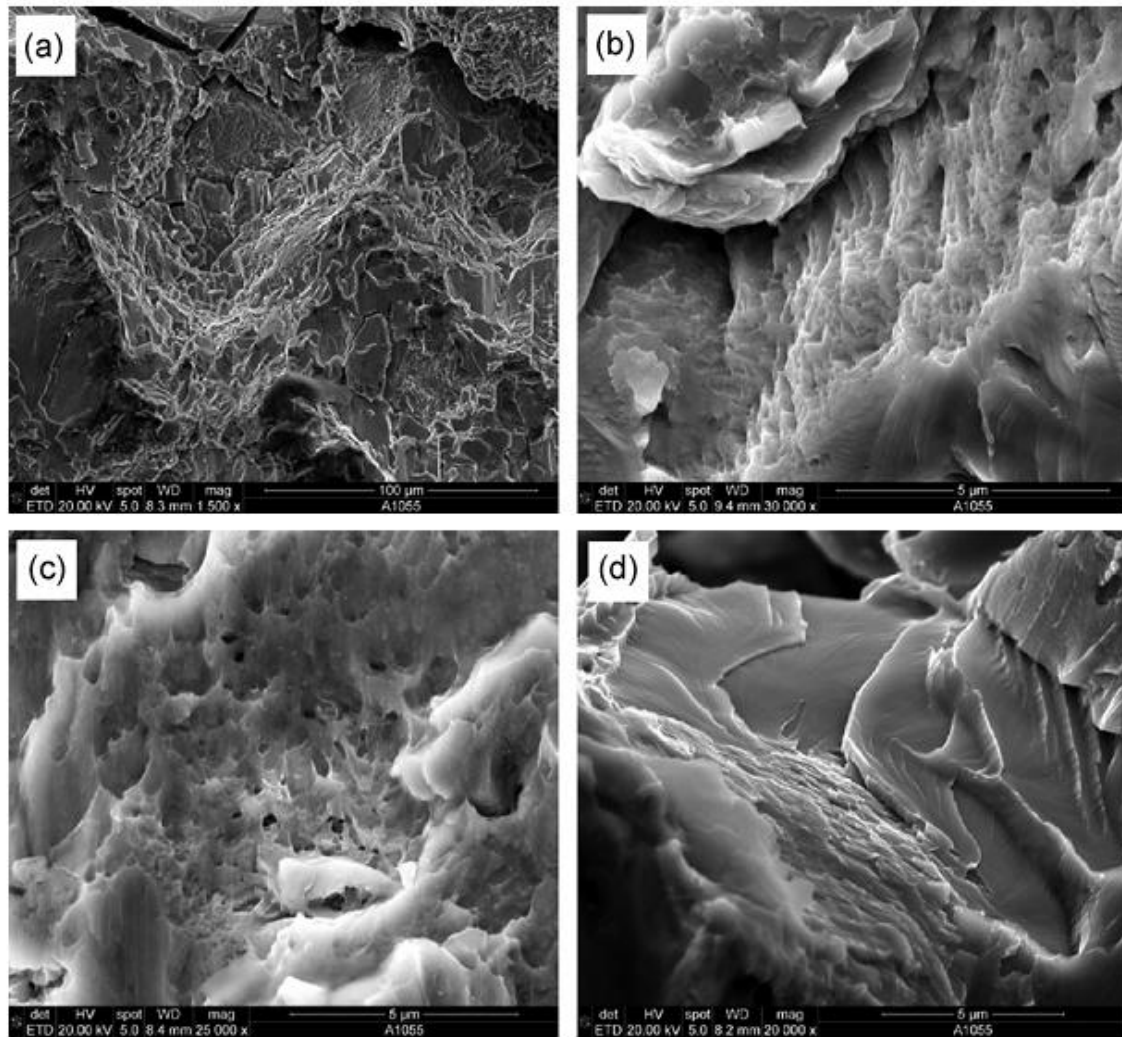


Figure 15. SEM secondary electron images of the fracture surface of a NbCrMo_{0.5}Ta_{0.5}TiZr alloy samples after compression deformation at room temperature.

Literature results from [23]

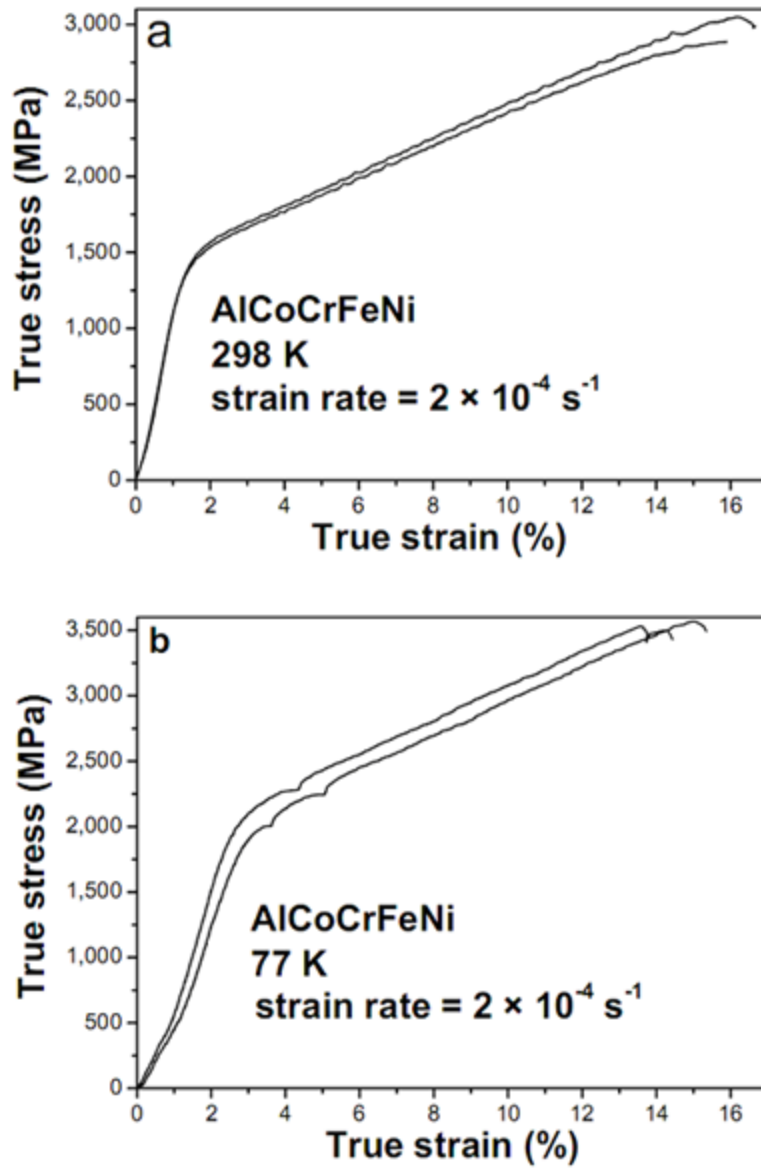


Figure 16. The compressive true stress-strain curves of the AlCoCrFeNi HEA at (a) 298 K and (b) 77 K. The yield strengths and fracture strengths at cryogenic temperatures increase distinguishably, compared to the corresponding mechanical properties at ambient temperature. Literature results from [35]

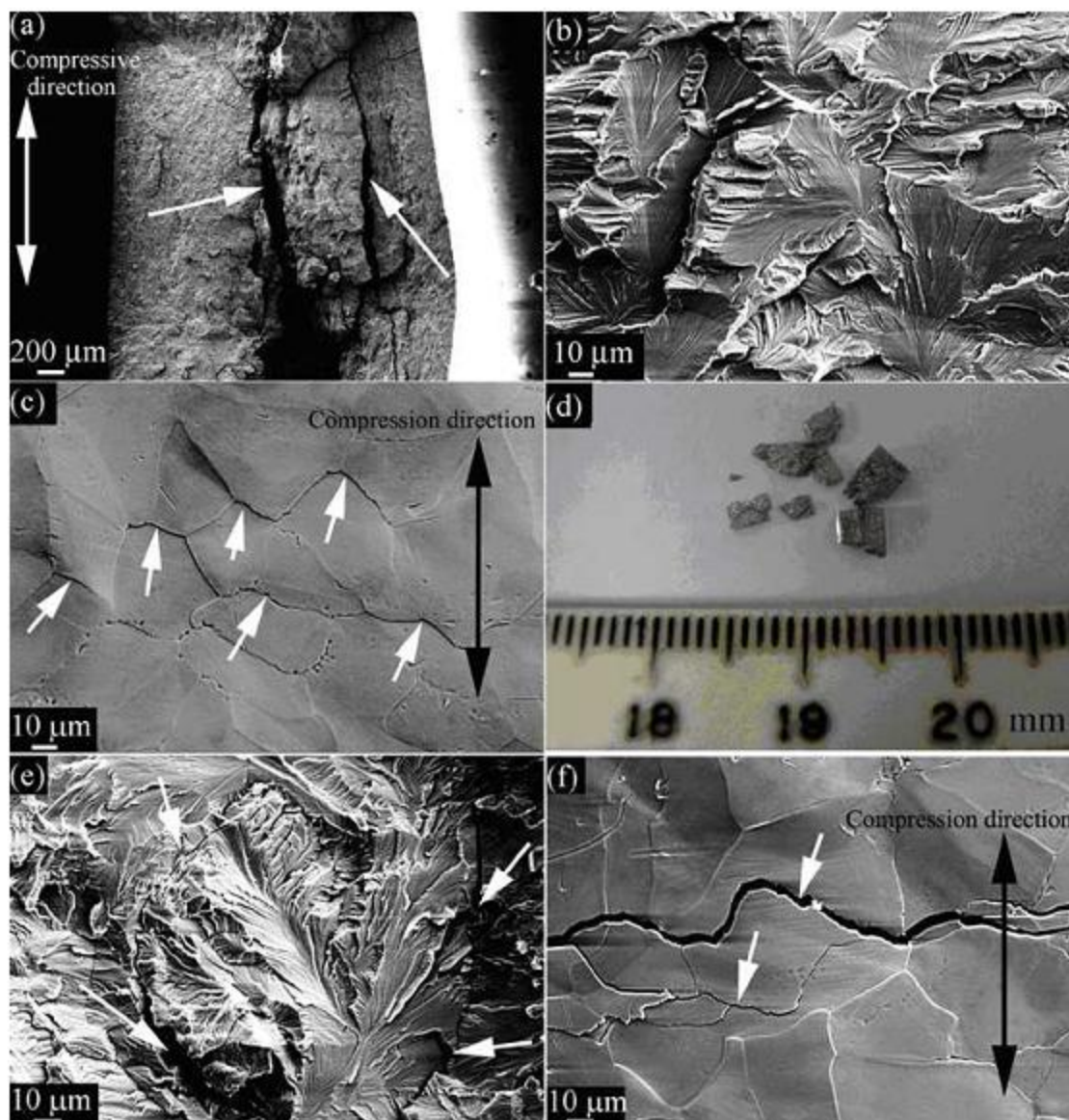


Figure 17. The low and high magnifications for the fracture surfaces of the AlCoCrFeNi HEA at 298 K shown in (a) and (b), respectively; The lateral surface of the deformed sample of the AlCoCrFeNi HEA at 298 K shown in (c); The low and high magnifications for the fracture surfaces of the AlCoCrFeNi HEA at 77 K shown in (d) and (e), respectively; The lateral surface of the deformed sample of the AlCoCrFeNi HEA at 77 K shown in (f). Literature results from [35]

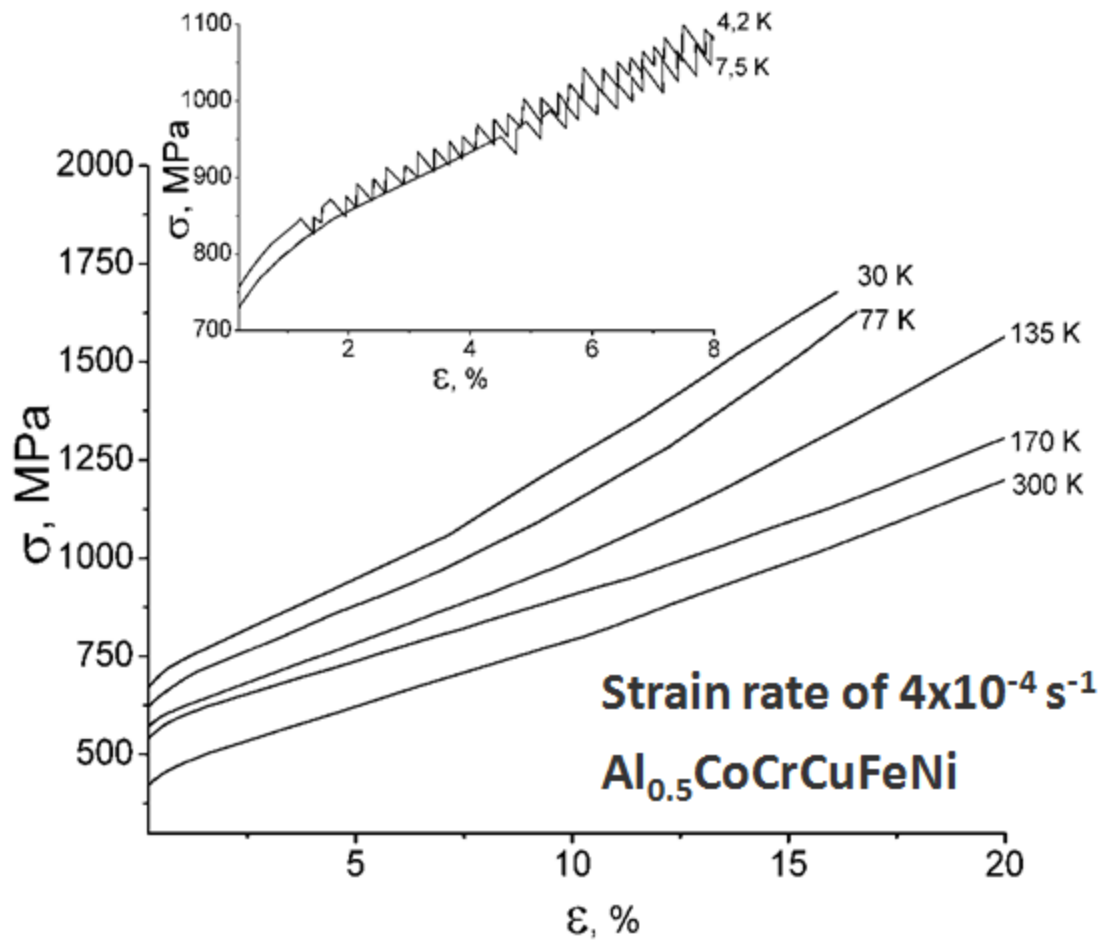


Figure 18. At all temperatures to 4.2 K the $\text{Al}_{0.5}\text{CoCrCuFeNi}$ HEA possess high plasticity under compression. At temperatures below 15 K, the curves take a serrated shape. The inserted figure illustrates a typical serrated stress-strain curve. Literature results from [36]

