Microstructure, mechanical and corrosion behaviors of AlCoCuFeNi-(Cr,Ti) high entropy alloys

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Abstract

The equimolar AlCoCuFeNi-(Cr,Ti) HEAs were synthesized by nonconsumable arc melting to investigate the effects of Cr and Ti on the mechanical and corrosion properties of the HEAs. The results showed that as-cast AlCoCuFeNi-(Cr,Ti) HEAs have a multi-phase microstructure, of which the solid-solution face-centered cubic (FCC), body-centered cubic (BCC) phases, and intermetallics can be observed. Ab initio molecular-dynamics (AIMD) simulations exhibit the existence of the preferred short-range ordering of Al-Ni, Co-Cr, Cr-Fe, and Ti-Co pairs in the AlCoCuFeNiCrTi liquid structure. The AIMD simulations are consistent with the experimental observation during solidification. The segregations and the FCC Cu-rich phase appear in the AlCoCuFeNiCrTi alloy, which is in agreement with AIMD calculations. The Cr addition to AlCoCuFeNi facilitates the formation of the BCC phases in the AlCoCuFeNiCr alloy, which can be explained by the larger Ω and smaller δ values. The addition of large Ti atoms facilitates the formation of the FCC phase, which is due to the fact that Ti will easily induce the breakdown of the BCC solid-solution of the AlCoCuFeNi alloy in terms of decreasing the Ω value and increasing the δ value. The Cr addition improves the corrosion resistance of AlCoCuFeNi alloys.

Keywords: High entropy alloys; Chromium, Titanium; Microstructure; Properties

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1. Introduction

Industry alloy systems are based on one or two principal elements to form the matrix, in the addition of minor alloying elements to improve mechanical behavior and other properties. As the amount of the minor alloying element increases, intermetallic compounds, which are normally hard and brittle, are usually formed. Although the strength of the alloys may further improve, the plasticity of the alloys often drops. In contrast, new unique materials, high-entropy alloys (HEAs), have been developed, which show and confirm their high strength/hardness [1-9], outstanding wear resistance [10, 11], exceptional fatigue and toughness [12-17] and low-temperature strength [17, 18], great structural stability [19], good corrosion resistance [20-22], and antioxidation [20-25].

HEAs, which were firstly proposed by Yeh et al. [1, 6], are generally defined as those alloys containing at least five principal elements, each having the atomic percentage between 5% and 35%. Due to the high configurational entropy effect, especially at high temperatures, HEAs tend to form a simple solid solution, such as face-centered cubic (FCC) structure, body-centered cubic (BCC) structure, hexagonal close-packed (HCP) structure, or their mixtures [1-17, 26-28]. Even though extensive studies focus on the single-phase solid-solution HEAs, multi-phase HEAs are still promising [29]. There has been extensive research based on the Al-Co-Fe-Ni-Cr system [8, 9, 30-33] and Al-Co-Cu-Fe-Ni-Cr system [3, 5, 11-14, 33-40]. The main difference between these systems is the presence of the Cu-rich phases in the latter. This is because Cu has positive mixing enthalpies with most of other elements, and, thus, is repelled to the inter-dendrite (IR) region [5, 12, 34]. Additionally, the remnant Cu in the dendrite region also clusters and forms various kinds of precipitates [5, 7, 35, 41]. The researchers also found that the Cu element can enhance the FCC phase formation [37].

The additions of both Cr and Ti can affect the microstructures and properties of HEAs in various ways [12, 42-44]. However, there are some contradictory conclusions in the reported literatures. For example, Liu et al. [40] found that the Cr addition can improve the compressive strength and toughness, but reduce the ductility of $\text{AlTiCr}_x\text{FeCoNiCu}$ ($x = 0.5 \sim 2.5$) HEAs prepared by the vacuum-arc furnace. However, Fu and the coworkers [41] reported that the Cr addition decreased the compressive strength and Vickers hardness of the twinned $\text{CoFeNiAl}_{0.5}\text{Ti}_{0.5}\text{Cr}$ alloy after the combination of mechanical alloying (MA) and spark-plasma sintering (SPS). Meanwhile, Chem et al. [12] reported that the Ti addition led to the formation of the CoCr-like phase and suppression of the B2 phase, and, thus, increased the hardness of the $\text{Al}_{0.5}\text{CoCrCuFeNiTi}_x$ ($x = 0 \sim 2.0$) alloy. Zhou and the coworkers [9] studied the microstructure and mechanical properties of the AlCoCrFeNiTi_x ($x = 0 \sim 1.5$) system at room temperature, and found that the

alloy system is mainly composed of a simple BCC solid solution and showed excellent mechanical properties. Meanwhile, Qiu et al. [44] also found that the minor Ti element addition can enhance the corrosion resistance of $\text{Al}_2\text{CoCrCuFeNiTi}_x$ ($x = 0 \sim 2.0$) coatings prepared by laser cladding in the 0.5 mol/L HNO_3 solution.

Motivated by these previous investigations of the effects of the Cr and Ti additions on the microstructures and mechanical properties of multi-phase HEAs, in the current study, the as-cast $\text{AlCoCuFeNi}-(\text{Cr,Ti})$ HEAs with an equiatomic ratio were prepared, and, then, the alloying effect of Cr and Ti on the microstructures and properties of these alloys were investigated, using both experimental methods and computational simulations.

2. Experimental procedures

Four equiatomic ratio HEAs, including AlCoCuFeNi (I), AlCoCuFeNiCr (II), AlCoCuFeNiTi (III), and AlCoCuFeNiCrTi (IV), were prepared by the arc melting and casting method, where the purity of all components is greater than 99.9% (weight percent). Melting and casting were performed in a pure argon atmosphere and in a copper crucible. Repeated melting was carried out at least four times to improve the chemical homogeneity of the alloy [3, 5, 6].

