

Effects of Al Content on Corrosion Behavior of High Entropy Alloys—A Review



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1 Introduction

Most of the conventional alloys are based on primary elements, and additional elements are added as per desired properties to improve the mechanical properties. With increasing alloying elements and minor elements, conventional alloys have the disadvantage of forming unstable and fragile intermetallic phases [1, 2]. Ye et al. [3] proposed a concept of a new class of material called that is called “high entropy alloys” (HEAs) about 16 years ago. High entropy alloys consist of 5 or more elements with a concentration of around 5–35% in the equimolar or nearly equimolar ratio [3, 4]. The effects such as high entropy, sluggish diffusion, lattice distortion, and cocktail are generally observed in HEAs. Out of these effects, the most significant effect is high entropy effect that is more in case of HEAs compared to conventional alloys. This high entropy will not make the formation of the intermetallic compound and favor the formation of disordered solution states [4]. HEAs possess some superior properties compare to conventional alloys such as high hardness, good elastic modulus, elastic strain, good wear resistance, fracture strength, thermoelectric property, catalytic property, and corrosion resistivity [1, 5–8]. Although the cost of HEA may be higher than typical conventional alloys because it consists of multiple elements, it is still cheaper than many superalloys and Ti alloys [4].

Generally, HEAs are solid solutions that consist of a simple face-centered and body-centered cubic structure or a mix of both [1, 4]. HEAs are applicable for special applications such as engine materials, nuclear materials, tool materials, hard-facing materials, marine structures, chemical plants, and functional coatings [9, 10]. HEAs are manufactured by many techniques such as laser cladding [2, 5], arc melting [11, 12], and powder metallurgy [13]. For more improvement in surface performance,

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cladding is important, which provides another layer on substrate materials without reforming the composition of bulk material. Laser cladding is widely used for HEAs coating, having advantages over a large heat-affected zone, poor process stability, and low deposition rate [1].

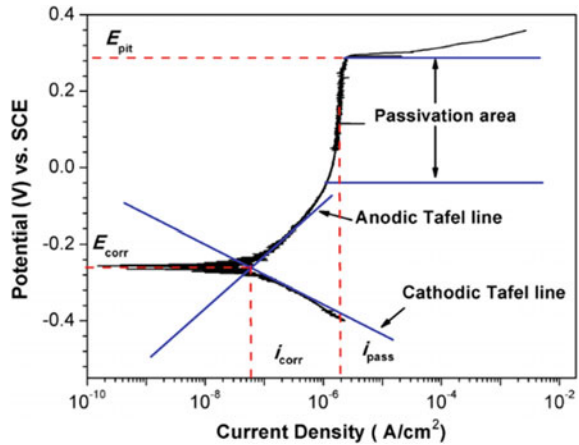
Corrosion is the gradual deterioration of material mainly because of chemical or electrochemical reaction between the material and the surrounding environment. More than three percent of GDP is affected by corrosion [13]. Corrosion is responsible for 25% of induced failure of total equipment failures in the oil and gas industry [14]. HEAs and coatings are alternative to conventional alloys and show good corrosion resistance and mechanical properties. The effect of corrosion on HEAs mainly depends on composition and its molar proportion. So, it is necessary to investigate the effect of a particular composition and molar fraction. Previous researchers already investigated the effect of various compositions and their molar fractions, such as Al [5, 6, 15–17], Ti [17], Mo [18], and Cu [19]. Al is a more preferable element in the design of HEAs as it has a low melting point temperature and also has a large atomic radius and can be easily dissolved in Fe, Co, Ni, and other elements [20]. In this paper, the corrosion behavior of HEAs coatings by varying Al content in the past decade has been summarized. The present study will help the researchers to work in this domain.

2 Corrosion Measurement Technique

Corrosion measurement is the practice of studying and acquiring the information of corrosion damage to the material. There are numerous techniques to measure corrosion behavior such as weight-loss technique, surface analysis techniques, polarization technique (Tafel polarization technique), electrical resistance technique, and non-destructive technology such as visual inspection, liquid penetrate inspection, magnetic particle testing, and radiographic inspection.