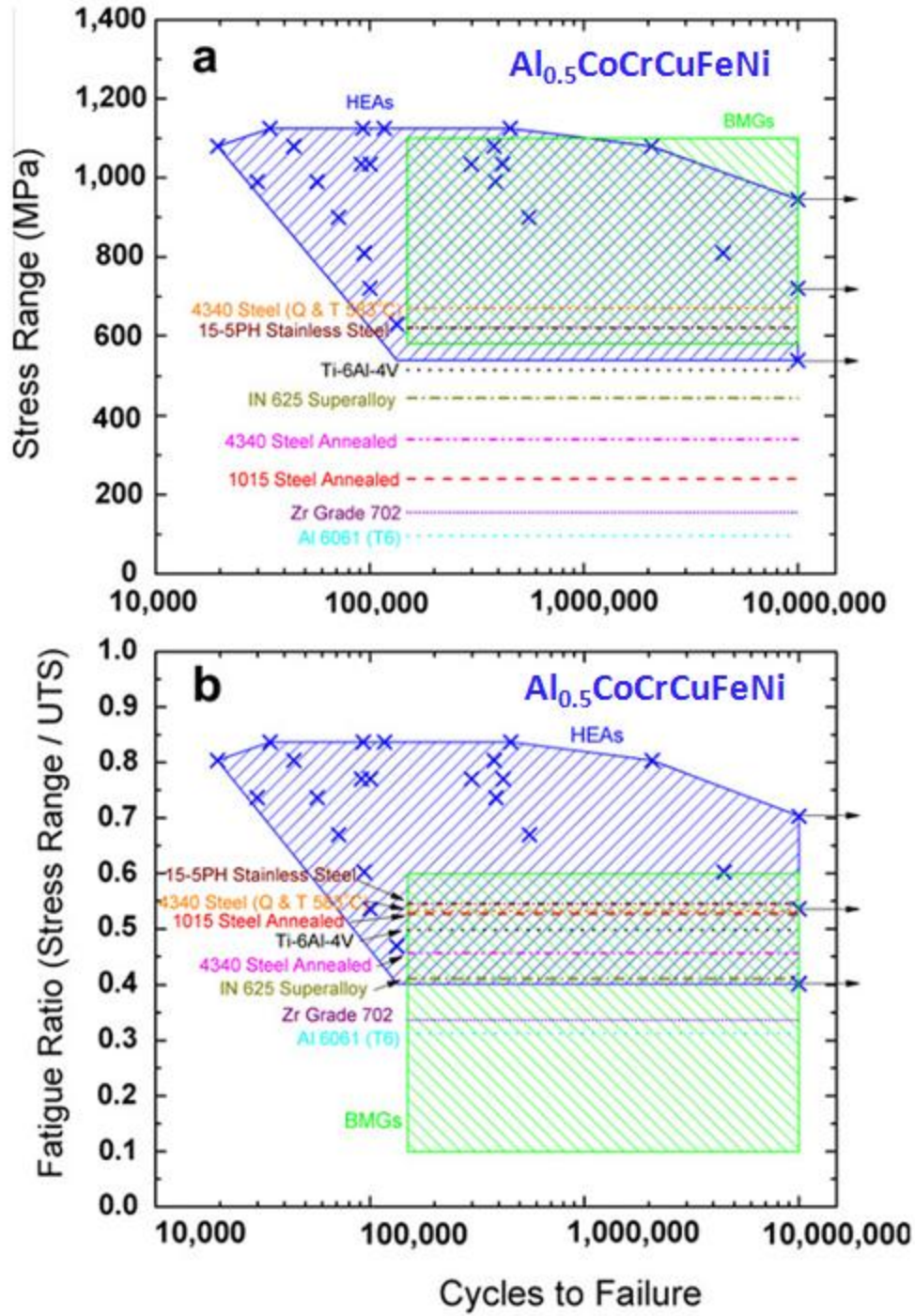


Figure 19. S-N curves comparing the fatigue ratios of the Al_{0.5}CoCrCuFeNi HEA, other conventional alloys, and bulk metallic glasses. Literature results from [16]

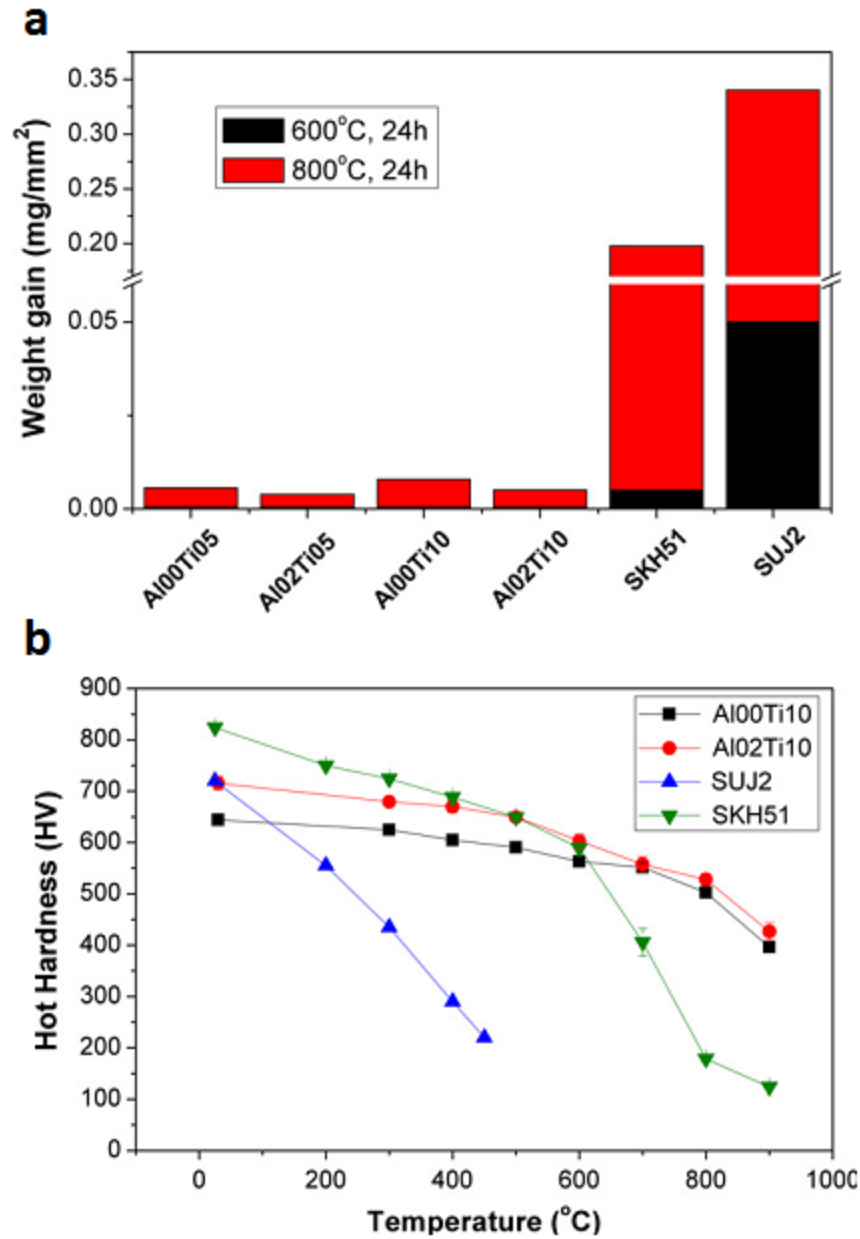


Figure 20. (a) Weight gain test of Al00Ti05, Al02Ti05, Al00Ti10, Al02Ti10, SUJ2 and SKH51 specimens at 873 and 1073 K for 24 h. The data is presented as weight increase per unit area after test. (b) Hot hardness vs. temperature plots for Al00Ti10, Al02Ti10, SUJ2 and SKH51 specimens from room temperature to 1173 K. Literature results from [37]

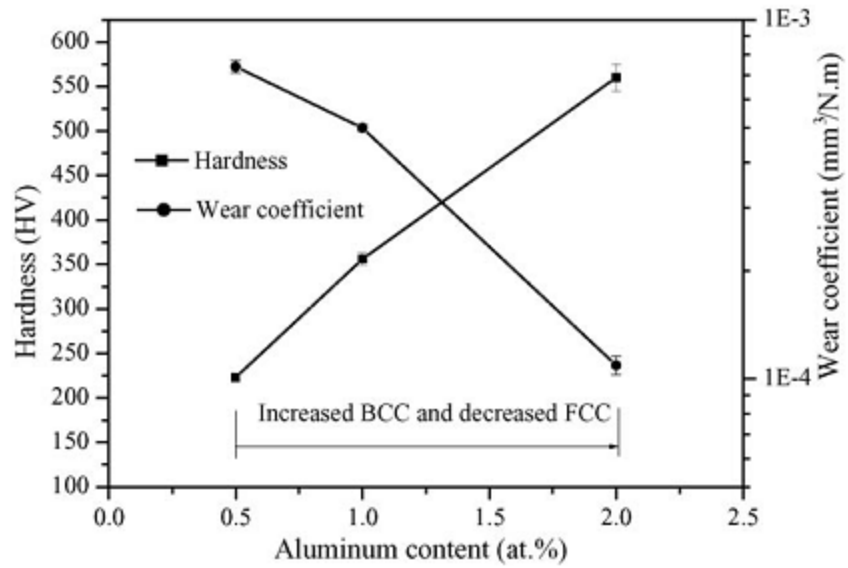


Figure 21. Vickers hardness and wear coefficient of Al_xCoCrCuFeNi alloys with different aluminum contents. Literature results from [38]

2. Microstructural Characterization of High-Entropy Alloys

2.1. Introduction

The relatively simple crystal structures of HEAs, like simple body-centered cubic (*BCC*) or face-centered cubic (*FCC*), found in the arc-melting and copper-mold-casting process, are usually nonequilibrium and unstable. After heat treatment, such as forging, annealing, and aging, additional phases can form and make the HEAs more complex. Indeed, the additional phases form common in HEAs system, such as ordered/disordered phases, intermetallic/solid solution phases, and matrix/precipitate phases. Furthermore, thermodynamics and kinetics of phase transformations in HEAs are still unclear. For example, the $\text{Cu}_{0.5}\text{CoCrFeNi}$ HEAs system aged over a range of temperatures (up to 1,623 K) exhibits to form a Cr-rich and a Cu-rich precipitate phases from as-cast *FCC* matrix [39]. A second *FCC* phase precipitates from the as-cast ordered *BCC* matrix and the *FCC* phases become dominated after the CoCrFeNiCuAl alloy annealed at 1,273 K for 2h [40]. After homogenization at 1,373 K for 24 h, additional *BCC* phase and Widmanstätten needlelike precipitates of the Cu-rich phase formed from the as-cast condition of *FCC* dendrite and a Cu-rich *FCC* interdendrite [41]. After thermomechanical treatments, intermetallic σ phase was found in the $\text{Al}_x\text{CoCrFeNi}$, and $\text{Al}_x\text{CoCrCuFeNi}$ HEAs systems [28, 42, 43], and some unidentified phases also appeared [30, 44].

As for mechanical properties, people usually seek for single phase HEAs to get the solid solution strengthening mechanism, because they take it for granted that a large volume of secondary intermetallic phases will deteriorate mechanical properties. Another method

for strengthening metals without losing toughness is grain refinement through the heat-treatment process [45]. Meanwhile, literature shows that the tensile ductility and toughness of HEAs improved at both room temperature and elevated temperatures after thermomechanical treatment [28, 30]. It means that thermomechanical treatment is also necessary in HEAs if we expect their applications at elevated temperatures, even though additional phases will precipitate and form.

The present work focuses on one of the earliest quinary HEAs system, AlCoCrFeNi (denoted as Y5E in this article), first reported in 2007 by Zhang et al. [19]. It belongs to the $\text{Al}_x\text{CoCrFeNi}$ high entropy alloy system, which is one of the most well-developed and refined HEA systems [19, 24, 31-33, 42, 46-51]. The Y5E alloy shows high compressive yield strength ($\text{YS}=990 \text{ MPa}$) with reasonable ductility at a temperature of 773 K [25]. This alloy's high strength at elevated temperatures makes it a promising structural material. In the literatures, through this or that experimental method, some people claimed that the Y5E alloy possessed a single-phase *BCC* crystal structure [32, 48], but others found additional ordered *BCC* phase [47, 50] and even *FCC* phase in the as-cast condition with the same composition [42, 51]. However, no publications have yet been available in the open literature, and there is limited knowledge on the long-term phase stability and high-temperature tensile properties of such a potential composition in extreme-environment condition. The attention in this paper will be stressed on the thermodynamics and kinetics of phase transformations in HEAs. We will discuss how nonequilibrium and equilibrium phases can be identified in the HEAs system. An

example of using the proposed approach will be presented by applying it to AlCoCrFeNi HEAs system.