The crystalline structures of the ingots were identified via X-ray diffraction, using a Rigaku D/max 2550 diffractometer with Cu K_α radiation. Specimens cut from the ingots were polished and etched with *aqua regia* ($\text{HNO}_3:\text{HCl} = 1:3$, volume fraction) for microstructure characterizations, using scanning-electron microscopy (SEM, FEI Nano SEM 230). The chemical compositions of the different phases were analyzed by the energy dispersive spectroscopy (EDS). Thin-foils specimens were prepared by conventional techniques of cutting, mechanically grinding, polishing, twin-jet electropolishing, and, subsequently, were observed under a transmission-electron microscope (Tecnai G2 F20, FEI Company, Netherland) with the selected area electron diffraction (SAED) analysis. Hardness measurements were conducted, using a Vickers hardness tester (Micromets 5104) under a load of 50 N for 20 s. Five random indents were made for each sample. Compression tests were performed on samples with a dimension of $\phi 4 \text{ mm} \times 8 \text{ mm}$ using Instron 3369 testing machine at room temperature and at a strain rate of $1 \times 10^{-4} \text{ s}^{-1}$. The tests were repeated three times. Fracture strength was measured by the maximum stress that a material can withstand during compression tests before breaking. After fracture, fracture strain is measured by the elongation over the gauge length using an extensometer, according the following equations:

$$\varepsilon_f = -\frac{L-L_0}{L_0} \quad (1)$$

where L is the gauge length after fracture and L_0 is the gauge length before compression tests.

Cylinder specimens with a dimension of 10 mm in diameter and 5 mm in length were used for the immersion-corrosion tests. These specimens were mounted in the epoxy resin with only one side being exposed as a working surface for immersion corrosion tests. These specimens were ground through 2000-grit SiC paper and polished using diamond grinding paste. Prior to immersed corrosion tests, each epoxy-prepared sample was weighed. The immersion corrosion tests were carried out in a H_2SO_4 solution with 0.5 M (mol/L) H_2SO_4 solution plus water bath (XMTD-4000). The corrosion rates were investigated at two temperatures (298 K and 366 K). The specimens were removed from the solution after immersion for 50 h and ultrasonically cleaned for 5 minutes in an alcohol solution to remove possible corrosion products. After rinsed in distilled water, these specimens were dried and weighed again. According to the actual weight loss of specimens, the average corrosion rates, by neglecting the weight loss of the mounting epoxy, were calculated using the following equation [45]:

$$V = \frac{8.76 \times 10^4 \times W}{t \times A \times D} \quad (2)$$

where W is the total weight loss (in g) after the exposure time, t (in h), D the density of the alloy (in g/cm^3), and A (in cm^2) the surface area of the specimen.

The electrochemical experiments were conducted, using the CHI660C electrochemical test equipment at 298 K and 366 K. The typical three-electrode electrochemical system consists of a platinum electrode as the counter electrode, and a saturated calomel electrode as the reference electrode. The HEAs samples were used as the working electrode with a surface of about 0.5 cm^2 exposed to the 0.5 mol/L H_2SO_4 solution. The polarization test was conducted by sweeping the potential from the cathode to anodic directions at a scan rate of 1 mV/s. Each polarization experiment was run after holding the electrode for 1 minute at the open circuit potential to allow for a steady state to be achieved. The 0.5 mol/L H_2SO_4 and the three electrodes were put into the water bath to conduct tests at certain temperatures. The electrochemical tests were conducted at least three times to confirm a good reproducibility. Electrochemical characteristic parameters, such as corrosion potential (E_{corr}), corrosion current density (i_{corr}) can be derived from the potentiodynamic polarization curves by linear fitting at 298 K and 366 K. In addition, the polarization resistances (R_p) were calculated by means of the Stern–Geary equation according to $i_{\text{corr}} = (\beta_a \times \beta_c) / [2.3 \times R_p (\beta_a + \beta_c)]$, where β_a and β_c were the anodic and cathodic Tafel slopes that were obtained from polarization curves. Following the polarization experiment, the specimens were

cleaned by ultrasonic washing and then dried in a drying cabinet. Subsequently, the morphology of the corroded surface of each specimen was examined by SEM.

3. *Ab initio* molecular-dynamics (AIMD) simulations

The computer simulation for the AlCoCuFeNiCrTi (IV) alloy was carried by the AIMD simulations, which were performed, using the plane-wave pseudo-potential software, Vienna *Ab Initio* Simulation Package (VASP) [46, 47] in a canonical ensemble, i.e., the constant mole, volume, and temperature, with the atomic-configuration relaxation and temperature controlled by a Nose thermostat [48]. Projector augmented-wave (PAW) potentials [49] and the revised Perdew-Burke-Ernzerhof [50] gradient approximation to the exchange-correlation functional were used. Cubic supercells of 196 atoms (a cell parameter of 13.7107 Å) was built for AlCoCrCuFeNiTi (IV) with a liquid density of 6.56 g/cm³, which was determined by adjusting the cell volume so that the pressure was zero at equilibrium. The simulations were performed at the Γ point only (i.e., the origin of the first Brillion zone), with a time step of 1 fs. A "medium" precision setting, as described in VASP, was used. Spin polarization was not considered. The electronic-energy-convergence criterion was set to the 1×10^{-4} eV/at. The AIMD simulations were performed with the plane-wave cutoff energy of 295.45 eV at 2,073 K for a total simulation time of 30 ps. The atomic structure in the liquid state can reveal the useful information about the preferred interatomic bonding that may impact the formation of disordered solid solutions during solidification [5, 6, 51-53]. The partial pair distribution function (PDF) gives the information about the probability of such bond formation by measuring the intensity of near-neighbor pairs against the total random distribution, and partial PDF (g_{ab}) was calculated, using:

$$g_{ab}(r) = \frac{V}{N_a N_b} \frac{1}{4\pi r^2} \sum_{i=1}^{N_a} \sum_{j=1}^{N_b} \langle \delta(|r_{ij}| - r) \rangle \quad (3)$$

where V is the volume of the supercell, N_a and N_b are the numbers of elements, a and b , $|r_{ij}|$ is the distance between elements, a and b , and the bracket, $\langle \rangle$, denotes the time average of different configurations.

