

A Review on Corrosion Resistance Properties and Behaviour of High Entropy Alloys

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Abstract: *The urgent need of corrosion resistant materials comes into existence to prevent most of the gross domestic products which gets destroyed by corrosion. Traditional high entropy alloys are composition of atleast 5 major metal elements as not similar to basic conventional alloys having one or two major elements. A large varied microstructure and properties can be seen in HEAs. Random arrangements of several elements forming exceptional solid solutions can be used for corrosion resistant properties due to locally disordered chemical environment. This review consists of corrosion resistant HEAs study in various environment for different HEA coatings. Various methods are analysed and discussed on alloying elements, the environmental effect and process adopted. Moreover, the possible future work in this regard has been suggested.*

Keywords: *high-entropy alloy, coating, aqueous environment, corrosion resistance*

1. Introduction:

The estimated cost of corrosion has increased to \$1 trillion (2013) from \$276 billion (1998) in the United States (U.S.) [1,2]. Metallic materials corrosion of metals and alloys is an electrochemical interaction among them and their working environment which is unfavorable for materials to function which becomes necessity to prevent. The corrosion behavior study and mechanism of degradation of metals and alloys should be a major concern for developing corrosion resistant materials for cost effective and benefits. Many of the corrosion resistant materials commonly used in industry includes cobalt-chromium alloys, stainless steel, etc. The fundamental mechanism of corrosion is to form a passive film on the surface which shields the metals and alloys beneath and protects from further corrosion. Microstructure plays an important role along with composition in the corrosion behavior of metallic materials [3]. This can be witnessed when corrosion resistance in stainless steel gets worsen due to presence of carbides at grain boundaries which have a tendency to form a Cr-depleted zones. Further this can be reduced by different heat treatment methods [4]. Hence, apart from process parameters such as different heat treatment and various metallurgical factors plays an important role in studying and developing corrosion-resistant metals or alloys.

Lately, a new development in advanced structural materials have been proposed and developed so-called High-Entropy Alloys (HEAs) or Multi-Principal-Element Alloys (MPEAs) [5-17]. Where conventional alloys have one or major principal elements HEAs generally comprise of five or more elements in equiatomic or near equiatomic ratios forming disordered solid solution phases. Face-centered-cubic (FCC) and/or body-centered-cubic (BCC) phases are more likely to be formed. As compared to conventional alloys better corrosion resistance can be observed in single-phase and multi-phase HEAs. Alike stainless-steel Al, Mo, Cr, etc are some of the passivating elements which when present in HEAs forms a passive layer. Impurities and inclusions are sites for corrosion initiation which can be avoided in HEAs [18]. HEAs have exceptional microstructural stability, good mechanical properties and admirable corrosion resistant since they form single

phase solid solution exhibiting homogenous chemical compositions [19, 20]. These exceptional properties lead HEAs to various practical applications of corrosion resistant. Many investigations have been reported on corrosion behavior of HEAs in different environments which have more superior corrosion resistance than conventional alloys like stainless steel (SS) [21].

2. Corrosion Resistance of HEA Coatings

Recent investigations have been done on HEA coatings through different methods obtaining varied thickness for diverse microstructure, properties and applications. Some of the obtained processes are magnetron sputtering, chemical vapor deposition, electro-spark deposition, laser cladding, electrodeposition. Many HEA coatings discovered reasonable thermal stability, homogeneous microstructure, good wear and corrosion resistance properties. This review discusses corrosion resistance of different HEA coatings in various environments.