2.2. Experimental Methods

The as-cast samples of the Al₂₀Co₂₀Cr₂₀Fe₂₀Ni₂₀ (mole percent) alloy, denoted as Y5E-AC, were prepared by arc-melting the constituent elements with a current of 500 amps in a water-cooled, copper hearth, using a Large Bell Jar (ABJ-900) arc melter of Materials Research Furnaces, Inc. The elements were all at least 99 weight percent (wt. %) pure, and the melting was done in a vacuum of at least 0.01 torr under a Ti-gettered argon atmosphere. The melting and solidification processes were repeated several times to improve the homogeneity of the sample. Finally, the re-molten ingot was cast into 6mm diameter rods. The final composition of the alloy is confirmed through quantitative analysis, by Inductively Coupled Plasma Optical Emission Spectrometers (ICP-OES) in Dirats Laboratories, Westfield, MA. Carbon percentage was quantitatively analyzed by a Combustion method. Hydrogen, Oxygen, and Nitrogen were quantitatively analyzed by an Inert Gas Fusion (IGF) method. Several samples were heat treated after casting. These samples are referred to as Y5E-HP. The heat treatment consisted of hot isostatic pressing (HIPing) and annealing. The samples were soaked at 1,373 K / 207 MPa for 1 hour, and then the furnace power was shut down, and the samples were cooled to 773 K under 207 MPa after which the pressure was released to 1 atmosphere (0.1 MPa) while the samples continued to cool down to room temperature. The HIPed samples were then placed in a horizontal tube furnace, vacuumed with a rough pump and then the tube was filled with high purity argon, which continuously flew at a rate of ~ 200 ml/min. The samples were

held at 1,423 K for 50 hours. The densities of the alloy samples were measured with a helium pycnometer AccuPyc 1330 V1.03. The phases of the samples were analyzed using a high energy synchrotron X-ray diffraction in a beamline 6-ID-D, Advanced Photon Source (APS), Argonne National Laboratory. The samples for X-ray diffraction were in the form of powders. The microstructures were investigated by Scanning Electron Microscopy (SEM) including EDS and EBSD, and the EDS data was used to resolve the *BCC_A2* from *B2* phases, which give indistinguishable diffraction, but distinct EDS signals.

2.3. Results and Discussion

According to thermodynamics, the equilibrium state and the corresponding microstructures of HEAs result from the stability competition among all the phases in a multicomponent system. HEAs in as-cast condition usually have lesser phases than the ones in heat-treated condition, because the former almost are still in metastable or nonequilibrium state. In order to recognize the relationship between nonequilibrium and equilibrium phases in HEAs, an effective way is needed to determine and/or predict the multicomponent phase diagrams. Traditionally, binary and ternary phase diagrams have been established purely through experimental methods. For multicomponent systems, a phenomenological method, called Computer Coupling of Phase Diagrams and Thermochemistry (CALPHAD), has been widely applied for the study [52]. Through this thermodynamic method, not only the known thermodynamic properties can be determined, but the unknown thermodynamic properties can be predicted. The application of the CALPHAD approach in aiding materials design has been widely

discussed [53, 54], and especially recently, successfully used in the AlCoCrFeNi HEAs systems by Zhang et al. [14].

As an example of using the proposed approach above, simultaneously-acquired EBSD crystallographic maps and EDS elemental maps of the nonequilibrium microstructures of as-cast condition (named Y5E-AC) are showed in Figure 22. The flowery dendrites can be seen in the Figure 22a, and more clearly in Figure 22d-h. The dendrites are embedded within individual grains of the matrix phase. The dendrites span $\sim 40\ \mu\text{m}$, and the growth of branched dendrites starts from a common center in arbitrary directions (Figure 22b). The dendrite arm thickness was $\sim 20\ \mu\text{m}$, and the average grain size of Y5E-AC in the region of equiaxed dendritic grains is estimated to be $\sim 75\ \mu\text{m}$. The EBSD data was forced to index as single-phase *BCC_A2*, because *BCC_A2* and *B2* phases are indistinguishable via EBSD. The data shows that the Y5E-AC pseudo-single-phase ferrite (red color) and grain boundaries are marked in black (Figure 22c). Dark and light regions inside the grains can be clearly seen in EDS element mapping (shown in Figure 22d-h). They are indicating different compositions of dendritic and interdendritic regions due to constitutional segregation during solidification, and the qualitative segregation characteristics can be visualized: Co is uniformly distributed, while Al and Ni solidify first in the dendrite cores, ultimately forcing Cr and Fe into the interdendritic regions.

After one hour HIPing at 1,373 K and fifty hours annealing at 1,423 K, the nonequilibrium phases become more equilibrium ones. The grain boundary becomes more clear and thicker (shown in Figure 23a-c). The grain boundary has lower energy than the matrix. Thus after 50 hours of annealing the grain boundary is expanding and

being accumulated by some precipitates. At the same time, the sample is soaked at 1,373 K / 207 MPa for 1 hour, and the flowery dendrites are broken into small pieces, and some round precipitates can be found in the matrix. Constitutional segregation can still be clearly observed. The refinement of EBSD data using EDS information determines four HIP/annealing-induced equilibrium phases, and the relative intensity of each element map (Figure 23g-k) give a qualitative sense for the segregation characteristics of that constituent: (1) Co is still the relatively most uniformly distributed element, but some segregation (darker orange color in Figure 23h) can be found; (2) broken dendrites (grey color in Figure 2a) are *B2*, rich in Ni and Al, while small Cr-rich and Fe-rich precipitates are observed in the dendrite cores; interdendritic regions are *BCC_A2* (red color in Figure 23a) and σ (blue color in Figure 23a), both rich in Cr and Fe; (3) the grain-boundary-like phase (green color in Figure 23a) is *FCC_A1*: rich in Co and Fe.

High energy X-ray (Synchrotron) diffraction, combined with EBSD and EDS data, confirms the two phases above existing in the nonequilibrium case (Y5E-AC), and the four phases existing in the equilibrium case (Y5E-HP). Figure 24 shows the X-ray diffraction patterns of Y5E-AC and Y5E-HP. Only one set of the diffraction peaks for *B2* in the as-cast condition can be easily identified in the Y5E-AC pattern (see Figure 24), and the lattice parameter is $a = 0.2875$ nm. It is, however, quite possible that there is also additional disordered *BCC* phase, also named the *BCC_A2*, with the same lattice parameter as *B2*. *BCC_A2* is a disordered *BCC* phase and only fundamental peaks [(110), (200), (211), (220), etc.] are present, which have exactly the same positions as the fundamental peaks from the *B2* phase with the same lattice parameter. A thorough

Rietveld analysis is required to separate these phases from synchrotron X-ray data. Otherwise, the peaks from the *BCC_A2* phase are shielded by the peaks from the *B2* phase (when the lattice parameters are the same) and not recognizable. It is possible to identify intensity between superlattice peaks and fundamental peaks of the ordered structure, to tell *BCC_A2* + *B2* from just *B2*, but the most straightforward way is TEM.

For the heat-treated condition with an equilibrium case (Y5E-HP), the HIP and annealing processing increased the intensities of the peaks of the *BCC_A2* and *B2* phases. Heat treatment also decreases the lattice parameter of the *B2* phase from $a = 0.2875$ nm to 0.2869 nm. This trend can be due to a slight change in the chemical composition of this phase caused by the annealing and formation of additional phases. In addition, another two phases, *FCC_A1* and σ , are found after the HIP and annealing, which agrees with the EBSD and EDS results. The lattice parameter of *FCC_A1* is determined to be $a = 0.3596$ nm. From these phases, only the *FCC_A1* phase seems to be disordered because no superlattice peaks are present from this phase [no such superlattice peaks like (100), (110), (210), (211) etc.; only fundamental (111), (200), (220), and (311)]. Similarly as the nonequilibrium case, it can also confirm through EDS mapping, shown in Figures 4g-k, that there is also additional *BCC_A2*. To identify the σ phase, three strongest peaks of the phase, are matched with the synchrotron pattern. The σ phase mentioned here is one Cr-Fe rich intermetallic phase with $P4_2/mnm$ (#136), discovered by Bergman et al. [55]. The three strongest peaks, (410) (411) (331), as well as (002) are found in the synchrotron pattern. Another three main peaks of σ phase, (330) (202) (212), are shielded by the peaks from the other phases.

Figure 25a shows the simulation of nonequilibrium solidification by Scheil model [56]. The calculated solidification path for the Y5E alloys, which indicate that the primary solidified phase is *B2*. Then the disordered *BCC_A2* phase will form with the temperature decreasing. According to the simulation as shown in Figure 25a, only 7% of the liquid is consumed to form the primary *B2* and the next 20% of liquid forms *BCC* phases (both *BCC_A2* and *B2*). Then, the rest of liquid solidifies into *BCC* + *FCC_A1* duplex structures. Furthermore, the temperature drops less than 15 K for the *BCC* + *FCC_A1* mixture to finish solidification. Thus, the *FCC_A1* phase may not be able to form due to the high cooling rate (nonequilibrium) of the alloy preparation using the drop-casting method. It should also be pointed out that, the simulation shows that the *BCC* structure is a mixture of the ordered *B2* and disordered *BCC_A2* owing to this special solidification (rich Al and Ni dendrite solidified first, and then interdendritic regions formed). This is consistent with the experimental observation for nonequilibrium microstructures of Y5E-AC in this work.

Using the thermodynamic database we developed in this study [14], an equilibrium line calculation is performed for the Y5E alloy as shown in Figure 25b. As shown in our calculation, the *FCC_A1* phase is in equilibrium with the *BCC* phases after heat treatment, which is consistent with the experimental data in this work and those in the literature [42, 48]. Note that the fraction of *FCC_A1* phase is around 50%, and we may not be able to obtain this amount since the Y5E-HP alloy may not yet reach equilibrium due to the sluggish diffusion of elements in HEAs and the short annealing period (50 hrs). As shown in Figure 25b, the σ phase does form in the temperature range of 733-1073 K.

However, Chou et al. [42] did not observe the σ phase at 773 K and 823 K, which is not surprising, since the precipitation is diffusion controlled process and a certain amount of phase is necessary for phase identification by regular lab X-ray diffraction. As mentioned previously, the σ phase was observed in the Y5E-HP microstructure, which was annealed beyond the thermodynamically predicted existing temperature range (733-1073 K). There are two possible reasons for this discrepancy: one reason may be due to unreasonable thermodynamic parameters for the σ phase in the current thermodynamic description; the other reason may be due to the localization of certain alloying elements within this alloy forming the σ phase. For example, a certain amount of Co can improve the stability of σ phases in higher temperatures, up to 1,556 K (such as the binary Co-Cr σ phase [57, 58]), which is higher than the annealing temperature 1,423 K. Indeed, a small amount of Co was observed in the σ phase, as shown in Figure 25h. Further experimental and thermodynamic investigation on this issue will be carried out in the future study. Thus, excluding the uncertainties from experimentation and thermodynamic calculations, the thermodynamic prediction shown in Figure 25 agrees qualitatively with the experimental observation of this study, as shown in Figure 23 and Figure 24. Further systematic phase transformation studies for the Y5E alloys will be necessary, especially in the solid state, for the quantitative comparison.

2.4. Summary

In summary, we discussed one proposed approach about how nonequilibrium and equilibrium phases can be identified in the HEAs system, what phases are usually found

in the as-cast or heat-treated condition, and what are thermodynamics and kinetics of phase transformations in HEAs.

The presentation of the results AlCoCrFeNi HEAs system as an example proves that the proposed approach is effective and suitable. Through TEM and EBSD, the nonequilibrium microstructures are identified to have large grains with clear intragranular dendritic structures containing two phases, *BCC_A2* and *B2*. The equilibrium microstructures have smaller grains, but with blocky wall-like phase along boundaries and along former-dendrite arms. Four phases, including *FCC_A1*, *BCC_A2*, *B2*, and σ phase, can be found in the equilibrium microstructures. Phase maps, high energy X-ray, and thermodynamic calculation identify the nonequilibrium and equilibrium microstructures.

We hope this study will pave the way for the characterization and optimization of the Y5E alloys and the similar HEAs system microstructures.

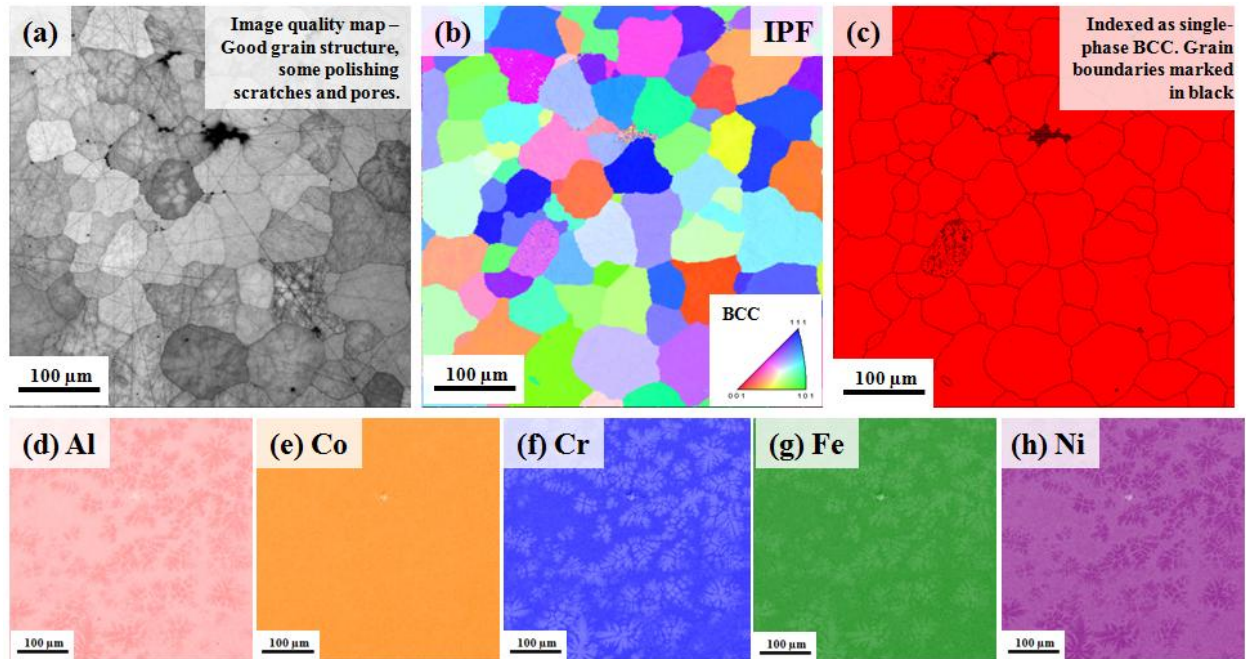


Figure 22. The EBSD and EDS element mapping images of the nonequilibrium microstructures of the Y5E-AC alloy. Index of EBSD shows that the Y5E-AC has single-phasing BCC_A2 (red color) and grain boundaries are marked in black (c), but there are still two phases, BCC_A2 and B2, in as-cast conditions through EDS element mapping (d-h).