By examining the atomic trajectory, the diffusion constants were obtained by plotting the mean square displacement (MSD) versus time using the following equation:

$$D_i = \lim_{t \rightarrow \infty} \frac{\langle |R_i(t) - R_i(0)|^2 \rangle}{6t} \quad (4)$$

where D_i is the self-diffusion constant of species, i , and $R_i(t)$ and $R_i(0)$ denote the atomic position of

species, i , at time, t , and $t = 0$, respectively. The angular brackets represent an average over all the same species.

4. Results

4.1 Microstructures of as-cast HEAs

The x-ray diffraction patterns of AlCoCuFeNi alloys with Cr or/and Ti additions are shown in Figure 1. Four alloys are composed of the FCC phase, disordered BCC phase (an A2 phase), and ordered BCC phase (a B2 phase), which were identified to be present in their microstructures (Table 1). The literatures reported that the equiatomic AlCoCuFeNi HEAs are composed of FCC and A2 phases [5, 6, 37]. When the Cr element was added, the dominant phases of the AlCoCuFeNiCr (II) alloy switched to the BCC (A2, B2) phase, and the amount of the FCC phases obviously decreases. However, there are two FCC phases [“1” ($L1_2$) and “2” (FCC) phases] in the AlCoCuFeNiCr (II) alloy. Two FCC phases are clearly visible from two overlapping peaks (Figure 1), corresponding to the two {111} and {200} planes with slightly-different lattice parameters. The similar phenomena were also reported in literatures [8, 54]. The XRD peak intensities of the AlCoCuFeNiTi (III) alloy suggest that the volume fraction of the FCC phase is higher than that of the A2 phase, which means that the Ti addition promotes the FCC formation and depresses the disordered BCC formation. Moreover, contrary to what was reported [12], no Ti_2Ni -like phases were identified in the AlCoCuFeNiTi (III) alloy. When both Cr and Ti are added, the peak intensity of the A2 phase in the AlCoCuFeNiCrTi (IV) alloy obviously increases, indicating the transition from the FCC to BCC phases. Figure 1 also shows that there are some small peaks of Laves phases in the alloys of AlCoCuFeNiTi (III) and AlCoCuFeNiCrTi (IV). It indicated that the Ti addition affected the solidification of the based alloys.

The lower and higher magnification SEM graphs of the as-cast AlCoCuFeNi-(Cr,Ti) alloys are shown in Figure 2. The chemical compositions of the alloys analyzed by EDS are summarized in Table 2. Due to the similar microstructure between the disordered BCC (A2) and ordered BCC (B2) phases, they cannot be obviously distinguished by SEM. The AlCoCuFeNi (I) alloy includes the FCC and BCC (A2/ B2) phases (Figures 2a and 2b). The regular FCC phases, which are Cu-rich, are dispersed in the AlCoCuFeNi (I) alloy (bright in contrast). The BCC (A2/B2) phases have the high contents of Al and Ni elements (dark in contrast). With the additional Cr, the morphology of the FCC phase further evolved into dendrites, while the BCC phase is converted into a lamella-like structure known as the

Widmanstätten-side plates (Figures 2c and 2d) [8]. It indicates that the solidification mode of the AlCoCuFeNiCr (II) alloy is affected by the Cr addition. The dendrites in the AlCoCuFeNiCr (II) alloy are the Cu-rich FCC phases. The Co-Ni-rich BCC phases are the heterogeneous nucleation on the surface of the Cu-rich FCC phases. Meanwhile, the nano-sized basket precipitates in the AlCoCuFeNiCr (II) alloy have higher contents of Al and Ni elements than other regions (Figure 2d). These basket precipitates are identified to be the BCC phases [5]. After adding the Ti element, the microstructure of the AlCoCuFeNiTi (III) alloy consists of the coarse petal-shaped structure cell, and the cell size of 62 μm is relatively large (Figures 2e and f). The petal-shaped structure cell includes the BCC phases (A2/B2), which are Al-, Co-, Ni-, and Ti-rich elements. The Al-Ni-rich BCC (A2/B2) and Cu-rich FCC phases are also observed in the AlCoCuFeNiTi (III) alloy. While adding both Cr and Ti to the AlCoCuFeNi HEA (Figures 2g and h), the petal-shaped structure cell size of the AlCoCuFeNiCrTi (IV) alloy is about 50 μm , and the microstructure was evidently refined, indicating that the Cr and Ti additions can promote the refinement of the grains of the as-cast alloys. Moreover, the Cu segregation becomes more evident (Figure 2h). The nano-sized spherical precipitates in the AlCoCuFeNiCrTi (IV) alloy are the Cr-Fe-rich BCC (A2/B2) phases. The Al-Ni-Ti-rich BCC phases are also observed in the AlCoCuFeNiCrTi (IV) alloy (Figure 2h).

