



Corrosion of Eutectic High-Entropy Alloys: A Review

Kaiyang Li ¹^(b), Yunlong Zhai ¹, Minjie Lai ², Min Song ³, Shanfang Zou ⁴, Guojie Huang ⁵^(b), Khurram Yaqoob ⁶^(b), Zhangwei Wang ^{2,*} and Naiqiang Zhang ^{1,*}

- ¹ School of Energy Power and Mechanical Engineering, North China Electric Power University, Beijing 102206, China; kaiyang.li@ncepu.edu.cn (K.L.); zhaiyunlong2022@163.com (Y.Z.)
- ² State Key Laboratory of Solidification Processing, Northwestern Polytechnical University, Xi'an 710072, China; mj.lai@foximail.com
- ³ State Key Laboratory of Powder Metallurgy, Central South University, Changsha 410083, China; msong@csu.edu.cn
- ⁴ Optimal Material Technology Co., Ltd., Chengdu 610000, China; zsf829750@163.com
- ⁵ China Nonferrous Metals Innovation Institute (Tianjin) Co., Ltd., No.86, Ziguang Road Automotive Industrial Area, Xiqing District, Tianjin 300393, China; hguojie@126.com
- ⁶ School of Chemical and Materials Engineering, National University of Sciences and Technology, H-12, Islamabad 44000, Pakistan; khurram.yaqoob@scme.nust.edu.pk
- * Correspondence: z.wang@csu.edu.cn (Z.W.); zhnq@ncepu.edu.cn (N.Z.)

Abstract: High-entropy alloys (HEAs) are emerging as a new family of alloys with equal/nearequal amounts of constituting elements and outstanding properties. In particular, eutectic highentropy alloys (EHEAs) with alternate lamella phases possess both high strength and ductility, offering the advantage of conquering the strength–ductility trade-off that could hardly be achieved by conventional alloys. While the mechanical behavior of EHEAs has been widely studied, the corrosion behavior is still not fully understood. Furthermore, the environment-induced degradation could largely decide the service life of EHEA as engineering alloys, and the eutectic structure may have a special influence on the corrosion process. This article systematically reviews the corrosion studies of EHEAs by pointing out the structural features of EHEAs, summarizing the general corrosion issues for EHEAs and identifying the specific corrosion performance of different EHEA systems. It is found that EHEAs feature micro-galvanic corrosion due to their eutectic crystal structure, and such a corrosion mode is further affected by testing time, heat treatment, temperature, and applied potential. All the corrosion-affecting factors are summarized, and future research directions are suggested, aiming at ensuring the wide engineering application of EHEAs with both high strength–ductility and corrosion resistance.

Keywords: eutectic high-entropy alloy; corrosion; galvanic corrosion; passive film

1. Introduction

1.1. Emergence of Eutectic High-Entropy Alloys

For the past several thousand years, alloys have been fabricated by selecting one or two main elements and several other minor alloying elements and then mixing these elements to prepare metallic materials with the desired properties. The as-prepared alloys are often located at the corners and margins of multicomponent phase diagrams, and the properties of the alloys almost reach their limit after long-term research and development.

To overcome the conventional limitations, a breakthrough was made by designing alloys at the central region of multicomponent phase diagrams. The prepared alloys are considered as high-entropy alloys (HEAs). HEAs are featured with at least four principal elements in equal or near-equal atomic percentages, and the high configurational entropy of these elements often results in an unexpected solid solution phase rather than multiple phases [1]. The unique compositional and microstructural features provide HEAs with four major characteristics, namely, high-entropy effect, lattice distortion effect, sluggish



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). diffusion effect, and cocktail effect [2]. Benefiting from the above effects, HEAs often have superior properties over conventional alloys, such as high strength and hardness, high fracture toughness, remarkable creep, fatigue and wear resistance, superior corrosion and irradiation resistance, hydrogen embrittlement resistance, and so on [3–7]. The emergence of HEAs offers a new vision for the development of high-performance engineering alloys.

Most HEAs have a single phase, like a face-centered cubic (FCC) or body-centered cubic (BCC) structure. FCC-structured HEAs, such as CoCrFeMnNi, often show high ductility but relatively low strength [8]. In contrast, HEAs with a BCC structure, like TiNbTaZrHf, usually exhibit high strength but low ductility [9]. Such a single-phase-induced strength–ductility trade-off dilemma has been a challenging problem for a long period of time [10]. In addition, single-phase HEAs often have poor castability and element segregation during solidification. All these drawbacks limit the further application of HEAs.

To deal with these shortcomings, Lu et al. [11] conducted a successful trial by developing a new class of HEAs, named eutectic high-entropy alloys (EHEAs). EHEAs have dual phases, often a hard one and a soft one. The EHEA is an ideal in situ composite with an intermetallic reinforcing phase (e.g., B2 phase or Laves phase) and a soft matrix phase (e.g., FCC phase). Both the reinforcing material and matrix are high-entropy solid solution phases with alternate lamellar arrangements, which could offer a unique combination of high strength and ductility [12,13]. The eutectic structure-induced, unprecedented mechanical properties effectively overcome the strength–ductility trade-off, thus offering EHEAs great potential in various engineering fields [14]. The tunable microstructure and attractive mechanical strength make EHEAs suitable substitutes for conventional engineering alloys (like Fe-, Ni-, and Al-based alloys) as structural materials.

Additionally, EHEAs often show good liquidity and castability as eutectic alloys and retain the excellent characteristics of HEAs. Such features make EHEAs good candidates as ship propellers, pumps, and valves, which require alloys with both good castability and high mechanical performance [15].