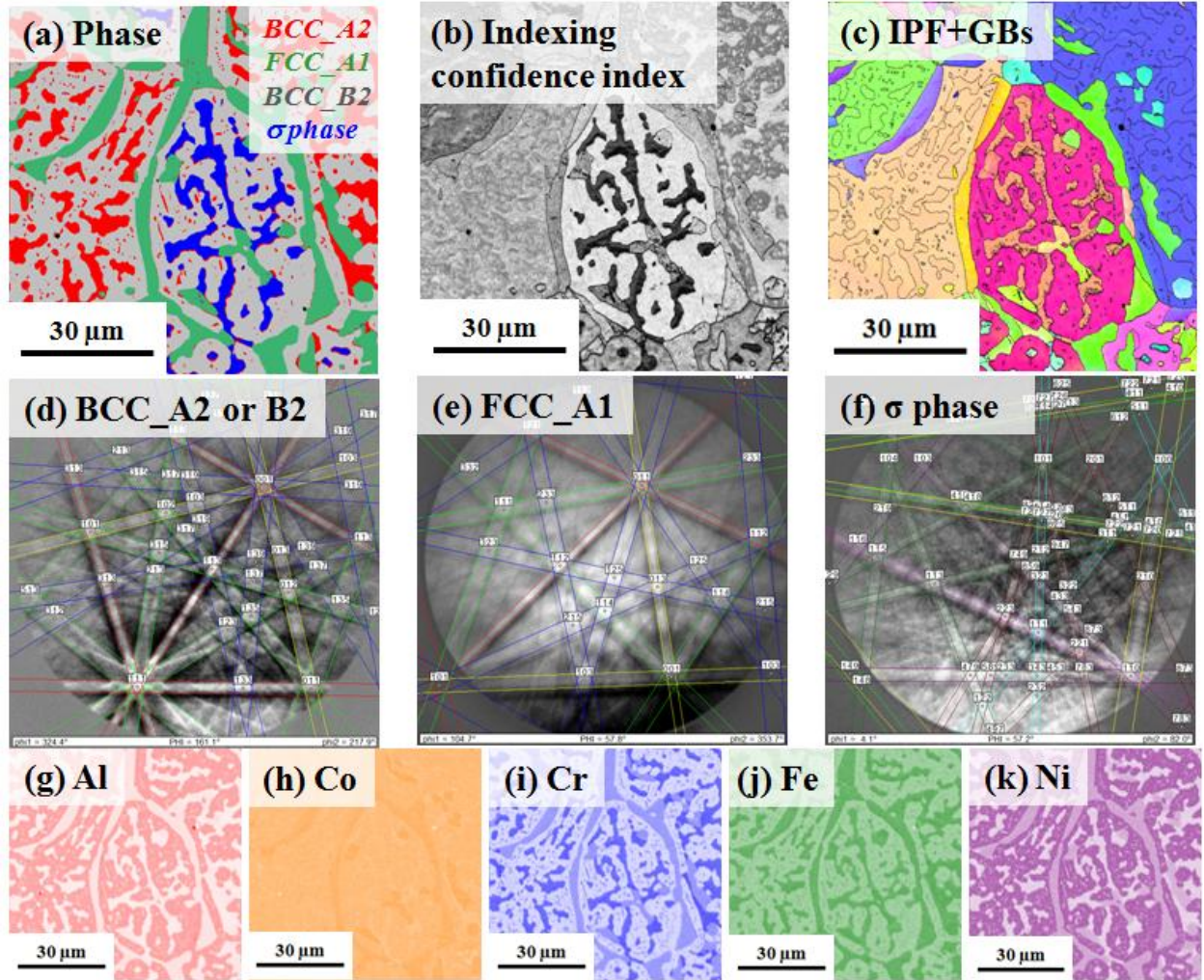


Figure 23. The equilibrium phase map in Y5E-HP is shown. The refinement of EBSD data (d-f) using EDS information determines four HIP/annealing-induced equilibrium phases, and the relative intensity of each element map (g-k) gives a qualitative sense for the segregation characteristics of that constituent.

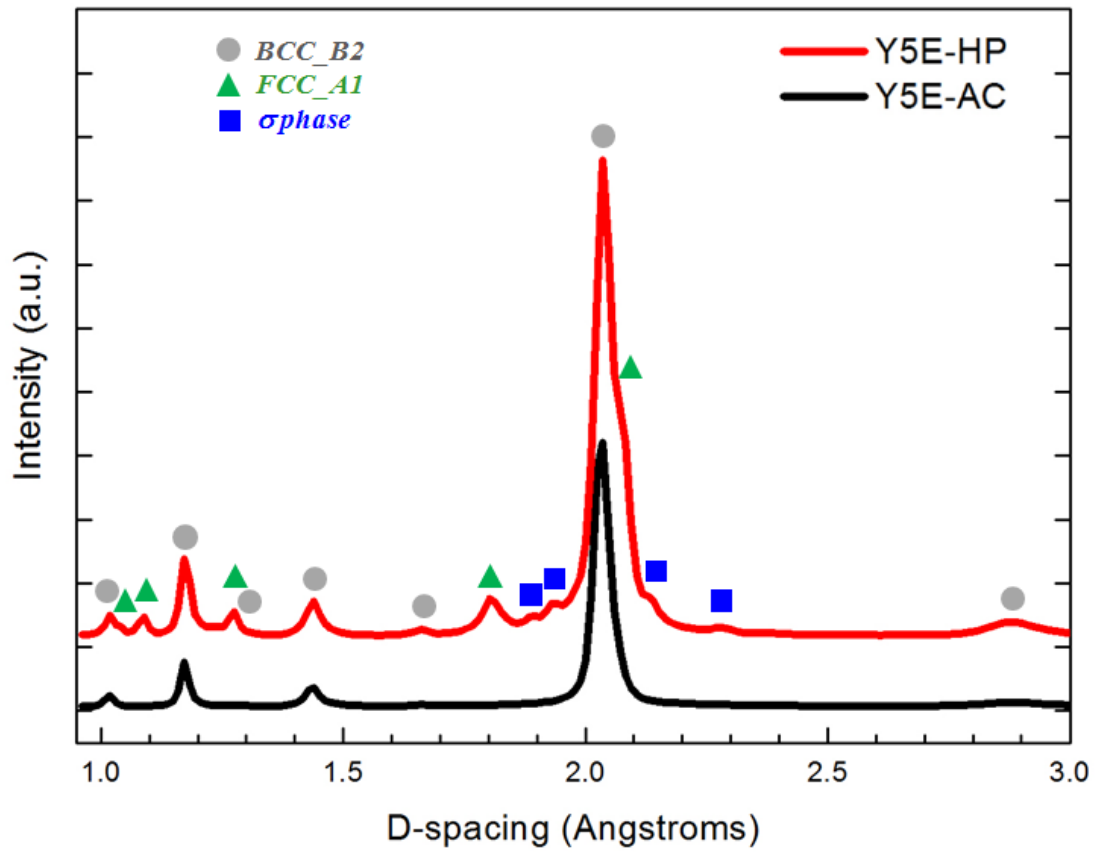


Figure 24. The high energy X-ray diffraction (Synchrotron) patterns of Y5E-AC and Y5E-HP. Only one set of the diffraction peaks for B2 in the as-cast condition can be easily identified in the Y5E-AC pattern (black color). However, another two phases, *FCC_A1* and σ phase, are found after the HIP and annealing, which agrees with the EBSD and EDS results.

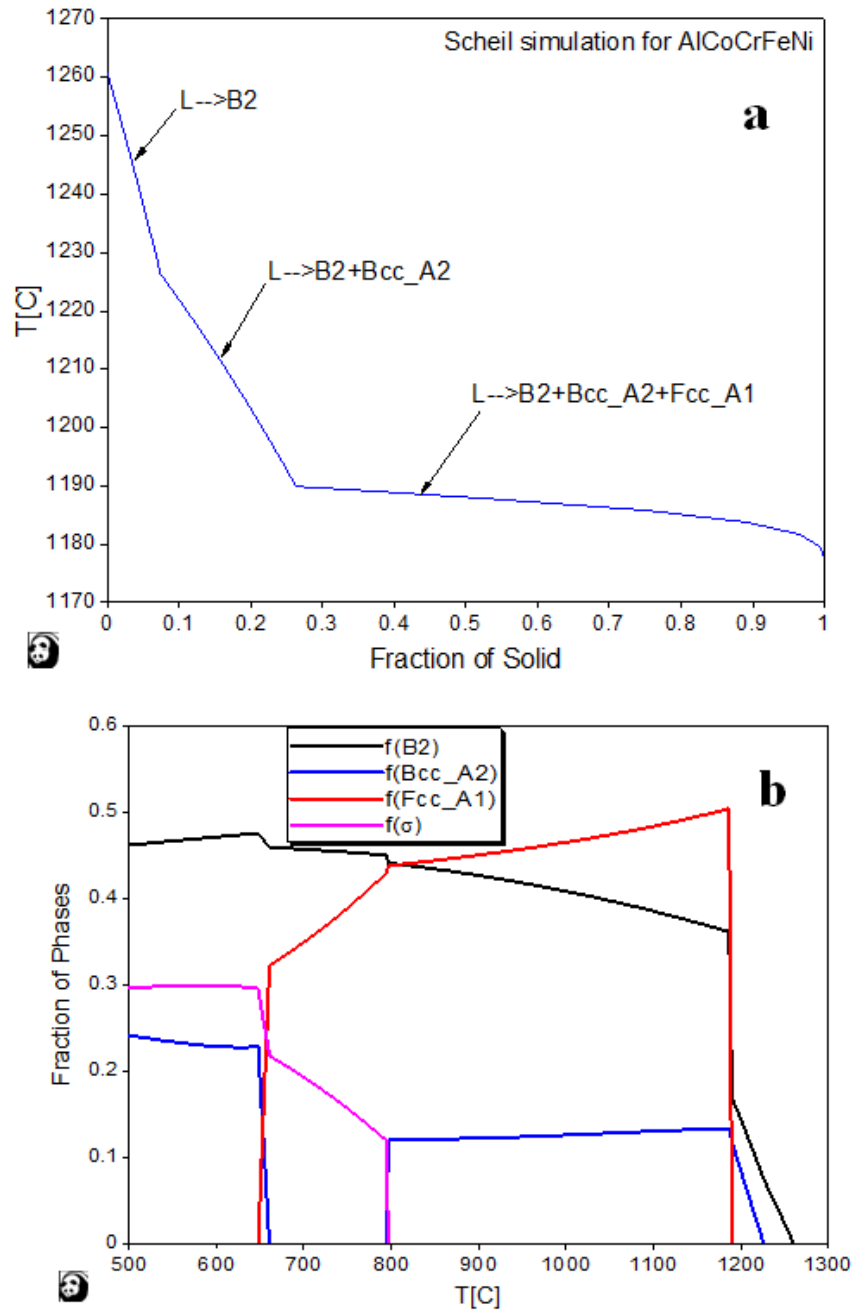


Figure 25. Thermodynamic modeling of (a) nonequilibrium solidification by Scheil model and (b) equilibrium phase diagram.

3. Tensile Behavior and Fracture Mechanisms of High-Entropy Alloys

3.1. Introduction

Owing to particular microstructures, HEAs are sometimes stable against heat treatment [6, 59, 60]. HEAs also have shown exceptional integrated mechanical properties, including both high strength and reasonable ductility during compression [22, 61, 62]. High ductility under tension of many HEAs is still expected for their applications. Most publications reported only compression property and hardness results [24, 62, 63], while only few papers reported tensile properties of HEAs [60, 64-66]. All of them were focused on HEAs which have face-centered-cubic (FCC) or FCC combined with body-centered-cubic (BCC) structures. Compared with the BCC crystal structure, FCC alloys usually have higher ductility but lower strength. However, BCC structures are sometimes preferred in extreme environmental engineering, especially nuclear industry applications. First, FCC has a greater number of close-packed-plane structures than BCC, which means that there is more free volume in BCC structure. The irradiation-induced interstitials and vacancies can migrate and recombine with each other more easily. Second, more free volume makes BCC higher ability to accommodate irradiation-induced defects. For FCC, due to its close-packed structure, the irradiation-induced defects incline to aggregate into large defect clusters, decreasing its irradiation tolerance. Third, BCC-structural HEAs have greater strength at high temperatures, compared to FCC-structural one. Thus, if HEAs become potential candidates for advanced reactors, which require operating

temperatures in excess of 1,023 K for the next 80 years, we preferentially pay high attention to BCC-structure materials instead of FCC.

The present work focuses on a quinary BCC multi-principal alloy, which is AlCoCrFeNi (denoted as Y5E in this article). This alloy was first reported by Zhang et al., [19]. The Y5E in as-cast condition alloy shows exceptionally high compressive strengths (990 MPa) at a temperature of 773 K [25], which is promising. It is expected to be one of the emerging structural materials. Unfortunately, no publications have yet been available in the open literature, and there is limited knowledge on the high temperature tensile properties of such a potential composition, or even BCC multi-principal alloy in the extremely environmental engineering. In this paper, microstructure and tensile properties at elevated temperatures of the Y5E alloy were studied and discussed.