Figure 3 shows the TEM micrographs and corresponding SAED patterns of the samples. Figure 3a reveals the bright-field (BF) image of the AlCoCuFeNi (I) alloy, and the corresponding SAED patterns of the FCC and disordered BCC (A2) phases. Figure 3b indicates the BF image of the AlCoCuFeNiCr (II) alloy and SAED patterns of the FCC and A2 phases. Meanwhile, Figures 3c and 3d show the bright field (BF) images of the AlCoCuFeNiTi (III) and AlCoCuFeNiCrTi (IV) alloys and the corresponding SAED patterns of the FCC and BCC (A2/B2) phases.

4.2 Liquid structures of AlCoCuFeNiCrTi (IV)

The predicted partial PDF by the AIMD simulations is presented in Figure 4. All the partial PDFs show noticeable preference in the first-nearest-neighbor pairs, e.g., the AlNi, CoAl, CoTi, CuCu, and CrFe pairs. In contrast, the AlAl, CoCu, CrCu, CuFe, and TiTi pairs are among those least favorable pairs. The significant contrast in the partial PDFs indicates that the existence of the local chemical short-range order (SRO) in the liquid may intensify during solidification and serve as favorable nucleation embryo sites for crystalline phases [5]. As pointed by Gao and the coworkers [5, 6, 51, 55], a uniform PDF distribution suggests that the lack of SRO tends to favor solid solutions. Therefore, the predicted PDFs

hint the formation of multi-phases in the as-cast state of the AlCoCuFeNi-(Cr,Ti) HEAs (Figure 2).

The MSD plot shown in Figure 5 demonstrates the linear behavior. The as-determined diffusion constants (D_0 [10^{-5} cm²/s]) are listed in Table 3. D_0 is the highest for Ni, followed by Cu, while it is the smallest for Ti that has the largest atomic size among the elements in the alloy.

4.3 Mechanical properties and fracture-surface study

Figure 6 shows the stress-strain curves of the investigated AlCoCuFeNi-(Cr,Ti) HEAs under compression at room temperature. The compression properties and Vickers hardnesses of the alloys are summarized in Table 4. The yield strength ($\sigma_{0.2}$), fracture strength (σ_f), fracture strains (ε_f), Vickers hardness (HV), and hardening coefficient (n) of the AlCoCuFeNi (I) alloy are 1,060 MPa, 1,452 MPa, 19.1%, 387 HV, and 0.458 respectively. When the Cr element was added, the fracture strength and Vickers hardness of the AlCoCuFeNiCr (II) alloy increase to 1,857 MPa and 459 HV, respectively. Meanwhile, the fracture strain and the hardening coefficient of the AlCoCuFeNiCr (II) alloy are increased to 24.6% and 0.536, respectively. The simultaneous appearance of the high strength and ductility is hardly seen in traditional metals and alloys. With the Ti addition, the strong work-hardening capabilities were observed in the alloys, AlCoCuFeNiTi (III) and AlCoCuFeNiCrTi (IV). The yield strengths of the AlCoCuFeNiTi (III) and AlCoCuFeNiCrTi (IV) alloys reach 1,612 MPa and 1,523 MPa, respectively, significantly more than those of the AlCoCuFeNi (I) and AlCoCuFeNiCr (II) alloys. The Vickers hardness of the AlCoCuFeNiTi (III) and AlCoCuFeNiCrTi (IV) alloys also increases to 623 HV and 510 HV, respectively. The hardening coefficients of the AlCoCuFeNiTi (III) and AlCoCuFeNiCrTi (IV) alloys are 0.414 and 0.455, respectively. However, the Ti addition decreases the fracture strains of the AlCoCuFeNiTi (III) and AlCoCuFeNiCrTi (IV) alloys (Table 4). Moreover, the simultaneous addition of Ti and Cr elements also decreases the maximum strength of the AlCoCuFeNiCrTi (IV) alloy. Table 4 also shows that in the four alloys, the AlCoCuFeNiCr (II) alloy has the highest hardening coefficient, while the AlCoCuFeNiTi (III) alloy has the lowest hardening coefficient, indicating that the Cr addition could improve the hardening coefficient, and the Ti addition could reduce the hardening coefficient.

The corresponding fractographic features were shown in Figure 7. Two typical fracture morphologies were observed for the AlCoCuFeNi (I) and AlCoCuFeNiCr (II) alloys (Figures 7a and b). The fracture surfaces reveal the deformed and sheared regions. Moreover, the AlCoCuFeNiCr (II) alloy exhibits the heavy deformation. It indicates that the fracture mode of the AlCoCuFeNiCr (II) alloy is the

ductile rupture. The fracture surfaces of the AlCoCuFeNiTi (Ⅲ) and AlCoCuFeNiCrTi (Ⅳ) alloys (Figures 7c and 7d) consist of river-like patterns, indicating that the fracture morphology of the alloys exhibits the typical cleavage-fracture microstructures. Therefore, adding the Ti element is not beneficial to the ductility of HEAs (Table 4).