1.2. Classification and Constituent Phase

Until now, various EHEAs with different phase components and chemical compositions have been developed. They could be classified either by constituent elements or phase components. Based on the number of constituent elements, EHEAs could be classified as alloys consisting of four, five, six, or more elements. Based on the constituent phases, EHEAs could be classified as FCC + BCC [16], FCC + Laves [17,18], BCC1 + BCC2 (B2) [19], HCP + BCC [20], L1₂ (FCC) + BCC2 [21], FCC + intermetallic compounds [22], etc. Details of these classifications can be found in the referenced review, which presents the phase constituents of different EHEAs that have been discovered so far [23].

Obviously, the chemical composition and size of the dual phases vary across different EHEAs. A typical example could be taken as AlCoCrFeNi_{2.1}, the EHEA discovered by Lu et al. [11]. It is composed of a soft FCC (L1₂) phase and a hard BCC (B2) phase with a fine lamellar structure. Detailed structural images are presented in Figure 1. EDS analyses found that the FCC phase is featured with a high content of Fe, Co, and Cr, while the B2 phase is enriched with Al and Ni. Table 1 presents the chemical compositions of the FCC and BCC phases in AlCoCrFeNi_{2.1} reported by different research groups [24–26]. It is found that, for the nominal composition of AlCoCrFeNi_{2.1}, the actual chemical composition presented by different studies varies.

Table 1. Chemical compositions of FCC and BCC phases in AlCoCrFeNi_{2.1} EHEAs from different studies.

Phase	Al	Со	Cr	Fe	Ni	Ref.
L1 ₂ (FCC)	6.4	18.4	23.1	20.5	31.6	[24]
B2 (BCC)	15.7	15.1	14.0	14.9	40.3	
L1 ₂ (FCC)	8.66	18.47	20.53	19.48	32.85	[25]
B2 (BCC)	24.3	13.00	6.50	10.55	45.70	
L1 ₂ (FCC)	7.33	21.27	19.50	21.73	30.17	[26]
B2 (BCC)	27.09	13.72	8.75	11.93	38.51	



Figure 1. Microstructural characterization of as-cast AlCoCrFeNi_{2.1}1 EHEA. (**a**) XRD analysis, (**b**) EBSD results of the eutectic structure (red-BCC, blue-FCC), (**c**) SEM images, and (**d**) corresponding EDS images. Adapted from Ref. [27].

The width of lamella usually ranges from micro- to nanometer. One study finds that a casted AlCoCrFeNi_{2.1} shows fine lamellae BCC–FCC phases with each width below 0.5 μ m and island-shaped ones below 2 μ m. Analysis on SEM images by commercial software shows that the volume shares of L1₂ (FCC) phase and B2 (BCC) phase are 65% and 35%, respectively [24]. Yet in another study, L1₂ (FCC) phase and B2 (BCC) phase in AlCoCrFeNi_{2.1} take the volume share of 41.2% and 58.8%, respectively [28]. For Al_{0.8}CrFeNi_{2.2} EHEA system, the FCC has a size of 3–5 μ m and takes a volume fraction of 60%, while those of B2 phase are 1–2 μ m and 40%, respectively [29]. Its FCC phase is featured with high contents of Fe and Cr elements, while its BCC phase is rich in Al and Ni elements [29].

Because of the dual-phase feature, phase boundaries are unavoidable in EHEAs. Given that the phase boundary is a crucial factor affecting corrosion performance, some researchers revealed the detailed microstructure of phase boundary with high-resolution TEM [30]. In FeCrNiCoNb_{0.5} with FCC phase and C14 Laves phase, discrete atomic steps are observed as semi-coherent phase boundaries [31]. The lattice coherency represents the changed lattice constant and the residual stress, which is prone to corrosion attack upon the exposure to an aqueous environment.

1.3. Gaps in Corrosion Study

Although the excellent mechanical behavior of EHEAs has been well recognized, there is still limited understanding about its real service performance. The alloy degradation in the service environment due to the direct chemical interactions between alloy surface and aqueous solution, also known as corrosion, is a crucial aspect in engineering application. Corrosion could induce integrity loss or even premature failure, posing a potential threat to fortune and human safety. Thus, evaluating the corrosion resistance of EHEAs, understanding the related corrosion mechanisms, and finding effective strategies to reduce the corrosion degree are of great importance to extend the engineering service life of EHEAs.

Up to now, corrosion studies of single-phase HEAs have been conducted in various aqueous environments (such as acid solution, SO_4^{2-} -containing solution, and Cl⁻-containing solution) [32,33], and HEAs show outstanding corrosion resistance due to the uniform, compact, and dense passive layer with limited defects [34]. However, for EHEAs, while the complex microstructure makes a beneficial contribution to the excellent mechanical behavior, the accompanying impact on corrosion is still uncertain. On one hand, the

addition of noble elements like Al and Cr in EHEAs could help to form a compact oxide with high stability. On the other hand, the duplex phase and complex microstructure of EHEAs may induce inhomogeneity in the passive film and increase galvanic corrosion. The related EHEA corrosion studies have been conducted in different aqueous environments [28,35]. Some researchers point out that EHEAs have a comparable general corrosion resistance with conventional stainless steels, Ni-based alloys, or even single-phase HEAs [27]. Others, however, claim that the galvanic corrosion between dual phases in EHEAs leads to poor corrosion performance [28]. One possible explanation for such dilemma is that the complex microstructure in EHEA not only contributes to excellent mechanical behavior but also makes the corrosion process more complicated. Furthermore, the corrosion of EHEAs may be affected by several other factors, such as alloying elements, testing time, pre-heat treatment, and testing temperature [32]. All these factors could make a certain impact on the microstructure evolution of EHEAs and the formed passive films, thus further affecting the corrosion behavior. However, until now, there is still limited understanding on the corrosion behaviors and passivation of EHEAs with different chemical compositions, microstructures, and testing environments.