Metallic alloys in the as-cast condition often have features that can significantly degrade mechanical properties, which means that the mechanical properties of cast alloys are known to be usually inferior to the properties of wrought alloys. These features include defects such as casting porosity; composition gradients from nonequilibrium solidification; and residual stresses. However, casting porosity can be removed by hot isostatic pressing (HIPing). Compositional gradients can be removed by homogenization heat treatments. Residual stresses can be removed by stress relief annealing. If a cast product is HIPed or homogenized, then a stress relief anneal is generally not needed. The literature shows that, after HIPing, some HEAs no phase changes occur and the experimental density becomes extremely close to the density calculated using the rule of mixtures of pure elements [21, 67]. The Y5E alloy contains five different elements that

may have significant differences in melting temperatures, which increases the probability of composition gradients and residual stresses after casting. Characterizing the mechanical properties of as-cast HEAs runs a significant risk of measuring the limiting properties of these defects, rather than the actual capability of the alloy. Further, candidate materials for high temperature structural applications must have exceptional high-temperature stability of properties for extended periods of time. Such alloys should not only have stable grain structures, but also should avoid precipitation of unwanted or unexpected phases. Although the Y5E alloy has been shown to possess a single-phase BCC crystal structure in the as-cast condition, studies to establish the long-term phase stability are not widely available. In this paper, we also explored the high temperature mechanical properties and phase stability of Y5E at elevated temperatures subjected to long-term heat-treatment including annealing and HIPing.

Investigation on the relationships between microstructures and deformation mechanism of tensile testing is also a fundamental principle of materials science. In conventional alloys, e.g. TG6 high temperature titanium alloy, the fine α_L increased the resistance to dislocations slip, delayed the crack nucleation and decreased crack propagation velocity. The fracture model at room temperature, was a mixture of ductile fracture, transgranular cleavage fracture, and quasi-cleavage fracture, while at high temperatures ductile fracture was the primary fracture model [68, 69]. In bulk metallic glasses (BMGs), the compressive fracture angle, θ_C , and the tensile fracture angle, θ_T , deviate from the maximum shear stress plane (45 °), which are indications that the fracture behavior of the metallic glass under compressive and tensile load does not follow the von Mises criterion

[70, 71]. A combined fracture feature of veins and some cores is observed on the tensile fracture surfaces. The difference in the fracture mechanisms of the metallic glass is attributed to the effect of the normal stress on the fracture process. However, few papers reported the fracture mechanisms of HEAs, and they still remain unclear. In this paper, the deformation of each microstructural parameter and the accommodative deformations between them were studied, based on the microstructural analysis and predicted modeling. The crack initiation and fracture models at high temperature were discussed by the detection of fracture surface and region below the surface. The objective of this work was to verify the deformation mechanisms and fracture behaviors subjected to the thermomechanical treatment and to provide some support for the optimization of Y5E and even HEAs microstructures.

3.2. Experimental Procedures

The Al₂₀Co₂₀Cr₂₀Fe₂₀Ni (mole percent) alloy were prepared by arc-melting the constituent elements. The elements were all at least 99 wt. % pure, and the melting was done in a vacuum of at least 0.01 torr under a Ti-gettered argon atmosphere. The melting and solidification processes were repeated several times to improve the homogeneity of the sample. Finally, the re-molten ingot was cast into 6 mm diameter rods. The final composition of the alloy is confirmed through quantitative analysis, by Inductively Coupled Plasma Optical Emission Spectrometers (ICP-OES) in Dirats Laboratories, Westfield, MA. Carbon percentage was quantitatively analyzed by a Combustion method. Hydrogen, Oxygen, and Nitrogen were quantitatively analyzed by an Inert Gas Fusion

(IGF) method. The results are given in Table 1. It should be noted that the composition of each alloy is close to equiatomic, and non-metallic impurities are very limited.

To close porosity and remove compositional gradients presented in the as-cast condition, several samples were heat treated after casting. The heat treatment consisted of hot isostatic pressing (HIPing) and annealing. To close porosity presented in the as-solidified sample, it was HIPed at 1,373 K / 207 MPa for 1 hour. The HIPed samples were held at 1,423 K for 50 hours. The densities of the alloy samples were measured with a helium pycnometer AccuPyc 1330 V1.03. The weight of the samples was at least 3 g and was measured with an accuracy of ± 0.0001 g, while the volume of the samples was determined with an accuracy of ± 0.0001 cm³ by measuring the free volume of the loaded cell using He gas and ten purges. Five measurements per sample were used.

The microstructures and properties of the alloy were studied in the as-cast and heat-treated conditions. The cross sections of the samples were polished and etched with the Kalling's reagent, and the microstructures were investigated by metallographic microscope and a Leo 1525 Field Emission Scanning Electron Microscope (FE-SEM), equipped with a backscatter electron (BSE) detector and an energy-dispersive X-ray spectrometer (EDS). According to the American Society for Testing and Materials (ASTM) E8 / E8M - 09 Standard Test Methods for Tension Testing of Metallic Materials, the cylindrical tensile specimens (Figure 26) were prepared for tensile tests. The tensile samples had a gauge length of 30 mm and a cylindrical gauge cross-section of 3 mm in diameter. Uniaxial tensile experiments were conducted in air using an 810 Material Test System (MTS) machine equipped with a box furnace for heating up to

1,473 K. The tensile tests were performed at 973 K with a strain rate of $1 \times 10^{-4} \text{ s}^{-1}$. The microstructure morphology and fractography of alloys were investigated by using FE-SEM. The nanoindentation tests were performed in a Hysitron TriboScope (Minneapolis, MN) mounted on a Quesant atomic force microscope (AFM) (Agoura Hills, CA). The diamond tip was used with a cube-corner indenter. Constant loading and unloading rates were used in the indentation tests. The penetration depth and applied load were used in the characterization of the near-surface mechanical behavior of the Y5E.

3.3. Results

3.3.1. Deformation Behavior

Figure 26 showed true stress-strain curves of the Y5E alloy, in both as-cast and heat-treated conditions, tensile tested at 973 K. The values of Young's modulus (E), the yield stress (YS), σ_y , the ultimate tensile stress (UTS), σ_u , and the elongation to fracture (EL), ϵ , of the samples are given in Table 2. The values of E for the as-cast and heat-treated alloy samples are $102.6 \pm 0.2 \text{ GPa}$, tensile tested at 973 K. The values of YS for the as-cast and heat-treated alloy are 397 MPa and 295 MPa, respectively. After the heat treatment, a noticeable increase in tensile ductility occurs: the elongation increases from 1.0 % for as-cast condition to 11 % for heat-treated condition, while the UTS remained almost the same: 402 MPa in the as-cast condition and 412 MPa in the heat-treated condition. For comparison, tensile properties of other reported HEAs at 973 K are also listed in Table 2. Compared to other HEAs, the studied alloy exhibits relatively high YS, UTS, and plastic deformation.

3.3.2. Microstructural Characterization

3.3.2.1. Microstructure before Tensile Deformation

The microstructure of the as-cast AlCoCrFeNi alloy sample is showed in Figure 27a. The flowery dendrites can be seen, and the spanning length of dendrites is $\sim 40\text{ }\mu\text{m}$, and the growth of branched dendrites started from a common center in arbitrary directions. Our estimations show that the angle between primary dendrite arms is $\sim 90^\circ$, and between the primary and secondary arms are $\sim 60^\circ$, indicating preferable directions of the dendrite growth, probably $\langle 110 \rangle$ directions. The dendrite arm thickness was $\sim 20\text{ }\mu\text{m}$. The average grain size in the region of equiaxed dendritic grains is estimated to be $\sim 75\text{ }\mu\text{m}$. Dark-grey and light-grey regions inside the grains can be clearly seen in the as-etched samples, indicating different compositions of dendritic and interdendritic regions due to constitutional segregation during solidification. The qualitative segregation characteristics have been discussed in previous section.

After HIPing and annealing, the grain boundary becomes more clear and thicker (shown in Figure 27b). The average grain size of heat-treated samples is $\sim 70\text{ }\mu\text{m}$, almost similar to the one of as-cast samples. The grain boundary has lower energy than the matrix, so after 50 hours of annealing the grain boundary is expanding and accumulated by some precipitates. At the same time of sample soaked at 1373 K / 207 MPa for 1 hour, the flowery dendrites is broken into small pieces, and some round precipitates can be found in the matrix. Constitutional segregation can still be clearly observed.

3.3.2.2. Fractography after Tensile Deformation

The SEM images of fracture surfaces of the as-cast Y5E samples tensile tested at 973 K were shown in the Figure 28a-d. At the lower magnification of SEM (Figure 28a-b), the fracture showed that most grains undergo shear rupture, attributing to transgranular fracture. The fracture revealed the brittle behaviors in which some of the $\sim 75\ \mu\text{m}$ grains can be clearly seen on the surface, which were consistent with the Figure 27's results. The surfaces showed a coarse faceted appearance of the fracture surface. No dimples can be found in the fracture surfaces. Another fracture area (Figure 28b) showed that brittle, quazi-cleavage features dominated, with typical characteristics such as cleavage feathers, flat facets, and tongues. The plate precipitates and oxidation precipitates can be found in higher magnification images (Figure 28c-d). On the surface of the grain, those precipitates may cause the cleavage fracture. Some impurities, which may form during the fabrication, were ripened off during the tensile test. These results reflected that the as-cast samples exhibited almost no plastic deformation before fracture, leading to the reasonably elongation, 1 %, with the UTS of 402 MPa.

Fractographs of the heat-treated samples after 973 K tensile testing showed different features from the conditions above. The SEM images of fracture surfaces after tensile fracture at 973 K were shown in the Figure 28e-h, respectively. On the SEM images, the angular-faceted steps and river-pattern markings were observed on fracture surfaces, which was similar to the as-cast sample. However, at the same time, on higher magnification images, some plastically-formed dimples can be clearly observed, which revealed greater ductility as dimples with $\sim 1\ \mu\text{m}$ in diameter were presented. A mixed

type of brittle and ductile fracture was reflected by the presence of both river-pattern markings and numerous dimples of 1 - 5 μm in diameter. This trend may happen because cracks were formed along the grain-boundary during the tensile testing, and then the nearest grain region of more ductility suffered some plastic deformation. These findings were consistent with the greater elongation of 11 %, in comparison with the 1 % elongation for the as-cast condition.

3.4. Discussion

3.4.1. Fracture Mechanisms of As-Cast Alloys at Elevated Temperatures

The occurrence of failure by fast fracture, like uniaxial deformation, is necessarily associated with the presence of high local stresses and strain near stress concentrators. The stress distribution depends on the size and shape of the component and the change in geometry (such as holes, circumferential notch) [72]. For cylindrical tensile samples, the center line usually acts as stress concentrators or stress risers, and thus is a common location for fracture to commence. This reason results in axial tensile stresses being a maximum at the center. Also, we did find some existing shrinkage casting pores. Thus, center casting pores with cracks can be clearly observed in the cross-sections parallel to the loading direction in the deformed as-cast samples, as shown in Figure 29. In a tensile test of a metal, the initial elastic (and essentially linear) deformation is followed by plastic deformation during which the length increases and the cross section decreases [72]. However, for as-cast samples, a certain degree of a strain is quickly attained, where

further plastic deformation becomes much localized. Thus, the failure immediately was occurred after the elastic deformation and yielding, as seen in Figure 26. For brittle samples, cracks may be initiated at grain boundaries and grain-boundaries junctions, and lead to transgranular fractures. The formation of intercrystalline cracks under tensile condition at elevated temperatures has two situations: (a) cracks formed at the intersections of several grain boundaries; (b) the formation of voids at grain boundaries aligned perpendicular to the principal tensile stress [72]. It is very interesting that cracks did not form around the small existing casting pores in the dendrite (Figure 29b), while some bead-like and wedged-like cracks were only formed along the grain boundaries and grain-boundaries junctions (Figure 29b-c). This means that the grain boundaries are weaker than the small casting pores in the dendrite. We did find some oxidation precipitates and plate precipitates along the grain boundaries on the fracture surface, as shown in Figure 28c-d. Some impurities are also ripped out (Figure 28d). Meanwhile, the contour outlines of the center cracks are matched with the shape of dendrite, which means that they are not only cracks but also shrinkage casting pores. From these features, it is concluded that cracks initiated along grain boundaries and center casting pores. After the initiation of cracks, some precipitates and impurities along the grain boundaries in the as-cast samples, as well as existing residual stresses, may easily lead to fast fracture and showing integrated intergranular and transgranular fractures features.

3.4.2. **Facture Mechanism of Heat-Treated Alloys at Elevated Temperatures**

Figure 30 illustrates that no obvious shrinkage casting pores with gathered precipitates can be found in the cross-sections parallel to the loading direction, but some cracks can still be found in the grain boundaries. Both transgranular and intergranular fractures were observed on the longitudinal cross-section. Only transgranular cracks can be clearly found in the region below the fracture surface. We already know from our previous work that after 50 hours of annealing the grain boundary is expanding and accumulated by some *FCC_A1* precipitates, and matrix is *B2* structure. Thus, initial cracks were formed on the interface between *B2* and *FCC_A1* phases, as shown in Figure 30d-e. That is to say, the interfacial fracture was the major mechanism for heat-treated samples. The interface between *B2* (matrix) and *FCC_A1* (reinforcement, or “fibers”), the following discontinuities in properties need to be considered: (1) crystallographic: structures and lattice parameter difference; (2) moduli: difference in elastic modulus; (3) coefficient of thermal expansion (CTE). For example, in the heat-treated condition, the lattice parameter of *B2* is $a = 0.287$ nm, and the lattice parameter of *FCC_A1* is $a = 0.360$ nm, which show a large difference with distinct structures. In order to investigate the difference in elastic modulus, nanoindentation experiment of each phase was performed. The hardness and elastic modulus of *B2* and *FCC_A1* phases by nanoindentation are shown in Figure 31. The hardness of *B2* phase is more than twice of *FCC_A1* phase, and the elastic modulus of *B2* phase is ~ 8 % higher than the one of *FCC_A1* phase. As we know, cracks nucleate at the interfaces, as a result of the stresses produced by the elastic

incompatibility of the adjacent phases [73]. Because of the difference in compositions and orientations, the elastic moduli of *B2* and *FCC_A1* phases are different, which result in different elastic strains. The energy of adhesion is given by [73]

$$E_{Ad} = F_{S(a)} + F_{S(b)} - \gamma_{I(ab)} \quad [1]$$

where $F_{S(a)}$ and $F_{S(b)}$ are the solid surface free energies of metals *a* and *b*, respectively, and $\gamma_{I(ab)}$ is the interfacial free energy at the contacting surfaces. In this case, *a* is *B2* phase, and *b* is *FCC_A1* phase.