4.4 Corrosion study

The electrochemical-corrosion behavior of the as-cast alloys, which were immersed in a 0.5 mol/L H₂SO₄ solution, was studied, using a potentiodynamic-polarization method. The polarization curves for the various alloys conducted at 298 K and 366 K are shown in Figure 8a and 8b, respectively. The measured values of the electrochemical parameters of the alloys are listed in Table 5. In Figure 8a, all of the four alloys have passivation regions and over passivation regions at 298 K. While, the AlCoCuFeNi (I) has no passivation region when it was tested at 366 K, indicating that the passivation film was damaged at 366 K. All of the as-cast alloys conducted at 298 K have corrosion potentials (E_{corr}) in the range from -0.058 to -0.256 V vs SCE. However, the alloys, AlCoCuFeNi (I) and AlCoCuFeNiCr (Ⅱ), have the lower corrosion-current densities (i_{corr}) in the range of 5 ~ 8 $\mu\text{A}/\text{cm}^2$, whereas the alloys, AlCoCuFeNiTi (Ⅲ) and AlCoCuFeNiCrTi (Ⅳ) have the higher corrosion current densities in the range of 39 ~ 45 $\mu\text{A}/\text{cm}^2$ at 298 K.

The AlCoCuFeNiCr (Ⅱ) has a very high polarization resistance (R_p) of 14,450.3 Ω , while other three alloys have a lower polarization resistance (R_p) in the range of 1,100 ~ 2,300 Ω at 298 K. After tested at 366 K, the corrosion potentials (E_{corr}) of four alloys is from -0.158 to -0.368 V vs SCE. However, the AlCoCuFeNi (I) has a very low corrosion-current densities (i_{corr}) and high polarization resistance (R_p) with the value of 11.74 $\mu\text{A}/\text{cm}^2$ and 1,311.5 Ω , respectively. The other three alloys have the higher corrosion-current densities in the range of 779 ~ 3,380 $\mu\text{A}/\text{cm}^2$ and the lower polarization resistance (R_p) in the range of 29 ~ 36 Ω .

Figure 9 shows the SEM microstructure of the alloys after the potentiodynamic polarization in 0.5 mol/L H₂SO₄ at 298 K. According to the SEM images, surface examinations showed that the major type of corrosion was pitting corrosion. The results of EDS indicated that the corroded areas have lower Cu contents, which indicated that the Cu-rich FCC phases in the alloys were mainly eroded during potentiodynamic polarization. However, the Al-, Fe-, Ni-, Co- and Ti-rich phases were retained.

Figure 10 presents the corrosion rate for the investigated alloys, which were immersed in a 0.5 mol/L H₂SO₄ solution at two different temperatures (298 K and 366 K). When the Cr element is added,

the corrosion rate of the AlCoCuFeNiCr (II) alloy is 0.048 mm/year, lower than that of the AlCoCuFeNi (I) alloy, which is 0.14 mm/year at 298 K. However, the corrosion rate of the AlCoCuFeNiCr (II) alloy increases to 1.19 mm/year at 366 K. With the Ti addition, the AlCoCuFeNiTi (III) alloy exhibits the higher corrosion rates, which are 27.16 and 32.20 mm/year at 298 K and 366 K, respectively. It indicates that the Ti addition decreases the corrosion resistance of the based alloys. When adding the Cr element, the corrosion rate of the AlCoCuFeCrTi (IV) alloy is lower than that of the AlCoCuFeNiTi (III) alloy.

5. Discussion

5.1 Effects of Cr and Ti additions on the microstructures of the as-cast HEAs

Figures 1, 2, and 3 show that the Cr and/or Ti additions affect the microstructures of HEAs significantly. The addition of the Cr element (~ 16.7 at. %) to AlCoCuFeNi (I) facilitates the formation of the BCC phase in the AlCoCuFeNiCr (II) alloy. It is different from the results of Fu and the coworkers [43], who thought that the addition of Cr (~ 20 at. %) to the CoFeNiAl_{0.5}Ti_{0.5} alloy promoted the formation of the FCC phases. Meanwhile, the high magnified image shown in Figure 2d reveals the nano-scaled basket structure of the dendrite matrix. This basket structure can be regarded as the modulated plate resulting from the spinodal decomposition, which has been reported by Soffa and Laughlin [55]. Instead of the Cr addition, when Ti is added to the AlCoCuFeNi (I), the main phases in the AlCoCuFeNiTi (III) alloy are the FCC phases (Figures 1, 2e, and 2f). This trend indicates that the Ti addition (~ 16.7 at. %) promoted the formation of the FCC phases in AlCoCuFeNiTi (III). However, Qiu et al. [44] thought that the Ti addition, to a certain extent, promoted the formation of a BCC-dominant microstructure in Al₂CoCrFeNiCuTi_x coatings.

There are many factors, which may affect the microstructure of HEAs. According to the literatures, δ (the atomic-size parameter) [4, 6, 56], ΔS_{conf} (configurational entropy) [1, 4, 6], $\Delta\chi$ (the electronegativity difference) [6, 57], VEC (valence electron concentration) [6, 58], and Ω (the parameter of the entropy of mixing times the average melting temperature of the elements divided by the enthalpy of mixing) [6,56,59] are often selected to study the phase formation and stability of HEAs. The ΔS_{conf} , which is the macroscopic - comprehensive reflection of the atomic-intrinsic characteristic, reflects the atomic-binding energy. It is related to the electronegativity difference ($\Delta\chi$), electron density, etc. This is an important factor that affects the phase composition of HEAs. The atomic-size parameter (δ), which is adopted to describe the effect of the atom-size difference in the HEAs, also affects the phase compositions

of HEAs. Moreover, the *VEC* is the physical parameter to control the phase stability for FCC or BCC solid solutions.

The electronegativity difference ($\Delta\chi$) of a HEA alloy is defined as follows [56]:

$$\Delta\chi = \sqrt{\sum_{i=1}^n c_i (\chi_i - \bar{\chi})^2} \quad (5)$$

where n is the number of the components in an alloy, c_i is the molar fraction of the i -th component, χ_i is the Pauling electronegativity of the element, i , in the alloy, which can be obtained in Reference [60], and $\bar{\chi} = \sum_{i=1}^n c_i \chi_i$ is the mean value of the electronegativity for the alloy.