To address these issues, a systematic review covering the corrosion behaviors of EHEAs in different environments and revealing the related corrosion mechanisms is highly needed. Therefore, we intend to conduct a review paper by summarizing the microstructural features of EHEAs, describing the corrosion features induced by complex microstructure in EHEAs, scrutinizing the crucial factors that affect corrosion from both testing environment and material sides, reviewing the corrosion performance of different EHEA systems, summarizing the current research progress, and sorting out the future research directions. The related works are expected to show the corrosion performance of EHEAs in various environments, shed light on the corrosion mechanisms of EHEAs, evaluate the corrosion performance of EHEAs as the substitutes for conventional engineering alloys, and eventually, support the successful application and safe operation of EHEAs in various engineering fields.

2. General Corrosion Issues for EHEAs

2.1. Galvanic Corrosion

The corrosion resistance of metals and alloys is highly dependent on the properties of the surface passive film during direct interactions with the aqueous corrosive media [36]. The formation of a passive, compact, and continuous oxide layer is the key feature of a protective barrier [37]. In EHEAs, one of the most serious corrosion challenges is the galvanic corrosion between the dual phases. The galvanic corrosion could commonly be found in multi-phase alloys due to compositional and the resulting potential variations between different phases [38–40].

EHEAs usually have fine and alternate-distributed phases. The variation of enriched elements in different phases leads to the formation of different passive films. The difference in chemical compositions of the passive film in each phase convolutes the formation of local cathodes and anodes as galvanic corrosion cells, which may disrupt the chemical integrity of surface passive film and complicate the corrosion behavior of the EHEAs. In short, the composition difference of the dual phase leads to the heterogeneity of the passive film, thus different potentials for micro-galvanic corrosion.

It is well-recognized that the dual-phase feature of EHEAs inevitably brings galvanic corrosion in various media, like solutions containing H^+ , Cl^- , or SO_4^{2-} [29]. For instance, in AlCoCrFeNi_{2.1}, the most typical EHEA, the micro-galvanic corrosion between BCC (anode, Al-Ni-rich) and FCC (cathode, Cr-Co-Ni-rich) phases was found in 3.5% NaCl solution [24]. The enrichment of Cr and Co in the FCC phase brings about a more passive state of the oxide layer, thus making the BCC phase a sacrificed one. Related Density Functional Theory (DFT) calculation also proves that the BCC phase more easily adsorbs Cl^- than the FCC phase, thus making it more prone to localized corrosion [30]. The schematic diagram showing the selective dissolution of BCC phase in a Cl^- -containing solution is presented



in Figure 2. Several other studies also confirm such selective dissolution of BCC phase as anode in different solutions [28,41], which is identified as the initiator of corrosion.

Aggregation and absorption of Cl⁻ on passive films

Figure 2. Schematic diagram of the selective dissolution of BCC phase in Fe_{1.125}Ni_{1.06}CrAl EHEA in 3.5% NaCl solution [30].

To further investigate the preferentially dissolved phase, more information on the electrochemical feature is needed. Because of the alternative distribution of the dual phases and their small sizes as low as micrometers, the detailed characterization on the electrochemical properties of each phase is more difficult than the bulk phase. Up to now, several advanced techniques have been postulated or employed to investigate the galvanic effects by identifying the more prone-to-corrosion phase and showing the potential differences between different phases. For instance, scanning vibrating electrode technique (SVET) has been used to detect the active sites on metal surfaces with a high spatial resolution, thus providing an active site distribution map to determine the corrosion tendency of different phases [27]. It quantitatively analyzes the surface electric field and effectively evaluates the individual electrochemical response of each phase in AlCoCrFeNi_{2.1} EHEA, thus revealing the corrosion mechanism of galvanic coupling. Figure 3 is a typical SVET result showing the potential differences between the FCC and BCC phases in an EHEA. In another study, scanning Kelvin probe force microscopy (SKPFM) measurement was also employed by retrofitting a Bruker Dimension Icon AFM [35]. It successfully proved the low stability of the B2 phase after plotting the surface morphology and measuring the local contact potential difference [35]. For future studies, scanning electrochemical microscopy (SECM) is also utilized, which could further shed light on the corrosion process by measuring the in situ electrochemical reactions on EHEA surfaces using the scanning probe [42].

The negative effect of galvanic corrosion is obvious. The micro anode–cathode coupling may break the uniformity of the passive film, thus increasing the possibility of localized corrosion like pitting. Moreover, the corrosion is accelerated. For most EHEAs, like AlCoCrFeNi_{2.1}, the less-noble B2 (BCC) phase often has a smaller size, and its dissolution will result in its accelerated loss due to the so-called "area effect" [24].



Figure 3. (a) SEM image of AlCoCrFeNi_{2.1} and (b) SVET line scan results after immersion in 1% NaCl solution on different days. Adapted from Ref. [24].

2.2. Effect of Testing Time

Even the preferential dissolution of B2 or other less-noble phase is inevitable, there is still a question of what will happen when these less-noble phases are dissolved as corrosion proceeds. To investigate the effect of corrosion time, both short-term study with testing time of several hours and long-term study up to 30 days have been conducted on EHEAs [27]. It is generally found that time may shift the corrosion mechanism.