2.1. Coating by Laser Cladding

Coatings through laser cladding leads to well bonded, homogeneous and dense deposition which resulting in electrical and thermal effect on the substrate. The thickness obtained by laser cladding reaches range of millimeter which helps in rapid heating and cooling, low dilution of the base material [22]. Mainly processing parameters and alloying methods effects the properties and corrosion resistance of the coatings. Ye et al. successfully coated $Al_xCoCrCuFeNi$ HEA [23] on AISI 1045 steel substrate (0.43–0.50 wt % C, 0.60–0.90 wt % Mn) through laser cladding route and studied corrosion property. FCC and BCC structures were observed and the microstructure showed dendrites and interdendrites similar to cast sample. Though, as compared to cast HEA, segregation of Cu was less observed in interdendrite region [23]. Distribution of elements homogeneously improvised corrosion resistance property. 0.05 mol/L HCl [23] was used to study corrosion on as coated $Al_xCoCrCuFeNi$ and bare 314 L stainless steel. Better corrosion resistance was observed in as coated sample. Q235 carbon steel was used as substrate to study corrosion behavior of $Al_2CoCrCuFeNiTi_x$ and $Al_2CoCrCuFeTiNi_x$ coatings. The effect of Ti and Ni was demonstrated by Qiu et al. [24,25]. The adhesive property of coatings and substrate was found to be good. FCC + BCC phases was observed having equiaxed grains and columnar crystals. Fine microstructure with reduced elemental segregation credited to high entropy effect and rapid cooling which reduced the corrosion effect triggered by galvanic cell formation. Hence both the coatings ($Al_2CoCrCuFeNiTi_x$ and $Al_2CoCrCuFeTiNi_x$ coatings) reported better corrosion resistance as current density reduced from 2.4×10^{-1} to 2.7×10^{-3} as compared to Q235 steel. Corrosion behavior for $Al_2CrFeCoCuNiTi_x$ HEA coatings studied in 0.5 M HNO_3 solutions enhanced the corrosion resistance as Ti content increased. [24]. Also, corrosion resistance in the 0.6 M NaCl [25] first increases and then decrease as Ni content increased.

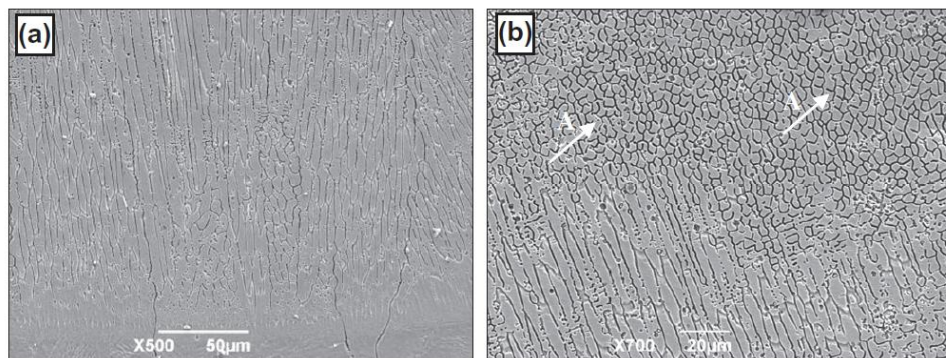


Fig. 1: Microstructure of the cross-sectional FeCoNiCrCu coating without Si, Mn and Mo additions: (a) at the interface region and (b) at the central region. [22]

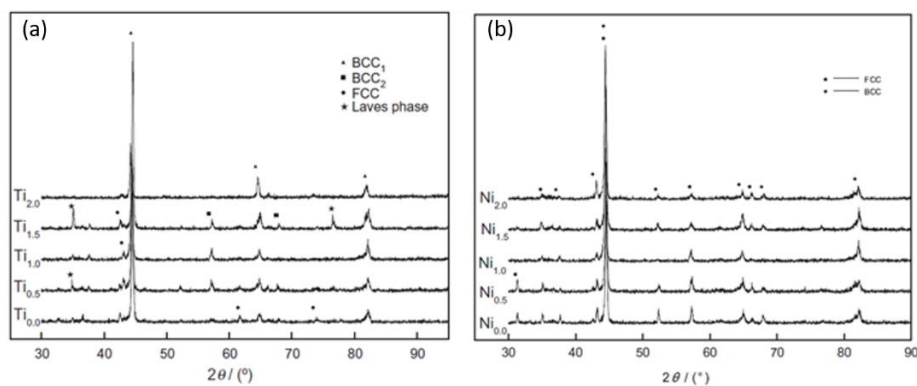


Fig. 2: (a) XRD diffraction pattern of $\text{Al}_2\text{CrFeNiCoCuTi}_x$ high-entropy alloy [24]. (b) XRD diffraction pattern of $\text{Al}_2\text{CrFeCoCuTiNi}_x$ high-entropy alloys [25].