Meantime, the atomic-size parameter, δ , is expressed as [4]:

$$\delta = 100 \sqrt{\sum_{i=1}^N c_i \times (1 - r_i / \bar{r})^2} \quad (6)$$

where n is the number of the components in an alloy, c_i is the molar fraction of the i -th component, r_i is the atomic radius, which can be obtained in Reference [60], and $\bar{r} = (\sum_{i=1}^n c_i \times r_i)$ is the average atomic radius.

Let us consider an equiatomic alloy in its liquid state or regular solid solution. Its ideal configuration entropy per mole can be calculated as follows [1, 4, 6]:

$$\Delta S_{conf} = R \ln n \quad (7)$$

where R is the gas constant, 8.314 J/(K.mol), and n is the number of the components in an alloy.

Moreover, the *VEC* for the HEAs can be defined as follows [57, 58]:

$$VEC = \sum_{i=1}^n c_i \times (VEC)_i \quad (8)$$

where the n is the number of the components in an alloy, c_i is the molar fraction of the i -th component, and $(VEC)_i$ is the *VEC* of the i -th element in an alloy.

The Ω parameter is introduced to predict the phase formation for HEAs. It represents the competition between the entropy and enthalpy, and can be calculated as follows [6, 56, 59]:

$$\Omega = \frac{T_m \Delta S_{mix}}{|\Delta H_{mix}|} \quad (9)$$

where $T_m = \sum c_i (T_m)_i$ is the melting point of the alloy, $\Delta S_{mix} = -R \sum c_i \ln c_i$ is the entropy of mixing, $\Delta H_{mix} = \sum_{i \neq j} 4c_i c_j \Delta H_{ij}^{mix}$ is the enthalpy of mixing in the liquid, and ΔH_{ij}^{mix} can be obtained in Reference [60].

According Equations (4) ~ (8), the physical parameters of the present alloys are summarized in Table 1. The calculated δ values are 6.99 and 6.69 for the alloys AlCoCuFeNiTi (III) and AlCoCuFeNiCrTi (IV), respectively, which are higher than those (5.61% and 5.19%) of the AlCoCuFeNi

(I) and AlCoCuFeNiCr (II) alloys (Table 1). A larger δ value is indicative of more severe lattice distortion. The Cr addition increases the Ω value to 5.06 and decreases the δ value to 5.19% for the AlCoCuFeNiCr (II) alloy, respectively. Zhang et al. [6, 56, 59] thought that larger Ω (≥ 1.1) and smaller δ ($\leq 6.6\%$) should be expected to form the HEA-stabilized solid-solution phase. So the Cr addition promotes the formation of mainly the BCC solid-solution phase in the AlCoCuFeNiCr (II) alloy, compared to AlCoCuFeNi (I).

The atomic radius of Ti is the largest among Fe, Co, Ni, Cu, Al, Cr, and Ti [60], and, thus, will easily induce the breakdown of the BCC structure of the AlCoCuFeNi (I) alloy (Table 2). Table 1 also shows that the Ti addition decreases the Ω value from 3.53 to 1.43 and 1.95, and increases the δ value to 6.99% and 6.69% for the AlCoCuFeNiTi (III) and AlCoCuFeNiCrTi (IV) alloys. So the Ti addition results in the multiphase formation in the AlCoCuFeNiTi (III) and AlCoCuFeNiCrTi (IV) alloys (Figures 1 and 2). Figure 2 shows that the Cu segregation is the typical behavior in the AlCoCuFeNi-(Cr,Ti) HEAs. Since the mixing enthalpies for a mixture of Cu and each of Co, Fe, Ni and Cr, are 6, 13, 4 and 12 kJ/mol [56], respectively, Cu is rejected into the liquid during solidification, and, hence, Cu-rich phases are formed in the regions (Figures 4 and 5). Figure 2 also presents that the Ti addition accelerates the Cu element to segregate and, thus, may result in the decrease of the ductility of HEAs (Table 4 and Figure 6).

Figure 4 suggests the existence of the preferred short-range ordering of Al-Ni, Co-Al, Co-Ti, Cu-Cu, and Cr-Fe pairs in the liquid structure. These structural features in the liquid are consistent with the experimental observation of Al-Ni-rich, Cr-Fe-rich and Al-Ni-Ti-Co-rich phases (Figure 2 and Table 2) during solidification. The preferred Cu-Cu pair correlation suggests that Cu tends to segregate in the liquid (Figure 4). This trend leads to the formation of a Cu-rich phase during solidification, which is also consistent with the experimental observations (Figure 2).

5.2 Effects of Cr and Ti additions on mechanical properties of as-cast HEAs

Table 4 and Figure 6 show that the Cr addition can simultaneously improve the strength, hardening coefficient, and ductility of the based alloy. Figure 1 indicates that the volume fraction of BCC phases in the AlCoCuFeNiCr (II) alloy is higher than that of the AlCoCuFeNi (I) alloy. The higher strength of the AlCoCuFeNiCr (II) can be attributed to the solid-solution strength and strong bonding effect among the alloy metallic elements [61]. On the other hand, the nano-sized basket precipitates, BCC phases, can also enhance the strength of the AlCoCuFeNiCr (II) alloy. The high ductility may be attributed to the phase composition of the AlCoCuFeNiCr (II) alloy. According to the basic structural factor, the structure with more slip systems leads to lower lattice friction during dislocation motion, and, thus, increases the

ductility of the samples [62]. The FCC structure has slip planes with the closest packing, while the BCC structure has no true close-packed slip planes. Thus, the critical stress for slip in the FCC structure is basically smaller than that of the BCC structure. As the “2” FCC phase precipitates from the BCC matrix phase, the FCC phases can increase the ductility of the AlCoCuFeNiCr (II) alloy.