In the initial stage, the EHEA often spontaneously forms a passive film, although its stability may be impaired due to the inhomogeneous nature. In one study, both SS304 and AlCoCrFeNi_{2.1} EHEA were exposed to 1% NaCl [24]. During the initial period of 0–2 h, open circuit potential (OCP) values of both alloys moved to a higher value, indicating surface passivation. However, the EHEA experienced a large potential drop during the rising trend, which was mainly caused by the localized breakdown of the passive oxide layer [24]. In comparison, SS304 showed a smoother transition towards the noble potential. Even though both alloys show an increasing trend on potential with time due to the formation of the protective oxide layer, the passive film on EHEA may be less stable. Since the passive film is less noble, the dissolution of B2 phase is thermodynamically favored. Several other studies also reported the preferential dissolution of B2 or other less stable phases in the initial corrosion period [28,41].

With extended time, micro-galvanic corrosion dominates the corrosion process, yet it shifts from phase dissolution to region dissolution. During the corrosion study of AlCoCrFeNi_{2.1} in 0.5 M H₂SO₄, Wei et al. [27] found the galvanic corrosion couple changed from FCC (cathode)–BCC (anode) to lamellar (anode)–irregular (cathode). Furthermore, the main corrosion form changed from the preferential dissolution of the BCC phase to the localized corrosion of the lamella region. During the initial stage, the preferential dissolution of BCC occurs due to the huge compositional difference between BCC and FCC phases, leading to the exposure of larger amounts of irregular FCC areas. Accumulation of these new FCC phases up to 30 days eventually evolved into new micro-galvanic corrosion cell between irregular area and lamellae, within which the lamella structure was dissolved as anode [27]. The cross-sectional images at 2 d and 30 d are shown in Figure 4.



Figure 4. Cross-sectional SEM images of AlCoCrFeNi_{2.1} after immersion in 0.5 M H₂SO₄ for different periods of time: (**a**) 2 d and (**b**) 30 d [27].

In another accelerated electrochemical test, it is found that the corrosion region of EHEA shifted from single phase to dual phases with time, which is related to the evolution of passive film composition on different phases. In NaCl and H_2SO_4 solutions, $Al_{0.8}CrFeNi_{2.2}$ experiences the selective dissolution of BCC phase in the initial stage, then the corrosion of both FCC and BCC phases in the later stage [29]. SVET was employed to provide the mechanistic explanation by plotting the potential map of different phases in the EHEA [24]. The potential evolution with extended time was measured at open circuit. The potential amplitude, which is related to the potential difference between two phases, dropped from 4 μ V at 1 day to 0.5 μ V at 5 days [24]. The reduced potential difference inhibited the selective dissolution of BCC phase but promoted the dissolution of both BCC and FCC phases. XPS analyses showed that the chemical compositions of the passive films in BCC and FCC phases were changing with time, thus leading to the variation in dissolution phase [27].

2.3. Effect of Heat Treatment

Heat treatment is a commonly used method to optimize the microstructure for improved mechanical properties [43–45]. From corrosion protection aspect, heat treatment like annealing/aging is usually not expected on most alloys since it may deteriorate the corrosion performance by changing both substrate and passive film. At elevated temperatures,

most alloys are thermodynamically unstable, and the microstructure might be changed due to the facilitated diffusions of elements and defects. The growth of certain phase and/or the formation of precipitates may change the composition of the substrate, thus affecting the passive film and bringing unexpected changes in corrosion properties [46]. In EHEAs, things are more complicated. The synergistic effects of heat treatment-induced phase growth, precipitates, and other factors could all make an impact on the corrosion behavior. Both positive and negative effects of heat treatment on EHEAs' corrosion performance have been reported [47].

The dual phases in EHEA tend to spontaneously grow at elevated temperatures. Shuang et al. [31] studied the effect of annealing temperatures (600 °C, 900 °C, and 1200 °C) on the growth of dual phases and the subsequent effect on corrosion. It is found that annealing, even within 60 min, leads to the growth of lamella in FeCrNiCoNb_{0.5}. When increasing the annealing temperature from 600 to 1200 °C, the average lamellar size increases from 140 (as-cast state) to 1500 (annealing at 1200 °C for 60 min) nm. Accordingly, i_{corr} (corrosion current) increases from 0.0229 to 0.217 μ A/cm² with a larger lamella size [31]. The size effect on passive film stability is obvious. It is explained that the larger phase inhibits the diffusion of metallic ions to form a thicker passive film, thus reducing the protectiveness and suffering more from the Cl⁻ attack.

Besides phase growth, the heat treatment-associated precipitates are often not expected since these precipitates always generate passive element-depleted area and induce local inhomogeneity of the passive film [48]. Yet in EHEA, one interesting study performed by Duan et al. [41] showed that aging-induced precipitates actually improved corrosion resistance. They applied 1000 °C/3 h solution treatment and 600 °C/100 h aging treatment on AlCoCrFeNi_{2.1} EHEAs. Through electrochemical tests in 3.5% NaCl, it is found that the corrosion resistance sequence could be aging treatment > as-cast > solution treatment. Further characterization of the microstructure was conducted using HRTEM. L1₂ precipitates with 5 nm size and rich in Cr-Fe were found in FCC phase while Cr-rich BCC precipitates with a size of 30 nm were found in B2 phase. Interestingly, these precipitates actually improved the corrosion performance of the EHEA. The beneficial effects of the precipitates are due to the following aspects [41]:

- The 5 nm L1₂ precipitate is too small to affect the Cr-rich passive film in FCC;
- In B2 phase, the Cr-rich BCC precipitates increase the stability of the passive film by increasing the Al content both in the B2 phase and the passive film;
- The BCC precipitates could inhibit the pitting initiation for its Cr-rich nature.

In the future, more related studies are needed to clearly illustrate the effect of heat treatments on microstructure evolution and the following corrosion behavior.