The ideal fracture strength, σ_{max} , of a crystalline solid can be defined as the tensile stress required to simultaneously rupturing all the atomic bonds between two adjacent atomic planes at a temperature of absolute zero [73]. The decohesion that characterizes the formation of two fracture surfaces is the reverse of the formation of an adhesive joint. The work of fracture, or the energy for decohesion, should equal the adhesive energy; as a consequence,

$$E_f = E_{Ad} = F_{S(a)} + F_{S(b)} - \gamma_{I(ab)} \quad [2]$$

The stress to separate the perfect lattice will start from zero, reach a maximum, and then drop to zero, approximating a sinusoidal variation from which an estimate of σ_{max} may be obtained in the form

$$\sigma_{max} = \left(\frac{E_Y F_S}{a} \right)^{\frac{1}{2}} \quad [3]$$

where E_Y and F_S are the Young's modulus and the solid surface free energies, respectively, and a is the lattice parameter. As a consequence, the cohesive stress at the interface between two phases is

$$\sigma'_{max} = \left[\frac{E_Y(F_{S(a)} + F_{S(b)} - \gamma_{I(ab)})}{2a} \right]^{\frac{1}{2}} \quad [4]$$

As a result, the interface cohesive stress will be smaller than that for phase interior:

$$\frac{\sigma'_{max}}{\sigma_{max}} = \sqrt{\frac{F_{S(a)} + F_{S(b)} - \gamma_{I(ab)}}{F_{S(a)} + F_{S(b)}}} \quad [5]$$

and fracture (crack nucleation and propagation) would be expected to be associated with, if not to give preference to, interface. Equation [5] illustrates that intergranular or interfacial fracture is expected to be favored in polycrystalline or multiple-phase metals and alloys, and that crack propagation might be expected to follow high-energy boundaries preferentially (as compared with twin boundaries or low angle boundaries, for example). This trend may be the reason that interfacial fracture is expected to be favored in the multiple-phase Y5E heat-treated alloy, since at least four phases are found in heat-treated samples, yet only two phases in as-cast samples.

3.4.3. The Reason for the Improvement of Plasticity

A noticeable increase in the tensile ductility occurred after the heat treatment. For example, during deformation at 973 K, elongation of the heat-treated alloy was 11 %, while the as-cast alloy showed elongation of only ~ 1.0 %. The ultimate tensile strength

was almost unaffected by heat treatment, and it was 407 ± 5 MPa at 973 K. The mechanical properties of the two alloys were correlated to its as-cast and heat-treated microstructures.

Firstly, for as-cast samples, the dendrites are intensively embedded in the grain matrix. Only *BCC_A2* and *B2* structures are found through XRD in previous section. For heat-treated samples, some round *D8b-sigma* precipitates can be found in the *B2* matrix, and a bright *FCC_A1* phase precipitated along grain boundaries. We already know that the interdendrites are weaker than dendrites in as-cast samples, which lead to the beadlike cracks initiated along grain boundaries. The mole fraction of *FCC_A1* phase on the grain boundaries during equilibrium solidification is more than 10 %, which may strengthen the grain boundaries. Meanwhile, *FCC_A1* has a higher packing efficiency and the slip planes are more closely packed than *BCC_A2* phase, and also the hardness of *FCC_A1* is much lower, as shown in Figure 31. Some dimples were found on the fracture surface of heat-treated samples (Figure 28h), which very possibly come from *FCC_A1* phase. Thus, we believe that the formation of *FCC_A1* phase along the grain boundaries may contribute to the improvement of plasticity, yet *D8b-sigma* precipitates and *B2* matrix still maintain the similar high UTS.

Secondly, another important reason for the improvement of plasticity may be contributed to reduce in number of pores. It is well known that the presence of defects has a profound impact on the mechanical properties of materials, and the control (reduce and/or intentional introduction) of defects is a key issue in material processing. As we mentioned before, casting porosity is usually removed by HIPing in commercial practice.

For HEAs, they usually contains more than five different elements that may have significant differences in melting temperatures, which increases the probability of not only porosity but also composition gradients and residual stresses as well after casting. Hence, this is our motivation to HIPing as-cast specimens. Different sizes of pores are found in the as-cast samples (Figure 29), but pores were closed after HIP treatment (Figure 30). Thus, we believe that reduce in number of pores is another important reason that contribute to the significant improvement of elongation during the tensile tests from 1.0 % to 11 %.

Thirdly, we believe residual stresses are removed by 50 hours of annealing. The as-cast samples were prepared by arc-melting method in a water-cooled, 6 mm diameter copper hearth, so the cooling rate is very high, compared to large ingot and other preparation method. This process easily introduces some residual stresses, after the original cause of the stresses (external forces from the copper mold and heat gradient between the cold mold and hot samples) has been removed. They remain in the as-cast samples, which is easily leading to brittle failure. We did find the existing of residual stresses when machining the tensile specimens. However, after long-term annealing (50 hours), we believe such kind of residual stresses are possible to be released and removed, which may reduce the influence on the fast failure.

To sum up, we believe that the formation of *FCC_A1* phase, less pores, and residual stresses removed, are some of the important reasons that contribute to the significant improvement of elongation. We propose that the one of optimization of Y5E and even HEAs and/or MPAs microstructures may be ~ 10 % of *FCC_A1* structures in the

BCC_A2 and/or *B2* matrix, which will have better combination of high strength and decent ductility.

3.4.4. Comparison with Conventional Structural Materials and BMGs

As shown in Figure 32, a stacked bar chart shows the elongation and specific strength of HEAs (this work) and other high temperature structural materials at 973 K (Table 4). The properties of Y5E heat-treated HEAs are overcoming the 304 stainless steel, duplex stainless steel, oxide-dispersion-strengthened (ODS) steel and other reported MPAs/HEAs, and comparable to the intermetallics, FeAl 787, and Ni-based superalloy, Inconel 690, at 973 K [28, 30, 74-82]. Among the reported HEAs/MPAs, Y5E both in as-cast and heat-treated conditions show highest specific strength. Since a noticeable increase in the tensile ductility occurred after the heat treatment, Y5E heat-treated alloys exhibited an excellent combination of high specific strength [58.9 MPa/(g/cm³)] and decent elongation (~ 11 %). We would like to discuss four advantages of HEAs in the following section. First, the densities of Ni-based superalloy and steel are ~ 8.9 and ~ 7.8 g/cm³, respectively, but the one of Y5E alloys is only ~ 7.0 g/cm³, which is ~ 21 % and ~ 10 % lower than Ni-based superalloy and steel, respectively. Second, the cost of Y5E alloys is ~ 7 % lower than Ni-based superalloy, because relatively more expensive Ni is replaced by cheaper Al and Fe. The prices of pure metals and several structural materials are shown in Table 3. Although the price of Y5E is still relatively high, the new MPAs/HEAs are emerging and having much lower price, such as AlCrCuFeMnNi. Third,

compare with conventional structural materials relatively complicated thermo-mechanical processing, most of MPAs have only metallurgical ingot preparation and simple heat-treatment, such as cold rolling, annealing. Hence, much more processes that can improve the mechanical properties are waiting for us to explore. Fourth, Y5E alloys have better room-temperature plasticity [24, 34, 35, 83] than intermetallics and BMGs. In brief, owing to lower density, lower cost, simpler process, and better room-temperature plasticity, we have reasons to believe Y5E alloys and other MPAs/HEAs are showing their potential to replace conventional structural materials.

3.5. Summary

- (1) The superior high-temperature tensile strength with the UTS of 402 MPa of the Y5E alloys in as-cast condition was sustained at the temperature of 973 K. However, it exhibited almost no plastic deformation before fracture, leading to the reasonably elongation, $\sim 1\%$. A noticeable increase in the tensile ductility occurred after the heat treatment. For example, during deformation at 973 K, elongation of the heat-treated alloy was 11 %, while the as-cast alloy showed elongation of only $\sim 1.0\%$. The ultimate tensile strength was almost unaffected by heat treatment, and it was 407 ± 5 MPa at 973 K. Such a thermo-mechanical processing was successfully proven to be an effective method for improving the toughness without decreasing the strength.
- (2) In as-cast Y5E alloy, fracture surfaces showed that brittle, quazi-cleavage features dominated. No dimples but the plate precipitates and oxidation precipitates can be found in high magnification fractography images. Casting pores with cracks can be

clearly seen below the fracture surface. Intergranular beadlike cracks were initiated along grain boundaries and center shrinkage pores in as-cast alloys. After the initiation of cracks, some precipitates and impurities along the grain boundaries, as well as existing residual stresses, may easily lead to final intergranular and transgranular fractures.

- (3) In heat-treated Y5E alloys, a mix type of brittle and ductile fracture was reflected by the presence of both river-pattern markings and numerous dimples of 1 - 5 μm in diameter through fractography. No obvious casting pores can be found in the cross-sections parallel to the loading direction, but intergranular cracks can also be found in the region below the fracture surface. Initial cracks were formed on the interface between *B2* and *FCC_A1* phases. Because the crystallographic, moduli, and CTE are of discontinuities and difference on the interface between *B2* and *FCC_A1*, interfacial fracture is expected to be favored in the multiple-phase Y5E heat-treated alloy.
- (4) The formation of *FCC_A1* phase, less casting pores, and residual stresses removed, are some of the important reasons that may contribute to the significant improvement of elongation. We propose that the one of optimization of Y5E and even MPAs and/or HEAs microstructures may be $\sim 10\%$ of *FCC_A1* structures in the *BCC_A2* and/or *B2* matrix, which will have better combination of high strength and decent ductility.
- (5) Because of lower density, lower cost, simpler process, and better room-temperature plasticity, compared to some existing materials, we have reasons to believe Y5E

alloys and other MPAs/HEAs are showing their potential to replace conventional structural materials.

Table 1. Chemical composition of Y5E in as-cast condition by ICP-OES in Dirats Laboratories

Element	Dirats Actual wt%	Dirats Actual at%	Intended at%	Difference at%
Al	10.81	20.25	20.00	0.25
Co	23.77	20.39	20.00	0.39
Cr	19.86	19.31	20.00	-0.69
Fe	21.75	19.68	20.00	-0.32
Ni	23.66	20.37	20.00	0.37
C	0.002	-	-	-
H	< 1 ppm	-	-	-
O	0.0042	-	-	-
N	0.0021	-	-	-

Table 2. Tensile behavior at 973 K for as-cast and heat-treated conditions and some of other HEAs for comparison. The values of Young's modulus (E), the yield stress (YS), σ_y , the ultimate tensile stress (UTS), σ_u , and the elongation to fracture (EL), ε , of the samples are given.

Alloys	Microstructures	E (GPa)	σ_y (MPa)	σ_u (MPa)	ε (%)
AlCoCrFeNi As-cast (This work)	<i>BCC_A2 + B2</i>	102.4	397	402	1.0
AlCoCrFeNi Heat-treated (This work)	<i>FCC_A1 + BCC_A2 + B2 + σ phase</i>	102.8	295	412	11
AlCoCrCuFeNi As-cast [28]	<i>BCC</i> matrix and <i>FCC</i> particles	-	350	360	4.7
AlCoCrCuFeNi Forged [28]	<i>BCC</i> matrix, <i>FCC</i> particles, and σ phase	-	63	91	63
Al0.5CoCrCuFeNi As-rolled [30]	<i>FCC</i> matrix and Cu-rich phase	-	180	185	5
Al0.5CoCrCuFeNi As-annealed [30]	<i>FCC</i> matrix and Cu-rich phase	-	160	180	12

Table 3. The prices of pure metals are shown [84]. The price of AlCoCrFeNi (Y5E) in comparison with that of other structural materials [Unit: US Dollars / Metric Tons (USD/MT)]

		Weight Percentage of Each Element (wt. %)					
Element	Metal Price (USD/MT)	AlCoCrFeNi (This Work)	AlCoCrCuFeNi	AlCrCuFeMnNi	Stainless Steel	FeAl	Inconel 690
Al	\$1,884	10.7%	8.5%	8.7%		25%	
Co	\$25,500	23.4%	18.7%				
Cr	\$13,459	20.6%	16.5%	16.7%	25%		28%
Cu	\$7,760		20.1%	20.4%			
Fe	\$355	22.1%	17.7%	17.9%	68%	75%	10%
Mn	\$3,979			17.6%			
Ni	\$16,000	23.2%	18.6%	18.8%	7%		62%
Alloy Price (USD/MT)		\$12,732	\$11,748	\$7,066	\$4,726	\$737	\$13,724

Table 4. Tensile properties at 973 K for Y5E-AC, Y5E-HP in comparison with that for some other high temperature structural materials [Density (ρ), Elongation (ε), Ultimate Tensile Strength (σ_{UTS}), Specific strength (σ_{UTS}/ρ)]