The addition of the Ti element improves the mechanical properties of the AlCoCuFeNiTi, especial the yield strength and Vickers hardness, but decreases the ductility of the alloys 3 and 4 (Figure 6 and Table 4). It indicates that the strengthening effect of the Ti element is beyond the Cr element. The Ti addition was found to have significant influence on the refinement of grains and increase of the ferrite/pearlite ratio, and, hence, has significant effects on the mechanical properties and toughness of medium carbon steels [63].

5.3 Effects of Cr and Ti additions on corrosion behavior of as-cast HEAs

Figures 8 and 10 show that the Cr addition can generally improve the corrosion resistance of the AlCoCuFeNi (I) HEAs, but the Ti addition decreases the corrosion resistance of the base HEAs at 298 K. Due to the heterogeneous composition which is the common phenomenon in the arc melting and casting method, the microstructure (Figure 2), stress, micro-anode region, and micro-cathode region are formed in the electrolyte solution. The anode and cathode areas constitute the corrosion cell. Therefore, the alloys with two-phase structures are corroded easily, and the difference of electrode potentials is greater, the i_{corr} variation between the micro-anode and micro-cathode regions is larger. From the phase-structure analysis (Figures 1, 2, 3 and 9), the corrosion resistance of the BCC solid solution is better than that of the FCC solid solution in the H_2SO_4 liquid. This trend shows that the AlCoCuFeNiCr (II) alloy with the Cr addition has better corrosion resistance than other alloys at 298K. Meanwhile, Cr is easy to form Cr_2O_3 , which being as a passivation film could prevent the HEAs further corrosion at 298 K. However, Cr addition decreases the corrosion resistance of the base HEAs at 366K. That is because the Cr_2O_3 passivation film breaks down at a higher temperature, and the passivation film could not be regenerated, which could accelerate localized corrosion.

6. Conclusions

- 1) The as-cast AlCoCuFeNi-based HEAs are found to have a dendritic structure, in which only FCC and BCC solid-solution phases can be observed. The additions of Ti and Cr can refine the grains of the as-cast alloys, but result in the segregation of Cu, and, thus, the formation of a FCC Cu-rich

phase. The microstructure of the Ti-containing alloys is different from that of the Ti-free alloy.

- 2) The addition of the Cr element (~ 16.7 at. %) to AlCoCuFeNi facilitates the formation of the BCC solid solution in the AlCoCuFeNiCr alloy, which can be explained by the larger Ω and smaller δ values.
- 3) The addition of large Ti atom (~ 16.7 at. %) facilitates the formation of the FCC phase, which due to the fact that the Ti will easily induce the breakdown of the BCC solid-solution of the AlCoCuFeNi alloy in terms of decreasing the Ω value and increasing the δ value.
- 4) Preferred short-range ordering of Al-Ni, Co-Al, Co-Ti, Cu-Cu, and Cr-Fe pairs exists in the liquid structure of the AlCoCuFeNiCrTi alloy. These structural features in the liquid are consistent with the experimental observation of the Al-Ni-rich, Cr-Fe-rich and Al-Ni-Ti-Co-rich phases during solidification. The preferred Cu-Cu pair correlation suggests that Cu tends to segregate in the liquid.
- 5) The AlCoCuFeNi alloy with the Cr addition has the highest fracture strength of 1,857 MPa, and the AlCoCuFeTi alloy has a high yield strength of 1,612 MPa. The addition of the Ti element increases the strength of AlCoCuFeNi, which results from the introduced fine precipitates, like Laves phases.
- 6) The Ti addition decreases the corrosion resistance of the FeNiCoCuAl alloys at both 298 K and 366 K, while the Cr addition improves the corrosion resistance of AlCoCuFeNi alloys without Ti.

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List of Tables

Table 1. Compositions and physical parameters of the alloys

Table 2. Nominal compositions of HEAs and chemical compositions (at. %) of different areas from
Figure 2

Table 3. Predicted diffusion constants of AlCoCuFeNiCrTi (IV) at $T = 2,073$ K.

Table 4. Mechanical properties of as-cast alloys.

Table 5. Dynamic parameters derived from the potentiodynamic-polarization curves by linear fitting at
298 K and 366 K.

Figure captions

Figure 1. XRD graphs of as-cast alloys.

Figure 2. SEM graphs of as-cast AlCoCuFeNi (I) (a, b), AlCoCuFeNiCr (II) (c, d), AlCoCuFeNiCr (III) (e, f), and AlCoCuFeNiCrTi (IV) (g, h).

Figure 3. TEM bright-field images and corresponding SAED patterns of the samples.

(a) AlCoCuFeNi (I), (b) AlCoCuFeNiCr (II), (c) AlCoCuFeNiTi (III), and (d) AlCoCuFeNiCrTi (IV)

Figure 4. Predicted partial pair distribution function of AlCoCuFeNiCrTi (IV) pertaining to (a) Al, (b) Co, (c) Cu, (d) Fe, (e) Ni, (f) Cr, and (g) Ti at $T = 2,073$ K.

Figure 5. Predicted mean square displacement of AlCoCuFeNiCrTi (IV) at $T = 2,073$ K.

Figure 6. The engineering stress-strain curves of as-cast alloys at the room-temperature.

Figure 7. SEM graphs of the fracture samples. (a) AlCoCuFeNi (I), (b) AlCoCuFeNiCr (II), (c) AlCoCuFeNiTi (III), and (d) AlCoCuFeNiCrTi (IV).