2.4. Effect of Temperature

The service temperature may change the passive film stability and thus affect the corrosion behavior. The effect of temperature was investigated by Song et al. [28]. AlCoCrFeNi_{2.1} was exposed to 0.005 M H₂SO₄ + 0.05 M NaCl solution at a series of temperatures (5 °C, 25 °C, 40 °C, and 60 °C). Based on the potentiodynamic (PD) testing results, the increases in i_{corr} (corrosion current) and i_{pass} (passive current) were observed with increasing temperature, which were mainly contributed by accelerated electrode reactions and a higher barrier to passivation, respectively. Interestingly, E_{corr} did not change with temperature, indicating that the thermodynamic tendency of corrosion was not affected. The SEM/EDS characterization after potentiostatic polarization tests showed that increasing temperature from 5 to 60 °C promoted the corrosion mode shift from local pitting to pitting + selective dissolution of the Al/Ni-rich B2 phase [28]. It seems that increasing temperature enhances the galvanic corrosion between L1₂ (FCC) and B2 (BCC) phases.

2.5. Effect of Applied Potential

Given that metallic elements like Cr, Fe, and Al have passive regions, a strategy was devised to inhibit galvanic corrosion between Cr-O-rich passive film and Al-O-dominated

passive film using anodic oxidation. Driven by this thought, Hasannaeimi et al. [24] applied anodic overpotential on AlCoCrFeNi_{2.1} EHEA. The overpotential values as +50, +150, and +250 mV vs. OCP were chosen based on the potentiodynamic curves of AlCoCrFeNi_{2.1} EHEA in 1% NaCl. Based on the SVET area map, increasing anodic overpotential results in higher activity in B2 phase [24]. Thus, applying anodic potential will intensify the galvanic corrosion between the L1₂ and B2 phases. Furthermore, it was found that pitting on B2 phase also became more pronounced with elevated anodic potential. At 0 V over-potential, there is no pitting but the preferential dissolution of B2 phase [24]. However, when the anodic potential was higher than the breakdown potential, more corrosion pits formed in the B2 phase.

3. Specific Corrosion Behavior of EHEAs

Up to now, several EHEA systems have been developed, featuring different constituent alloying elements. The alloying element affects the corrosion by changing the microstructure and the composition of the passive film. In this section, the related corrosion studies of different series of EHEAs are summarized as follows.

3.1. AlCoCrFeNi

By far, the most fully studied AlCoCrFeNi EHEA is AlCoCrFeNi_{2.1}. Cr and Al are the most important elements from corrosion aspect, playing a cooperative effect on surface passivation. During the interaction with an aqueous environment, Cr and Al are more prone to oxidation regardless of the high contents of Ni/Fe/Co in FCC and BCC phases. Cr and Al preferentially diffuse to the surface and are oxidized, leading to the enrichment of other elements in the sublayer [41]. In a typical AlCoCrFeNi_{2.1}, Cr in FCC could be as high as 23.28%, while in BCC the value is reduced to 4.66% [27]. Table 1 summarizes the Cr content in FCC and BCC phases of AlCoCrFeNi_{2.1}. It is found that Cr content is in the range of 19–23% in FCC phase and 6–14% in BCC phase. In conventional stainless steels, it is said that 12% Cr is the critical content to form a continuous Cr_2O_3 during the corrosion process [49]. The high Cr content in FCC phase will certainly ensure the selective oxidation of Cr and the formation of a continuous surface Cr_2O_3 layer when in contact with aqueous environments.

BCC phase is depleted of Cr, and its enrichment with Al facilitates the formation of Al_2O_3 as a passive film. Al is also prone to be oxidized and forms a surface oxide layer through selective oxidation. However, the protectiveness of Al_2O_3 is weaker than that of Cr_2O_3 . Cr_2O_3 oxides are compact and protect the base metal from corrosive ions' attack, while the formed Al oxides/hydroxides as a porous surface film, from which the corrosive ions could easily penetrate and cause pitting corrosion. This is related to the lower Pilling–Bedworth ratio of Al_2O_3 (1.28) than that of Cr_2O_3 (2.07) [50]. Such feature further results in a less compact oxide layer with lower stability, as it has been demonstrated in the comparative studies between Al alloys and Cr-forming stainless steels. Even though the less protective Al_2O_3 on BCC phase will form a micro-galvanic cell with Cr_2O_3 on FCC phase, it could still be passivated and protect the substrate to a certain degree. Therefore, the overall corrosion performance of $AlCoCrFeNi_{2.1}$ is usually equal to, if not better than, the conventional stainless steels like SS304 [27].

The effect of solutions on corrosion performance of AlCoCrFeNi_{2.1} was also investigated in pH-neutral and acidified (with 0.01 mol/L NaHSO₃) 3.5% NaCl solutions [28]. In both solutions, preferential corrosion of B2 phase occurs. In 3.5% NaCl solution, the AlCoCrFeNi_{2.1} could be passivated at 5–45 °C, while in acidified 3.5% NaCl, it could hardly be passivated. The passive film shifted from metal oxides to metal hydroxides due to the high acidity. The combined attack by H⁺ and Cl⁻ reduces the stability of the passive film, leading to dissolution. And the re-passivation rate cannot compete with the destruction rate [28].