Materials	ρ (g/cm^3)	ε (%)	σ_{UTS} (MPa)	σ_{UTS}/ρ [MPa/(g/cm^3)]	Reference
HEAs Y5E-AC	7.0	1.0	402	57.4	This work
HEAs Y5E-HP	7.0	11	412	58.9	This work
AlCoCrCuFeNi As-Cast	7.1	4.7	360	50.7	[28]
AlCoCrCuFeNi Forged	7.1	63	63	8.9	[28]
Al _{0.5} CoCrCuFeNi As-Rolled	7.6	5.0	185	24.3	[30]
Al _{0.5} CoCrCuFeNi As-Annealed	7.6	12	180	23.7	[30]
Duplex Stainless Steel	7.8	2.4	366	46.8	[75]
304 Stainless Steel	7.8	9.1	248	31.8	[75]
Ni-based Inconel 690	8.9	26	478	53.7	[76]
ODS Steel 0.3% yttria	7.8	11	272	34.9	[80]
Intermetallics FeAl 787	5.4	18	350	64.8	[81]

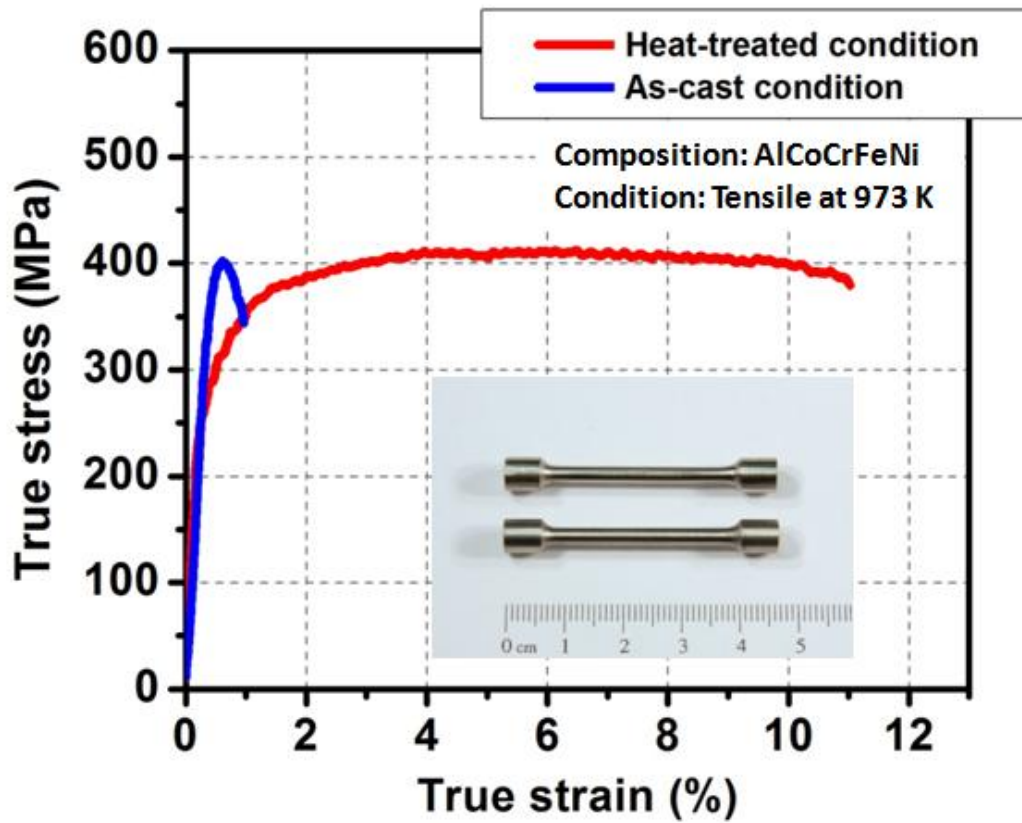


Figure 26. The true stress-strain curves of the Y5E alloy, both in as-cast and heat treated conditions, at the temperature of 973 K tensile testing. The inserted figure illustrates the cylindrical tensile specimen.

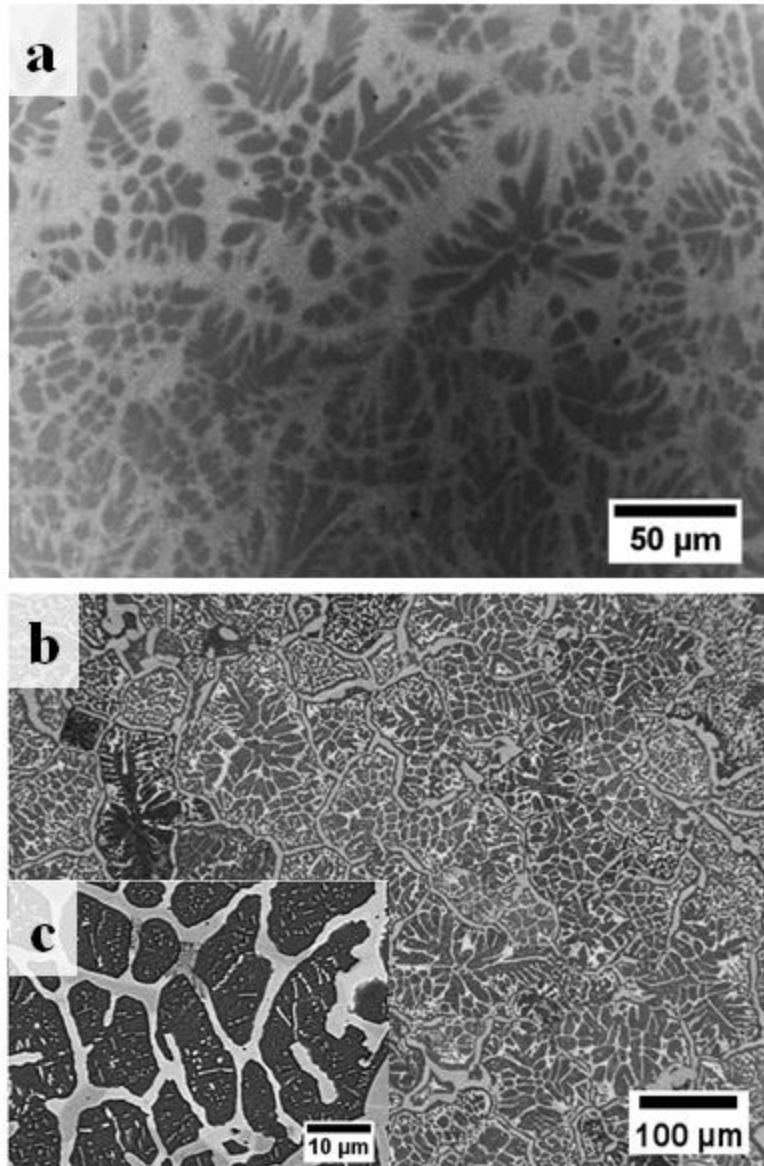


Figure 27. Electron microscopic images for as-cast and heat-treated Y5E samples. (a) Dendritic structure can be clearly seen after etching in as-cast condition. (b) HIPing and annealing causes phase separation in heat-treated condition. (c) The inserted figure is higher magnification of (b).

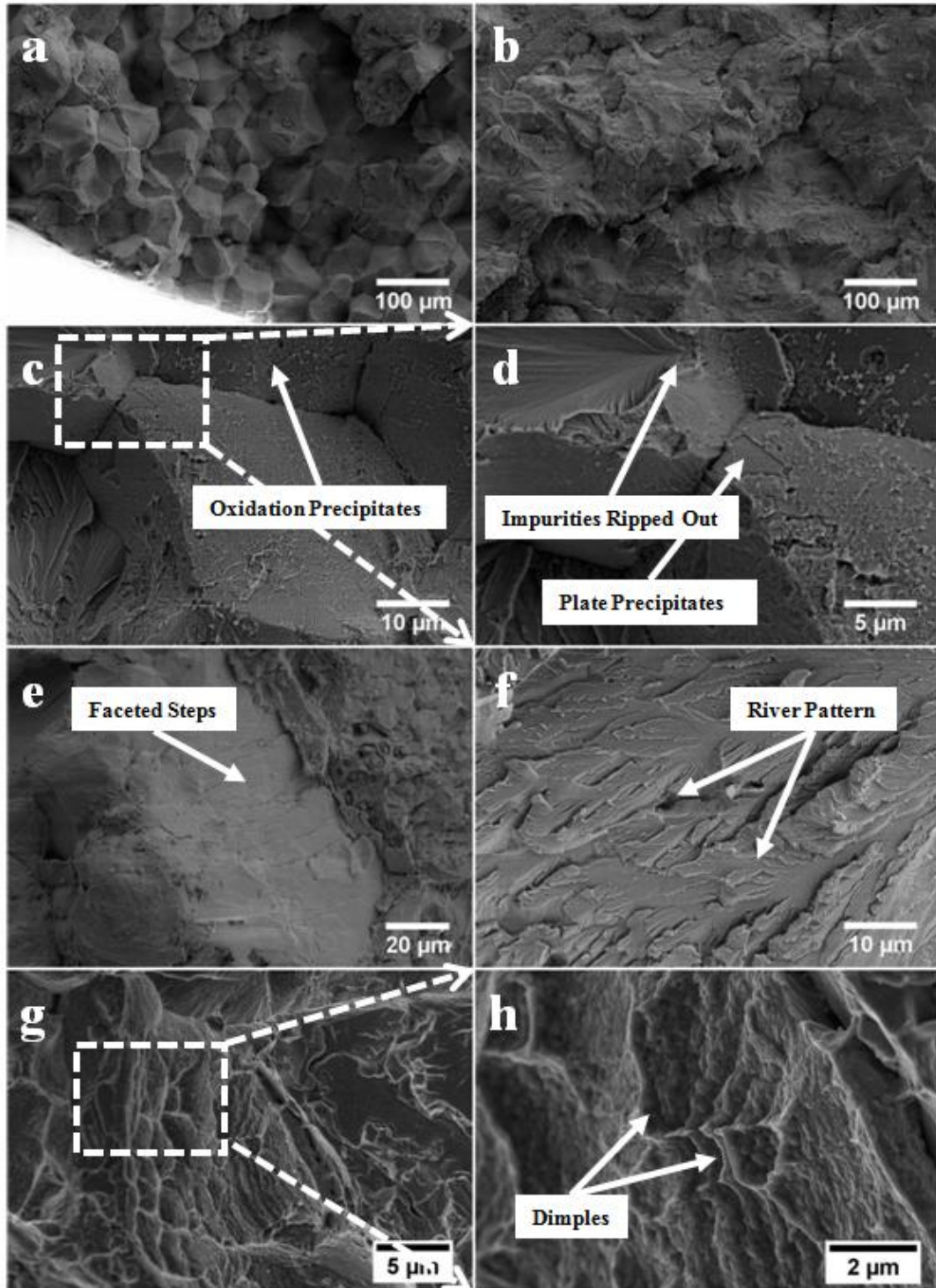


Figure 28. SEM fractographs of (a-d) as-cast and (e-h) heat-treated Y5E alloy after tensile tests at 973 K

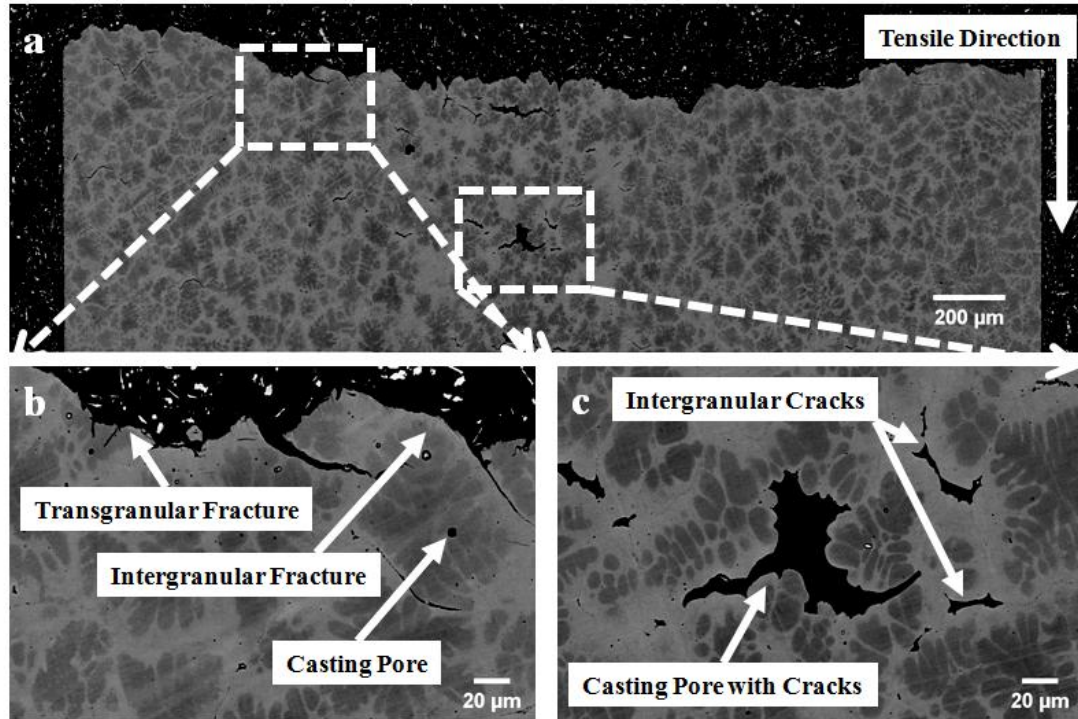


Figure 29. SEM images with back-scattered detector of a longitudinal cross-section of the as-cast Y5E after tensile tests at 973 K are shown. Microstructures below the fracture surface show casting pores with cracks. Cracks initiated along grain boundaries and interdendrites.