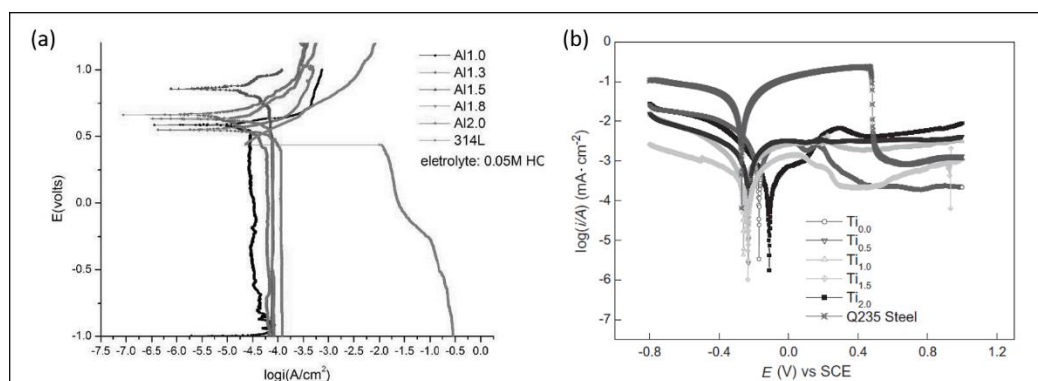


Fig. 3: (a) Tafel polarization (E - $\log i$) plots of $\text{Al}_x\text{FeCoNiCuCr}$ cladding coating and 314L stainless steel [23], (b) Potentiodynamic polarization curves for $\text{Al}_2\text{CrFeCoCuNiTi}_x$ high-entropy alloy coatings and Q235 steel in 0.5 mol/L HNO_3 solution [24].

The effect of Si (1.2 mol %), Mn (1.2 mol %), and Mo (1.2 mol %) addition was studied on Q235 steel CoCrCuFeNi HEA coating clad [22]. Poor adhesive property and non-homogeneous coating was demonstrated with no addition of Si, Mn, and Mo. Less segregation of components were witnessed with FCC solid solution. Addition of Si, Mn, and Mo lead to dendritic formation and improved coating quality as component segregation improved. As compared to Ni based superalloys (NiCrSiB), CoCrCuFeNi HEA coating have corrosion resistance when exposed to 5 vol % H_2SO_4 solutions.

2.2. Coating by Magnetron Sputtering

Magnetron sputtering process when used for HEA coatings comprised simple structures with homogeneous nanoparticles. This process results in smooth and dense AlCoCuFeNiV HEA coating [26]. The thin film synthesis may possibly be used in corrosive medium environments, like marine and petrochemical industry for wear resistant properties. The coating revealed FCC solid solution phase. With increase in deposition time, size of nanoparticle and thickness of coating film (from 0.275 μm to 2.688 μm) increased. Young's modulus of coating up to 189 GPa was obtained. The coatings obtained exhibited better corrosion resistance both in acid and salt corrosion media than 201 stainless steel since FCC structure did not reveal any elemental segregation further which can act as anti-corrosive protective materials. AlCoCrCuFeMn Coatings through magnetron sputtering also revealed Nano grains with homogeneous distribution and FCC structure likewise AlCoCuFeNiV HEA coating which had improved corrosion resistance as compared to 201 stainless steels [27]. Wide investigation is needed for HEA coatings through this route. Due to homogenization effect and improved corrosion resistance future studies for this method is attention seeking.