Figure 8. Potentiodynamic-polarization curves of as-cast alloys in the 0.5 mol/L H_2SO_4 solution at 298 K and 366K.

Figure 9. Surface images of as-cast alloys after potentiodynamic polarization in the 0.5 mol/L H_2SO_4 . (a) AlCoCuFeNi (I), (b) AlCoCuFeNiCr (II), (c) AlCoCuFeNiTi (III), and (d) AlCoCuFeNiCrTi (IV).

Figure 10. The corrosion rate for as-cast alloys in the 0.5 mol/L H_2SO_4 solution plus bath at 298 K (a) and 366 K (b).

Table 1. Compositions and physical parameters of the alloys

Sample	Phase composition	ΔS_{conf} (J·mol ⁻¹ ·K ⁻¹)	ΔH_{mix} (kJ·mol ⁻¹)	Ω	VEC	δ (%)	Δx	ΔT (K)
AlCoCuFeNi (I)	FCC + A2/B2	13.38	-5.76	3.53	8.20	5.61	0.130	16.0
AlCoCuFeNiCr (II)	A2/B2 + FCC	14.90	-4.78	5.06	7.83	5.19	0.138	15.8
AlCoCuFeNiTi (III)	FCC + A2/B2 + Laves	14.90	-16.56	1.43	7.50	6.99	0.165	23.6
AlCoCuFeNiCrTi (IV)	FCC + A2/B2 + Laves	16.18	-13.8	1.95	7.29	6.69	0.155	21.7

Table 2 Nominal compositions of HEAs and chemical composition (at. %) of different areas from Figure 2

Sample	Composition	Crystal structure	Al	Co	Cu	Fe	Ni	Cr	Ti
AlCoCuFeNi (I)	Nominal composition	-	20	20	20	20	20	-	-
	Cu-Co-Fe-rich	FCC	12.65	20.38	25.86	22.38	18.73	-	-
	Al-Ni-rich	BCC(A2/B2)	24.56	21.56	11.37	19.65	22.87	-	-
AlCoCuFeNiCr (II)	Nominal composition	-	16.67	16.67	16.67	16.67	16.66	16.66	-
	Cu-rich	FCC	11.31	15.60	29.31	14.58	17.52	11.67	-
	Al-Ni-rich	BCC(A2/B2)	25.58	16.82	10.91	14.27	20.09	12.22	-
	Co-Fe-rich	BCC(A2/B2)	11.94	19.77	16.18	19.41	15.99	16.72	-
AlCoCuFeNiTi (III)	Nominal composition	-	16.67	16.67	16.67	16.67	16.66	-	16.66
	Cu-rich	FCC	8.33	6.71	48.86	15.83	14.93	-	5.35
	Al-Ni-rich	BCC(A2/B2)	20.38	16.01	9.6	16.29	19.97	-	17.75
	Al-Co-Ni-Ti-rich	BCC(A2/B2)	21.93	19.87	6.55	14.75	18.50	-	18.40
AlCoCuFeNiCrTi (IV)	Nominal composition	-	14.29	14.29	14.28	14.28	14.28	14.29	14.29
	Cu-rich	FCC	6.52	2.15	77.91	3.57	6.34	1.65	1.86
	Fe-Cr-rich	FCC	2.55	9.47	7.13	33.83	7.11	30.76	9.14
	Al-Ni-Ti-rich	BCC(A2/B2)	20.08	16.35	7.55	8.64	22.30	3.29	21.77

Table 3. Predicted diffusion constants of AlCoCuFeNiCrTi at T = 2,073 K.

Element	Al	Co	Cu	Fe	Ni	Cr	Ti
D_o [10^{-5} cm ² /s]	3.89 ± 0.03	4.04 ± 0.02	4.32 ± 0.03	3.65 ± 0.03	4.69 ± 0.02	3.76 ± 0.05	3.57 ± 0.04

Table 4. Mechanical properties of as-cast alloys

Sample	σ_f (MPa)	$\sigma_{0.2}$ (MPa)	E (GPa)	ε_f (%)	HV	n
AlCoCuFeNi (I)	$1,452 \pm 5$	$1,060 \pm 4$	202 ± 6	19.1 ± 0.5	387 ± 5	0.458
AlCoCuFeNiCr (II)	$1,857 \pm 8$	$1,285 \pm 6$	219 ± 5	24.6 ± 0.7	459 ± 6	0.536
AlCoCuFeNiTi (III)	$1,816 \pm 6$	$1,612 \pm 7$	231 ± 7	12.8 ± 0.3	623 ± 8	0.414
AlCoCuFeNiCrTi (IV)	$1,588 \pm 7$	$1,523 \pm 5$	239 ± 5	8.1 ± 0.2	510 ± 5	0.455

Table 5. Dynamic parameters derived from the potentiodynamic polarization curves by linear fitting at 298 K and 366 K

Sample	E_{corr} (V vs SCE)		i_{corr} ($\mu\text{A}/\text{cm}^2$)		R_p (Ω)	
	298 K	366 K	298 K	366 K	298 k	366k
AlCoCuFeNi (I)	-0.058	-0.158	7.93	11.74	2273.5	1311.5
AlCoCuFeNiCr (II)	-0.075	-0.284	5.09	779.2	14450.3	29.2
AlCoCuFeNiTi (III)	-0.253	-0.374	44.76	3379	1144.9	36.0
AlCoCuFeNiCrTi (IV)	-0.256	-0.368	39.59	2246	1558.2	27.3

AlCoCuFeNiCrTi

AlCoCuFeNiCr