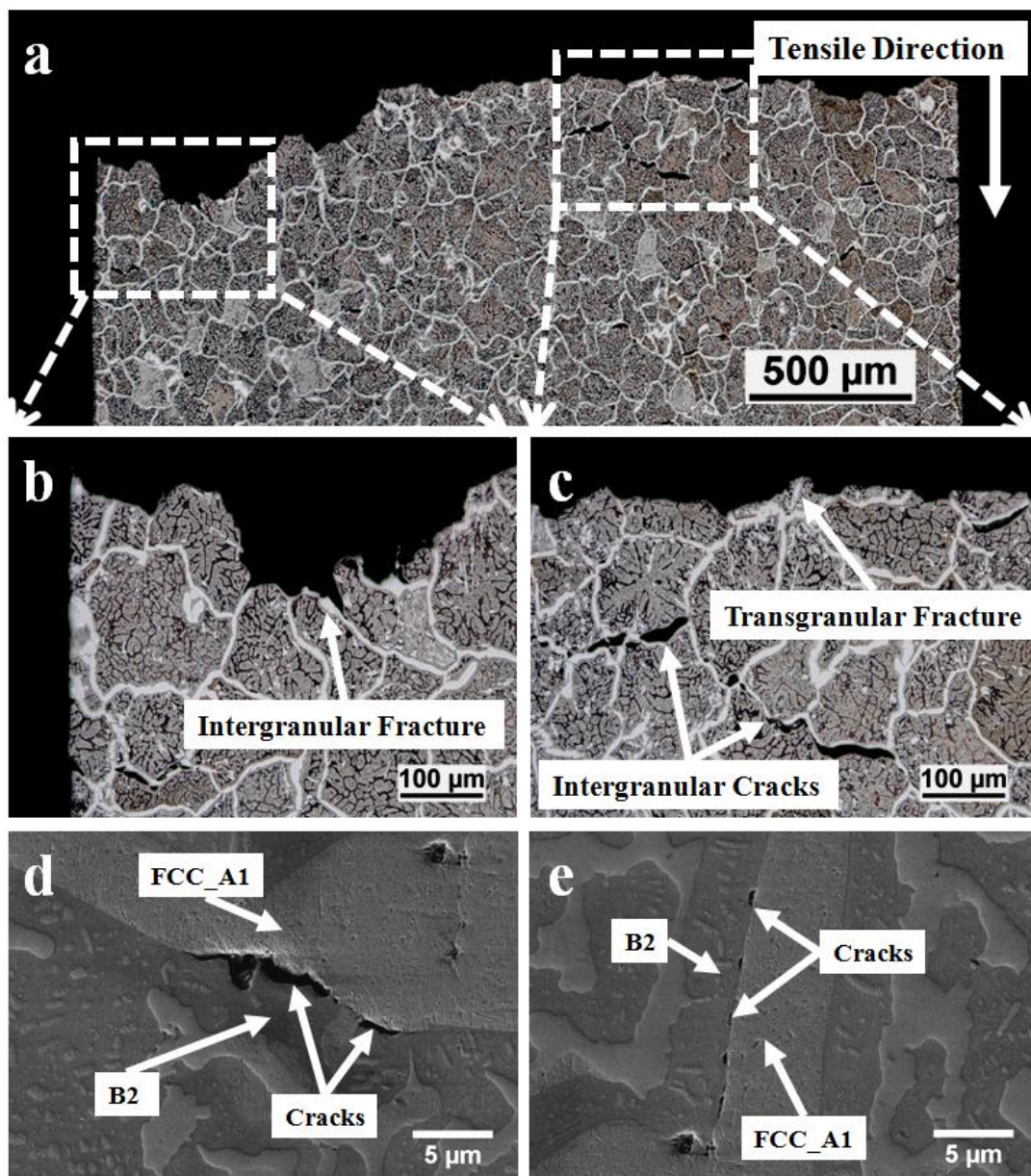


Figure 30. a-c: optical microscopic images of a longitudinal cross-section below the fracture surface in the heat-treated Y5E alloy after tensile tests at 973 K. d-e: cracks and pores with the high magnification of heat-treated samples. Cracks were formed on the interface between *B2* and *FCC_A1*.

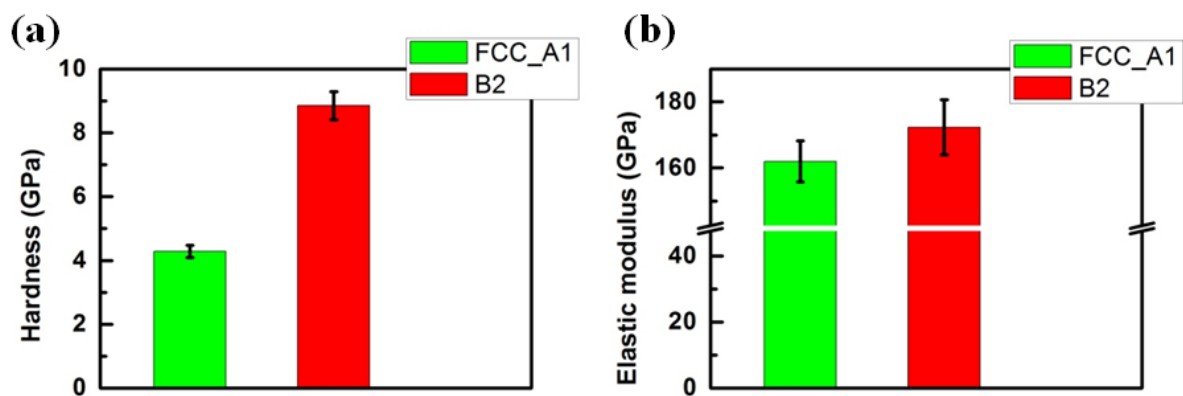


Figure 31. Hardness and elastic modulus of *B2* and *FCC_A1* phases by nanoindentation.

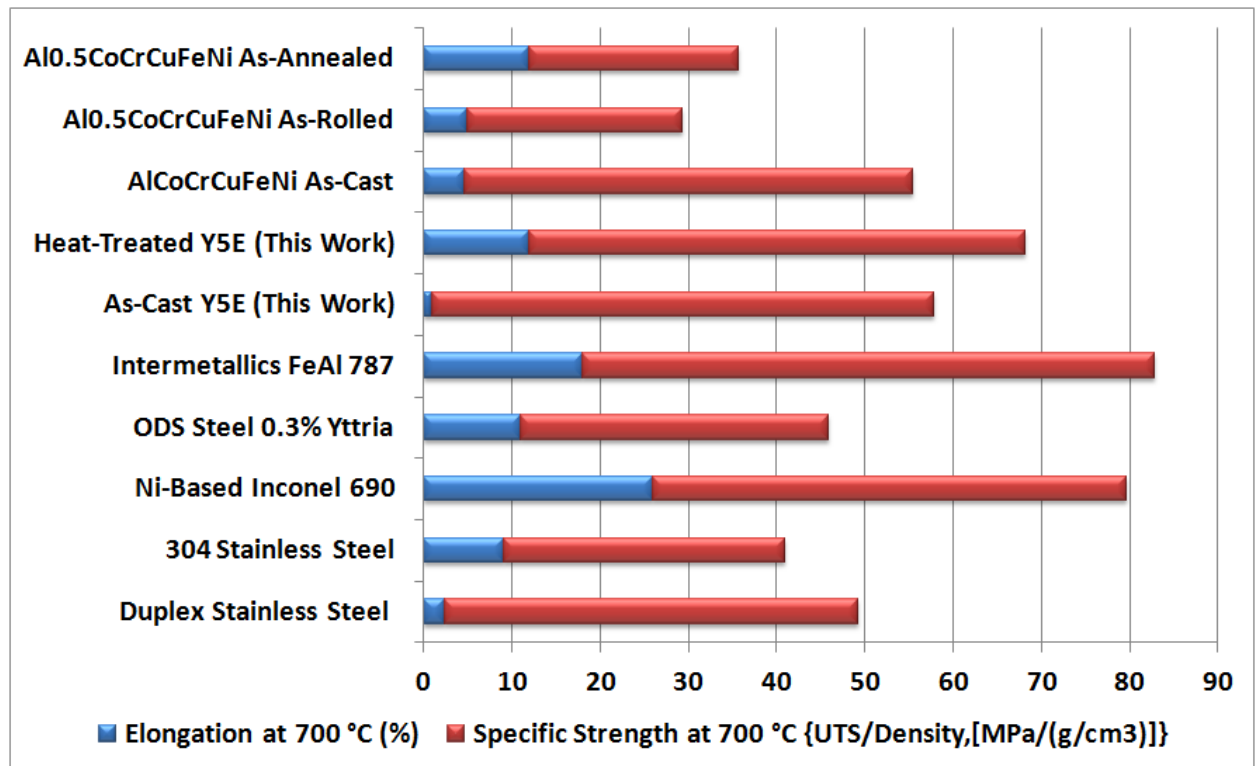


Figure 32. A stacked bar chart shows the elongations and specific strengths of as-cast and heat-treated Y5E (this work) and other high temperature structural materials at 973 K [28, 30, 74-82]. Compared to conventional structural alloys counterparts, Y5E in heat-treated condition has comparable combination of mechanical properties at elevated temperatures.

4. Summary and Conclusions

In this thesis, we firstly reviewed the mechanical properties of HEAs. Up to now, some HEAs with unique properties have been reported: e.g., high-strength body-centered-cubic (BCC) AlCoCrFeNi HEAs at room temperature, and refractory NbMoTaV at elevated temperatures. For room-temperature mechanical properties of HEAs, the yield strength can be varied from 300 MPa for the FCC-structured alloys to about 3,000 MPa for the BCC-structured alloys. The high specific yield strength of the Al_{0.5}CrCoCuFeNi HEAs can be sustained over to 1,100 K, and the TaNbMoW HEA can sustain its high specific strength to 1,800 K. For the Al_{0.5}CoCrCuFeNi HEA, there is no obvious ductile to brittle transition even the temperature is lowered to 4.2 K. Meanwhile, fatigue behavior of Al_{0.5}CoCrCuFeNi HEAs was studied and compared to many conventional alloys, such as steels, titanium alloys, and advanced bulk metallic glasses.

Secondly, we discussed one proposed approach about how non-equilibrium and equilibrium phases can be identified in the HEAs system, what phases were usually found in the as-cast or heat-treated condition, and what were thermodynamics and kinetics of phase transformations in HEAs. Through EBSD, the non-equilibrium microstructures were identified to have large grains with clear intra-granular dendritic structures containing two phases, *BCC_A2* and *B2*. The equilibrium microstructures had smaller grains, but with blocky wall-like phase along boundaries and along former-dendrite arms. Four phases, including *FCC_A1*, *BCC_A2*, *B2*, and σ phase, can be found in the

equilibrium microstructures. Phase maps, high energy X-ray, and thermodynamic calculation identify the non-equilibrium and equilibrium microstructures.

Thirdly, a noticeable increase in the tensile ductility occurred after the heat treatment: elongation of the heat-treated alloy at 973 K was 11 %, while the as-cast alloy showed elongation of only ~ 1.0 %. The ultimate tensile strength was almost unaffected by heat treatment, and it was 407 ± 5 MPa at 973 K.

In as-cast Y5E alloy, fracture surfaces showed that brittle, quazi-cleavage features dominated. No dimples but the plate precipitates and oxidation precipitates can be found in high magnification fractography images. Center shrinkage casting pores and casting pores can be clearly seen below the fracture surface. Intergranular beadlike cracks were initiated along grain boundaries and interdendrites in as-cast alloys. After the initiation of cracks, some precipitates and impurities along the grain boundaries, as well as existing residual stresses, may easily lead to final intergranular and transgranular fractures.

In heat-treated Y5E alloys, a mix type of brittle and ductile fracture was reflected by the presence of both river-pattern markings and numerous dimples of 1 - 5 μm in diameter through fractography. No obvious shrinkage casting pores can be found in the cross-sections parallel to the loading direction, but intergranular cracks can also be found in the region below the fracture surface. Initial cracks were formed on the interface between *B2* and *FCC_A1* phases. Because the crystallographic, moduli, and CTE were of discontinuities and difference on the interface between *B2* and *FCC_A1*, interfacial fracture was expected to be favored in the multiple-phase Y5E heat-treated alloy.

The formation of *FCC_A1* phase, less casting pores, and residual stresses removed, were some of the important reasons that may contribute to the significant improvement of elongation. We proposed that the one of optimization of Y5E and even MPAs and/or HEAs microstructures may be ~ 10 % of *FCC_A1* structures in the *BCC_A2* and/or *B2* matrix, which might have better combination of high strength and decent ductility. Because of lower density, lower cost, simpler process, and better room-temperature plasticity, compared to some existing materials, we have reasons to believe Y5E alloys and other MPAs/HEAs are showing their potential to replace conventional structural materials.

We believe our study will pave the way for the characterization and optimization of the Y5E alloys and the similar HEAs system microstructures. Meanwhile, it is our hope that our study will draw more attention of scientist to HEAs, and even provide some support toward the composition design of HEAs based on the composition-structure-property relationship. The fundamental understanding of microstructures will also lay down the foundation for the discovery of new HEAs with improved materials properties in extreme environments. HEAs as new class of advanced materials with competitive high strength at elevated temperature with reasonable ductility may become the next generation structural materials. The development of such novel materials will bring substantial impact to some extreme environmental engineering for wide applications.

5. Future Work

One kind of HEAs, AlCoCrFeNi, with balanced ductility and tensile resistance has been achieved by the studies included in this thesis. However, further improvements of the mechanical properties of this alloy will be needed for the applications such as turbine materials. The following studies may contribute an in-depth understanding of the mechanical properties and provide possible approaches to improve the properties of the designed alloys.

(1) The fracture mechanisms at room temperature have not been clearly identified. The dislocation structures before and after the tensile fracture will need to be investigated. Understanding the interaction between the dislocations and the solutes will provide the insights into the effects of the alloying elements on the ductility of the alloy.

(2) Hot and/or cold rolling has been shown to improve the ductility significantly in the literatures. However, how it is going to affect the creep resistance has not yet studied. The optimal grain size to achieve the balanced ductility and creep resistance will need to be determined.

(3) Large ingots (~ 5 kg) will be fabricated to investigate the differences between their properties and the previously fabricated experimental scale ingots.

(4) Kinetic models will be proposed to predict the precipitate size and distribution, as these features are believed to have significant effects on the tensile and creep resistance.

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7. Vita

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