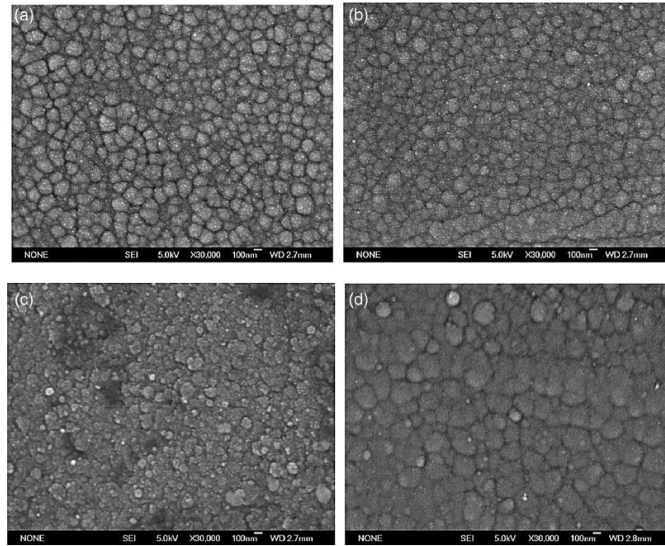


Fig. 4: FESEM surface morphology of the coatings at different time under 150 W plasma power. a.10 minutes, b. 20 minutes, c. 40 minutes and d 60 minutes [26]