Potentiodynamic polarization is one of the standard techniques to study corrosion behavior [13] because it is faster than a weight-loss method, and it separates cathodic reactions from anodic reactions; it is also a qualitative method. The important parameters such as corrosion current density (I_{corr}), corrosion potential (E_{corr}), pitting potential (E_{pit}), and passive current density (I_{pass}) are shown in potentiodynamic curve in Fig. 1. I_{corr} is a more detrimental parameter than E_{corr} , and it is used to calculate the average corrosion rate. Corrosion potential is a thermodynamic value, and it will change quickly with different corrosive environments compare to corrosion current density [5]. Corrosion potential gives only the corrosion tendency of the solution, while the corrosion rate is directly proportional to corrosion current density [13]. The intersection of the anodic Tafel line and cathodic Tafel line gives a point and projection of this point on the X -axis and the Y -axis gives I_{corr} and E_{corr} , respectively.

Fig. 1 Potentiodynamic polarization curve in 3.5% NaCl showing parameters [13]



3 Literature Review of HEAs Showing Effect of Al on Corrosion Behavior

Corrosion is the result of interactions between metals and the environment which results in degradation and wastage of material. Metals are extracted from ores, and pure metallic form is achieved. Metals are unstable in this form and tend to go back to ore form. Hence, corrosion is considered as the reverse of metal extraction.

Li and Shi [5] carried out the research on the corrosion behavior of $\text{Al}_x\text{CrFeCoNiCu}$ HEA coatings on AA5083. Laser cladding was used to prepare $\text{Al}_x\text{CrFeCoNiCu}$ HEA coating with different molar ratios of Al (x from 0 to 1.8) on the AA5083 surface, and the polarization test was carried out in a 3.5% NaCl medium to study corrosion behavior. It has been observed that with increasing Al content, initially, free corrosion current density (I_{corr}) decreases and then increases. I_{corr} is the deciding factor that gives an idea about corrosion rate, and its lower value indicates that material is having high corrosion resistance. Figure 2 shows the polarization curve of $\text{Al}_x\text{CrFeCoNiCu}$ HEA coatings by varying Al content, and it has been observed that up to $x = 0.8$, I_{corr} decreases, and then it shows increasing trends. The value of I_{corr} for Al content up to 0.8 is on the order of 10^{-7} , and then it increases to 10^{-6} while substrate material has I_{corr} on the order of 10^{-5} , larger compared to coating samples. Passive films fail mainly by Cl^- ions, the active Cl^- ions first attack at the interface and then penetrate through the oxide films [5, 13]. In HEAs, Cu segregation to the interdendritic region causes intergranular corrosion. Increasing Al content up to 0.8 promotes uniform distribution of Cu, which improves corrosion resistance. Further increasing Al content increases AlNi phase (B2), and its corrosion resistance is poor compare to BCC1 phase, so additional increasing Al content results in decreasing corrosion resistance [5].

Lee et al. [21] synthesized work on corrosion behavior of $\text{Al}_x\text{CrFe}_{1.5}\text{MnNi}_{0.5}$ HEA in aqueous environments (NaCl and H_2SO_4) for different Al content. Increasing Al

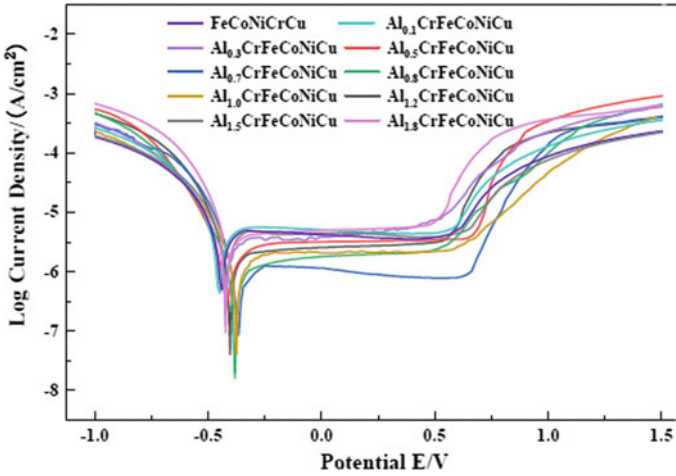


Fig. 2 Polarization curve for $\text{Al}_x\text{CrFeCoNiCu}$ HEA coatings [5]