3.2. AlCrFeNi

3.2.1. AlCrFeNi_{3.1} and AlCrFe₂Ni_{2.1}

Given that the Co element in AlCoCrFeNi_{2.1} is relatively expensive and has similar properties with Fe and Ni, a cost-effective strategy spontaneously comes into mind as replacing the expensive Co with cheap Fe or Ni. Such replacement is anticipated to reduce the cost and widen the engineering application of EHEAs. Following this enlightenment, Wu et al. [15] prepared Co-free AlCrFeNi_{3.1} and AlCrFe₂Ni_{2.1} EHEAs by vacuum induction melting and compared their corrosion performance with AlCoCrFeNi_{2.1}. The prepared EHEAs also have two phases, namely, Cr-Fe-Ni-enriched FCC phase and Al-Ni-dominated BCC phase. SEM images after polarization tests in 3.5% NaCl show that all samples experienced selective dissolution of BCC (B2) phase while their FCC phases remained intact. The corrosion resistance of the three EHEAs follows this sequence: AlCrFeNi_{3.1} > AlCoCrFeNi_{2.1} > AlCrFe₂Ni_{2.1}. The highest corrosion resistance in AlCrFeNi_{3.1} may be attributed to its high volume fraction of corrosion resistant FCC phase and the low Al/Cr ratio in BCC phase [15]. The high Ni content is favored for improved corrosion resistance. The addition of Fe, on the other hand, leads to a higher Al/Cr ratio in BCC phase, which facilitates the non-protective passive film of porous Al oxides/hydroxides [15].

3.2.2. $Al_xCrFeNi_{3-x}$

It seems that Ni plays a beneficial role while Al is not a good element for improving the corrosion resistance. To test this, one research group further investigated the effect of Al content in $Al_xCrFeNi_{3-x}$ (x = 0.6, 0.8, 1.0), and confirmed that the increase of Al from 0.6 to 1.0 reduced the corrosion resistance of AlCrFeNi EHEA [35]. Selective dissolution of B2 phase in EHEA was found in the 3.5% NaCl solution. High-resolution SKPFM was performed to detect the corrosion tendency of different phases. Al-Ni-enriched B2 phase had a higher V_{CPD} (local contact potential difference) and lower WF (work function) value than FCC phase, indicating it was more susceptible to the Cl⁻ attack and following dissolution. Increased Al led to lower corrosion resistance, as indicated by the higher stable potential in the OCP test, the reduced R_p in electrochemical impedance spectroscopy (EIS) measurements, and the higher i_{corr}/i_{pass} and lower E_{corr}/E_{pit} in polarization tests. Further characterizations were performed on the surface passive film for more details. XPS revealed that the stability was reduced with increasing Al content, as the O^{2-}/OH^{-} was decreased [35]. Mott–Schottky test also showed that the concentrations of charge carriers in the passive film were in the range of 10^{21} cm⁻³ and increased with increasing Al content. Thus, the sensitivity to pitting nucleation and adsorption of Cl⁻ increased [35].

3.2.3. Al_{0.8}CrFeNi_{2.2}

In another study, the corrosion performance of $Al_{0.8}CrFeNi_{2.2}$ in different solutions, namely, 0.5 M NaCl, HCl, H₂SO₄, and Na₂SO₄, was investigated [29]. It is found that the corrosion media has a great influence on the corrosion performance of $Al_{0.8}CrFeNi_{2.2}$. The selective dissolution of the BCC phase occurred in all media, and the combination of H⁺ and Cl⁻ induced the most severe corrosion with a corrosion rate of 127 μ A/cm².

3.2.4. AlCrFe_{1.125}Ni_{1.06}

During the solidification of arc melting fabrication process, $AlCrFe_{1.125}Ni_{1.06}$ EHEA experiences spinodal decomposition and splits into dual phases. In the corrosion tests with 3.5% NaCl, the preferentially dissolution also occurred on the phases rich in Al and Ni [30]. Both post-corrosion SEM observation and DFT calculation prove that the Al and Ni in BCC phase have higher interaction with Cl⁻ and are thus more prone to localized corrosion [30].

3.3. $(CoFe_2NiV_{0.5}Mo_{0.2})_{100-x}Nb_x$

In $(CoFe_2NiV_{0.5}Mo_{0.2})_{100-x}Nb_x$ EHEA, V and Mo are added since these two elements have high melting points, and their addition is expected to further enhance the lattice distortion and improve the mechanical behaviors [51]. Results showed that

 $(CoFe_2NiV_{0.5}Mo_{0.2})_{100-x}Nb_x$ was composed of FCC + Laves phases. With increasing Nb content as x = 0, 2, 4, 6, 8, 9, 10, 12, the Laves phase share increased and the EHEA shifted from hypo-eutectic to hyper-eutectic solidification. As for corrosion performance, higher Nb content decreased the corrosion potential and increased the passive window. The corrosion current first decreased and then increased, rendering an optimal 9Nb composition with the highest corrosion resistance. It is speculated that Nb had a complex influence on corrosion by increasing the passivity ability yet initiating more corrosion pits with early nucleation sites of Laves phase.

3.4. FeCrNiCoNb

Given that the formation of alumina is not desired in the BCC phase, Shuang et al. [31] prepared an Al-free FeCrNiCoNb_{0.5} EHEA through arc melting. The as-prepared EHEA has dual phases such as Nb-lean FCC phase and Nb-rich C14 Laves phase with near-equal volume fraction. It is found that the FeCrNiCoNb_{0.5} EHEA has excellent corrosion resistance (see Table 2) and grain size increasement due to annealing will reduce the thickness of the passive film, thus intensifying corrosion [31].

Table 2. Corrosion parameters of several EHEAs derived from potentiodynamic curves in different environments.