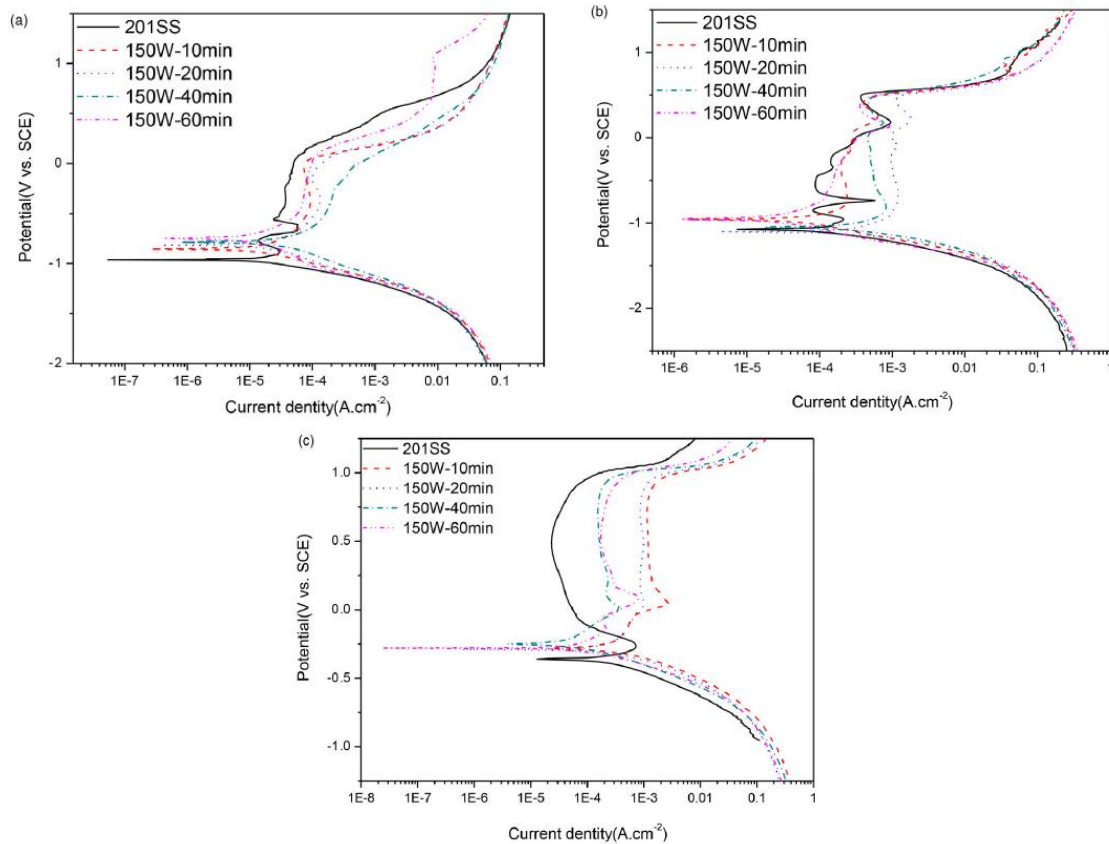


Fig. 5: The potentiodynamic polarization curves of the coatings in different corrosion mediums. a 3.5 NaCl, b 5% NaOH and c 10% H₂SO₄ [26].

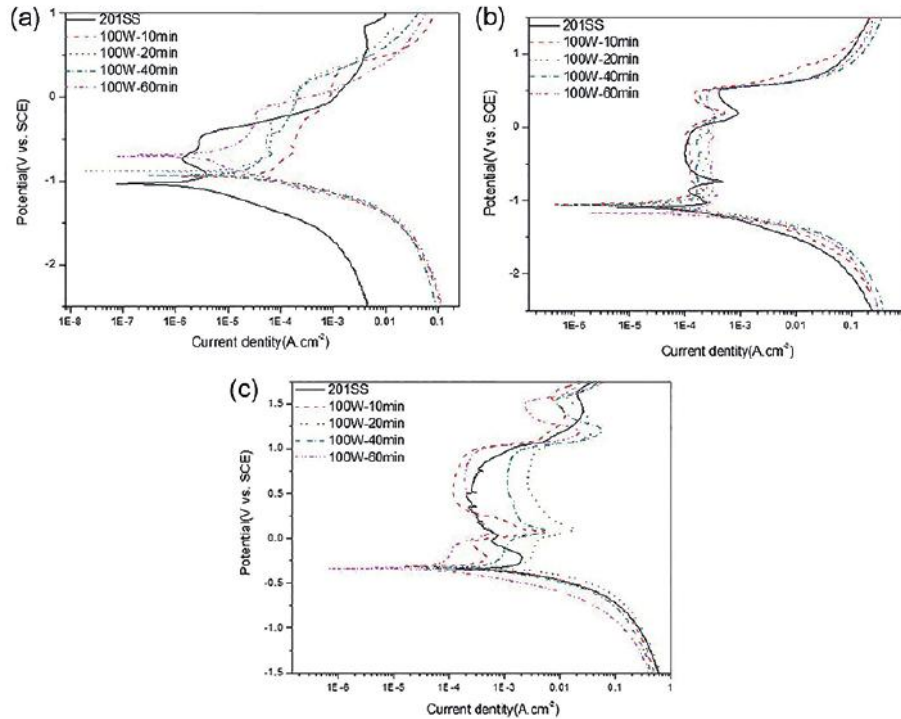


Fig. 6: The potentiodynamic polarization curves of the coatings in different corrosion mediums. (a) 3.5% NaCl, (b) 5% NaOH, (c) 10% H₂SO₄. [27]

M. Braic et al. [28] prepared (CuSiTiYZr)C coatings by co-sputtering by using pure Cu, Si, Ti, Y and Zr targets in an Ar + CH₄ atmosphere, at different CH₄/(CH₄ + Ar) flow rate ratios (0.25; 0.35; 0.50). 3.5% NaCl solution was used to investigate corrosion resistance. (TiZr)C reference coatings although having similar carbon content exhibited poor corrosion behavior than (CuSiTiYZr)C coatings.