content in acidic and chloride environment drops the corrosion resistance compared to Al-free alloys. It was observed that there is no pitting corrosion in Al-free HEA ($x = 0$) while in $\text{Al}_{0.3}\text{CrFe}_{1.5}\text{MnNi}_{0.5}$ HEA, there is a small surface attack of pits. An increasing trend of pitting corrosion was observed with increasing Al content, which indicates deep localized corrosion ($x = 0.5$). Al tends to form porous oxide films and increases localized corrosion. Corrosion current density and passive current density of $\text{Al}_x\text{CrFe}_{1.5}\text{MnNi}_{0.5}$ were measured lower in aqueous environments [21]. Sathyanarayana Raju et al. [12] successfully fabricated $\text{Al}_x\text{CoCuFeNiTi}$ by varying Al content from $x = 0$ to 1. It was observed that increasing Al content up to 0.25%, I_{corr} decreases, and then it increases. The corrosion rate will be lower in $\text{Al}_{0.25}\text{CoCuFeNiTi}$ compare to other HEA samples. Also, it was observed that as Al content increases in HEAs, the melting point of the alloy also increases and the density of the alloy decreases [12]. Ye et al. [2] carried out the research on corrosion behavior of $\text{Al}_x\text{FeCoNiCuCr}$ HEAs coatings on AISI1045 substrate material prepared by laser cladding. The corrosion test was performed in 0.05 M HCL electrolyte at room temperature. The current density for $x = 1, 1.3, 1.5, 1.8, 2$ was 29.2, 47.9, 31.4, 7.6, and 31.7, respectively. $\text{Al}_{0.3}\text{FeCoNiCuCr}$ shows the highest corrosion current density of $47.9 \mu\text{A cm}^{-2}$, which indicates a high corrosion rate where no passivation region, while $x = 1.8$ shows the lowest corrosion rate. It has been concluded that with increasing Al content, corrosion behavior exhibits little regularity in 0.05 mol/HCL electrolyte [2]. Muangtong et al. [22] studied the corrosion behavior of CoCrFeNi-X ($X = \text{Cu, Al, Sn}$) in chloride medium by adding Cu, Al, and Sn alternatively and compared with SS304 and SS316. It has been observed that CoCrFeNiSn possesses good corrosion resistance properties. Sn addition shows a wide passivation region and highest E_{corr} , which indicates good corrosion resistance. Al addition in HEAs shows weak corrosion property because it forms oxide of Al_2O_3 , weak in chloride solutions [22]. Zang et al. [23] performed a corrosion

test of $\text{Al}_x\text{CoCrFeNiTi}_{0.5}$ HEAs by varying Al content in aqueous solution. The aqueous solution was of 0.5 M H_2SO_4 at room temperature. As Al content increases, E_{corr} shows an increasing trend, and I_{corr} shows a decreasing trend, which concludes that pitting corrosion resistance increases significantly. $\text{Al}_{1.0}\text{CoCrFeNiTi}_{0.5}$ exhibits better corrosion resistance compared to other HEA samples. This trend was observed because BCC phase proportion increases as Al content increases and BCC plays better corrosion resistance [23].

Liu et al. [15] studied about corrosion of $\text{Al}_x\text{CoCrCuFeNi}$ in acidic, alkaline, and saline solutions, and the corrosive medium were HCL, NaOH, and NaCl, respectively. Figure 3 is showing polarization curve using different mediums for every attempt to study corrosion behavior. It was observed that free corrosion potential and free corrosion current values -0.378 V and 6.231×10^{-5} A cm^{-2} , respectively. From Fig. 3a, it is concluded that $\text{Al}_2\text{CoCrCuFeNi}$ corrodes faster in an acidic medium than in the alkali environment [15]. From Fig. 3b, it is observed that as Al content increases from 0.5 to 2.0, corrosion potential decreases from -0.230 to -0.378 V while corrosion current density increases from 5.237×10^{-7} A cm^{-2} to 6.231×10^{-5} . The corrosion test shows almost the same trend for rising and falling in E_{corr} and I_{corr} density in an alkali environment, as shown in Fig. 3c. As shown in Fig. 3d, both E_{corr} and I_{corr} decrease, and passivation film growth was observed with increasing