ЕНЕА	Solution	I _{corr} (μA/cm ²)	E _{corr} (mV, vs. SCE Unless Noted)	E _{pit} (mV)	I _{pass} (μA/cm ²)	Ref.	
	3.5% NaCl	0.7314	-265	119	-	[28]	
AlCoCrFeNi _{2.1}	3.5% NaCl + 0.01 mol/L NaHSO ₃	9.006	-322	-	-		
AlCoCrFeNi _{2.1}		0.87	-325.3	224.5	14.38		
AlCrFeNi _{3.1}	3.5% NaCl	0.41	-297.5	227.8	3.10	_	
AlCrFe ₂ Ni _{2.1}		3.53	-410.2	141.2	22.05	- [15]	
	0.5 M NaCl	0.33	-335	0.203	-		
Al CrEcNi	0.5 M Na ₂ SO ₄	0.2	-337	0.873	-	-	
Al _{0.8} CIFEINI _{2.2}	0.5 M HCl	127	-389	-	-		
	$0.5 \text{ M} \text{ H}_2 \text{SO}_4$	47	-351	0.936	-		
Al _{0.6} CrFeNi _{2.4}		0.049	-204.5 (vs. Ag/AgCl)	304.8	1.058	[35]	
Al _{0.8} CrFeNi _{2.2}	3.5% NaCl	0.244	-215 (vs. Ag/AgCl)	240.7	1.184		
Al _{1.0} CrFeNi _{2.0}		0.459	-254 (vs. Ag/AgCl)	207.3	1.483		
FeNiCrAl		0.1896	-281	-	-	[30]	
Fe _{1.125} Ni _{1.06} CrAl	3.5% NaCl	0.0093	-228	-	-		
$Fe_{1.125}Ni_{1.125}CrAl$		0.0634	-223	-	-		
CoFe ₂ NiV _{0.5} Mo _{0.2}		4.2606	-252.36	-	-	- - - [51] - -	
(CoFe ₂ NiV _{0.5} Mo _{0.2}) ₉₈ Nb ₂		4.0963	-318.8	-	-		
$(CoFe_2NiV_{0.5}Mo_{0.2})_{96}Nb_4$		3.1789	-322.87	-	-		
(CoFe ₂ NiV _{0.5} Mo _{0.2}) ₉₄ Nb ₆	3.5% NaCl	3.4967	-310.18	-	-		
(CoFe ₂ NiV _{0.5} Mo _{0.2}) ₉₂ Nb ₈		3.2805	-287.15	-	-		
(CoFe ₂ NiV _{0.5} Mo _{0.2}) ₉₁ Nb ₉		4.6428	-337.46	-	-		
(CoFe ₂ NiV _{0.5} Mo _{0.2}) ₉₀ Nb ₁₀		5.0078	-294.55	-	-		
(CoFe ₂ NiV _{0.5} Mo _{0.2}) ₈₈ Nb ₁₂		7.1288	-351.21	-	-		
FeCrNiCoNb _{0.5}	1 M NaCl	0.0229	-173	993	-	[31]	
Ni _{1.5} CrCoFe _{0.5} Mo _{0.1} Nb _{0.55}		0.335	-52 (vs. SHE)	1055		_	
Ni _{1.5} CrCoFe _{0.5} Mo _{0.1} Nb _{0.68}	3.5% NaCl	0.201	-45 (vs. SHE)	1070		[52]	
Ni _{1.5} CrCoFe _{0.5} Mo _{0.1} Nb _{0.8}		0.312	-73 (vs. SHE)	1100		=	

3.5. NiCrCoFeMoNb

Wen et al. [52] prepared the Ni_{1.5}CrCoFe_{0.5}Mo_{0.1}Nbx (x = 0.55, 0.68, 0.8) EHEAs and investigated the effect of Nb content on the corrosion and tribo-corrosion. In 3.5% NaCl solution, the Ni_{1.5}CrCoFe_{0.5}Mo_{0.1}Nbx EHEA shows better corrosion performance than most HEAs and commonly used Fe- and Ni-based engineering alloys. The high corrosion resistance is mainly attributed to the formation of a compact oxide layer mainly consisted of Cr₂O₃, together with other noble oxides like Nb₂O₅ and MoO₂/MoO₃. Increasing Nb reduces the number of point defects in the passive film and increases the share of Laves phase, thus improving the resistance to both corrosion and tribo-corrosion [52].

3.6. Corrosion Summary of EHEA

Based on the statement above, the corrosion behaviors of several EHEAs are summarized by extracting corrosion parameters from the potentiodynamic curves in aqueous solutions. See Table 2.

3.7. Comparison with Conventional Alloys

Several studies try to compare the bulk corrosion behaviors between EHEA and conventional alloys, aiming to find out if EHEA could be a suitable substitute for the conventional corrosion-resistant alloys like stainless steels and Ni-based alloys.

Even though the selective dissolution of BCC phase was achieved and EHEA AlCoCrFeNi_{2.1} exhibited a lower pitting potential than SS304, one study still showed that EHEA has the same level of corrosion current as stainless steel 304 (SS304) in 1% NaCl solution during the PD test [24]. Another study compared the electrochemical behaviors of OCP, EIS, and PD, and AlCoCrFeNi_{2.1} was found to have comparable corrosion resistance as SS304 in 3.5% NaCl solution [53]. One study even found that with proper fabricating method (gas atomization was applied), AlCoCrFeNi_{2.1} showed superior corrosion resistance than SS304 in 10% HCl and 3.5% NaCl solutions [54].

Figure 5 shows a comparison of the i_{corr} and E_{corr} derived from potentiodynamic curves of EHEA and other conventional corrosion resistant alloys in NaCl solutions at room temperature. The data is collected from related publications [15,28,30,35,51,55–66]. The i_{corr} and E_{corr} are treated as indicators of corrosion resistance of materials in electrolyte solutions. Evidently, the i_{corr} of EHEA is much lower than those of steels/stainless steels/duplex stainless steels, Al-based and Ni-based alloys, and HEAs, indicating the lower general corrosion rates. The E_{corr} of most EHEA is generally higher than those of Al-based alloys, Ni alloys, and HEAs, representing the lower tendency of corrosion. In general, the corrosion resistances of EHEAs are comparable or even superior to some of the conventional corrosion-resistant alloys (stainless steels, duplex stainless steel, carbon steel, Al-based alloys, and Ni-based alloys) in Cl⁻-containing environments.