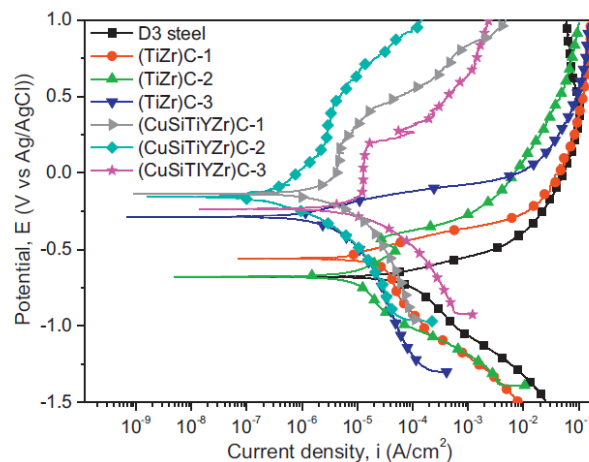


Fig. 7: Potentiodynamic curves of the investigated samples in 3.5% NaCl solution. [28]

2.3. Coatings by Electrodeposition

Corrosion properties gets affected by the elemental composition and high entropy alloy systems microstructure. Polarization curve is used for the measurement of corrosion behavior and properties of materials. The decrease in corrosion rate in potentiodynamic polarization curves is demonstrated by the shift towards lower corrosion current densities [29]. Corrosion resistance have been reported for coatings of high

entropy alloys through electrodeposition method. Authors studied high entropy alloy coatings and demonstrated corrosion potential (E_{corr}) of various compositions. The corrosion was carried out in neutral 3.5 wt.% NaCl solution. MnCrFeCoNi coating (-0.845 V vs Ag/AgCl) was found to be more noble than CrFeCoNiCu coating (-0.881 V vs Ag/AgCl). AlCrFeCoNiCu coating (-0.686 V vs Ag/AgCl) being the noble among reported composition. MnCrFeCoNi ($43.44 \mu\text{A}/\text{cm}^2$) had higher corrosion current density (i_{corr}) than that of AlCrFeCoNiCu ($24.66 \mu\text{A}/\text{cm}^2$). The polarization curves for all electrodeposited coated samples had no passive or trans-passive region pertaining to which there was no pitting corrosion in chloride environment as active dissolution of metals took place within applied potential range.

It is important to note that all the polarization curves (Figure 8) show no passive or trans-passive region, which implies that only active dissolution of metals occurred in the applied potential range and that there was no pitting corrosion in the chloride ion environment for all the electrodeposited high entropy alloy presented.

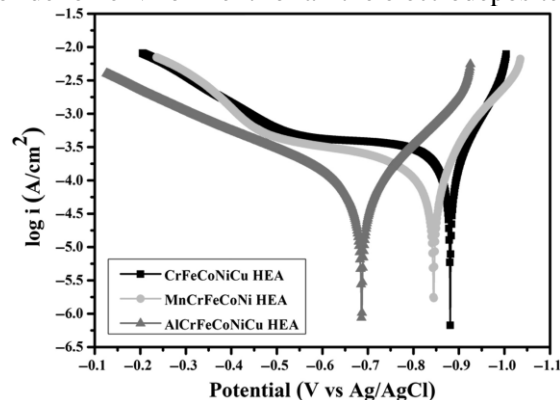


Fig. 8: The potentiodynamic polarization curves of electrodeposited high entropy alloys (HEA) system.[29]

3. Suggested Future Work

Since many publications have focused on HEAs exposed to different environment pertaining to aqueous corrosion several more environmental factors should be included further which could be focus on leading edge research area. The effect of residual stresses caused by hot forging and cold working which can cause stress corrosion cracking (SCC) [30] can be further investigated. Addition of Aluminum ($\text{Al}_x\text{CoCrFeNi}$ systems) can positively influence corrosion resistance since it yields high strength and have good corrosion resistance when added in HEAs. Welding leads to chemical composition and grain size changes due to uncontrolled melting and re-solidification in heat-affected zone (HAZ) region which could be further investigated. Structural metals for high performance and characterization of HEAs in aqueous electrolytes with an actual life-prediction model can be examined for Corrosion fatigue behavior [31]. Corrosion behavior can also be explored in heat treated and as cast conditions for single phase HEAs.

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