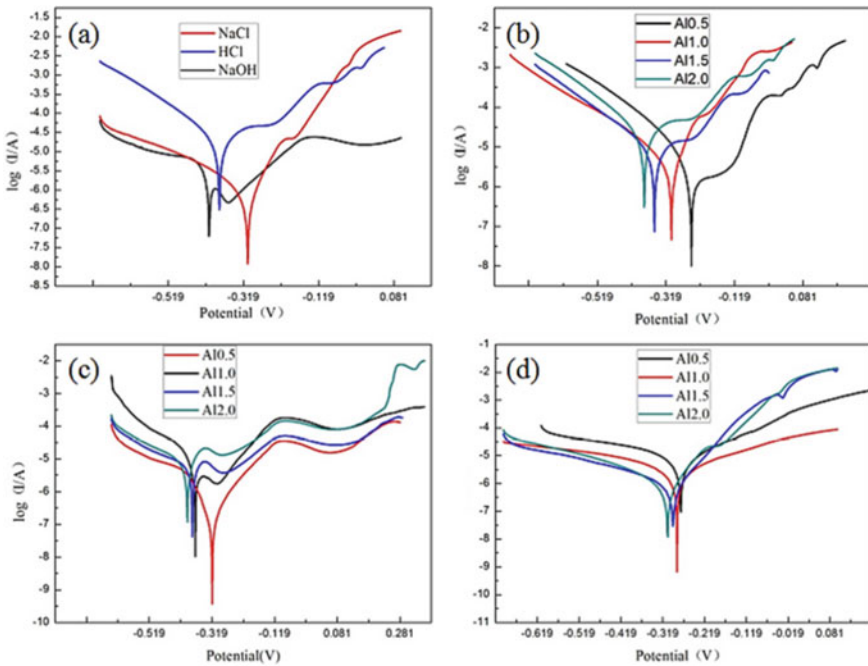


Fig. 3 a $\text{Al}_2\text{CoCrCuFeNi}$ HEA in various solutions; b $\text{Al}_x\text{CoCrCuFeNi}$ HEAs in (HCL + NaCl) solution; c $\text{Al}_x\text{CoCrCuFeNi}$ HEAs in (NaOH + NaCl) solution; d $\text{Al}_x\text{CoCrCuFeNi}$ in NaCl solution of 3.5 wt% [15]

Al content. Refinement of grain, dislocation, and increase grain boundary helps for the growth of the initial nucleation position in aspect to passivation film [15].

Bachani et al. [6] successfully deposited coatings of VNbMoTaWAl with different Al molar fractions on 304 SS and studied corrosion behavior in 0.5 M H₂SO₄. As increasing Al content, corrosion resistance of coatings can be improved significantly. The sample made of 2.37% Al contained VNbMoTaWAl coating was observed polarization resistance of 768,754 Ω cm⁻² that is highest, and a good passivation range was also observed [6]. Qiu et al. [17] studied corrosion property of Al_xCoCrFeNi in 0.6 M NaCl at 25 °C by potentiodynamic polarization test ($x = 0.3, 0.6, 0.9$). Passive window ($E_{\text{corr}} - E_{\text{pit}}$) was seen decreasing with increasing Al content because of the lower concentration of Cr in HEAs as Al increases. However unexpectedly, Al_{0.6}CoCrFeNi and Al_{0.9}CoCrFeNi show more E_{corr} and low I_{corr} which means better corrosion resistance than Al_{0.3}CoCrFeNi and Al-free alloys [17]. Raza et al. [24] successfully fabricated Al_xCrFeMoV HEAs by powder metallurgy, and samples were formed by varying Al content ($x = 0, 0.2, 0.6$ and 1.0). It has been observed that with increasing Al content by 0, 0.2, 0.6, and 1. E_{corr} values were observed $-397, -410, -460,$ and -307 mV_{SCE}, respectively. Interestingly, Al_{1.0}CrFeMoV was observed with the highest E_{corr} and lowest I_{corr} values. There is inconsistency in an observed trend due to volume fraction variation of the BCC2 phase [24]. Shi et al. [16] studied the corrosion behavior of Al_xCoCrFeNi in two conditions, namely forged and equilibrated, and observed that as fraction of Al content increases, E_{corr} decreases and I_{corr} increases. Further, increasing Al content also decreases critical pitting potential (E_p) and increases passivation current density (I_{pass}) indicates that localized corrosion rate is less in Al-free HEAs. For localized corrosion, E_p is a determining factor to measure corrosion behavior [16].

4 Conclusions

This paper reviews the effect of varying Al content in corrosion behavior of different types of HEAs and coatings of HEAs during the past decade. As volume fraction of the Al-rich phase increases in HEAs which results in decreasing volume fraction of other contents such as Cr and Cu. BCC phase is prone to attack by Cl⁻ ions in Cr depleted phase and results in decreasing corrosion resistance, while in HEAs containing Cu, corrosion resistance increases up to some level with increasing Al content because of uniform distribution of Cu in dendrite and interdendritic region but more addition of Al causes a change in microstructure and corrosion resistance decrease. From past research analysis, there is no clear trend that can be predicted for corrosion behavior as it depends on many factors such as elements of HEAs, electrolyte medium, and volume fraction of content although HEAs show better corrosion resistance and mechanical properties compared to conventional alloys. The coating of HEAs over conventional alloys or utilization of pure HEAs is advisable for better corrosion resistance property applications.

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