Figure 5. Comparison of i_{corr} and E_{corr} of EHEA and other engineering alloys (stainless steels, duplex stainless steels, carbon steels, Al-based alloys, and Ni-based alloys) in NaCl solutions [15,28,30,35,51,55–66].

To take the overall corrosion properties of EHEA into consideration, it could be concluded that the EHEA are corrosion resistant materials equal to or even superior to other conventional engineering alloys. The only problem associated with EHEA is the galvanic corrosion-induced localized failure, which needs further investigation. Overall, owing to the excellent mechanical properties and relatively high corrosion resistance, the future application of EHEA is very promising.

4. Research Summary and Future Directions

4.1. Research Summary

A brief overview of the corrosion behavior of EHEAs has been provided with an emphasis on the micro-galvanic corrosion and the related affecting factors. It is generally concluded that the dual-phase feature of EHEAs inevitably induces micro-galvanic corrosion in aqueous environments. Extending time may shift the corrosion mechanism from phase dissolution to region dissolution or from single phase to dual phases. Heat treatment has a complex effect as either facilitating or inhibiting corrosion, since heattreatment-induced phase growth, precipitates, other factors, and their synergistic effects have a complex impact on the corrosion behavior. Increasing temperature or applied potential in the anodic region enhances the galvanic corrosion. The corrosion performance of several EHEA systems (AlCoCrFeNi, AlCrFeNi, CoFeNiVMoNb, FeCrNiCoNb, and NiCrCoFeMoNb) was summarized from different aspects, including oxide layer, passive film stability, electrochemical parameters, degradation mechanism, environmental affecting factors, etc. Compared with other conventional engineering alloys (Fe-based alloys, Ni-based alloys, Al-based alloys, etc.), the EHEA generally shows comparable or even superior corrosion resistance in various solutions. The combined high strength/ductility and corrosion resistance implies the wide engineering application of EHEAs.

4.2. Future Directions

As an emerging new material, the ultimate goal of EHEAs is the wide application with the realization of both high mechanical strength and good corrosion resistance in a costeffective manner. While the mechanical behavior is well-recognized, the corrosion-related issues still call for further investigations. To fabricate corrosion-resistant EHEAs, more efforts are still needed for grasping the essence of alloying design, microstructure control, corrosion evaluation, and environmental factor identification. Therefore, some necessary future works are summarized from the following aspects.

4.2.1. Rational Alloy Design

The galvanic corrosion between Cr-rich FCC phase and Al-rich BCC phase is unavoidable. Such localized corrosion is especially detrimental during long-term corrosion and stress corrosion cracking in acidified/ Cl^- -containing environments. Therefore, it is hypothesized that the Al elements might be replaced by other alloying elements, such as Nb [27]. The added elements are expected to tailor the microstructure and passive film, thus inhibiting the micro-galvanic corrosion. Note that when selecting elements, thermo-calc prediction [67], high-throughput calculation [68], and other advanced tools could be the primary choices since these methods have already been proven very effective in alloy design.

4.2.2. Developing Theoretical Tools

Corrosion behavior could also be further studied by advanced theoretical tools. Up to now, one study combined DFT and first-principle calculations to investigate the Cl⁻ adsorption behaviors on different phases in EHEAs. The preferential dissolution of B2 phase is due to the higher adsorption energy and more available electrons on that phase [30]. It also manifests the possibility of theoretical calculation in deciphering the corrosion mechanisms. In future studies, more advanced theoretical tools, like machine learning [69], CALPHAD based on thermodynamics [70,71], kinetic calculation [72], and E–pH diagram [73], should be employed to calculate or predict the microstructure evolution, alloying effect, phase stability, passivation behavior, and/or other corrosion-related issues of EHEAs.

4.2.3. Explore the Effects of Processing

Several methods have been used to optimize the microstructure and improve the mechanical behavior of HEAs. Thermo-mechanical treatments (e.g., cold-rolling + annealing [74], cryo-deformation + annealing [75]) and thermal treatments (e.g., directional solidification [76]) could improve the mechanical behavior and achieve the strength–ductility trade-off to a great extent. During these processes, microstructure is often changed and optimized for better mechanical performance, yet the side effect on corrosion properties is unknown. Future studies, therefore, should figure out the relationships between processing-induced microstructure change and corrosion behavior.

4.2.4. Stress Corrosion Cracking

Stress corrosion cracking (SCC) is known as the development of cracks within alloy due to the simultaneous effects of external stress and corrosive environments [77]. The SCC crack tends to initiate from localized defects like pittings [78]. The micro-galvanic corrosion feature often results in selective dissolution of the BCC phase or formation of pitting, all of which are localized defects and are very likely to act as stress concentrators under the simultaneous effects of stress and chemical attack. It may be inferred that EHEA has very high SCC susceptibility, especially in Cl⁻-containing solutions. Further studies thus should make related SCC evaluations and ensure the safe operation of EHEA in suspicious environments.

4.2.5. Tribo-Corrosion

The interactions between engineering materials and surrounding environments consist of corrosion, stress, friction, and various other chemical and physical factors. Among them, the combination of friction and corrosion yields tribo-corrosion. Despite that many tribological studies have been conducted, the synergistic effect of both corrosion and friction as tribo-corrosion has rarely been explored in EHEA systems. Future studies should be conducted by employing the in situ tribo-corrosion measurement systems [40], namely, a real-time monitoring of the passive film properties of dual phases during abrasion.

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