Microstructure, Corrosion, and Mechanical Properties of High-Entropy Alloys

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Abstract

High entropy alloys (HEAs) concept was based on the idea that high mixing entropy can promote formation of stable single-phase microstructures and it is a new type of alloys composed of five or more main alloying elements, each making up between 5 at% and 35 at% of the total composition. HEAs have been shown promising characteristics of superior corrosion resistance, and have a huge possible compositional space, which is largely unexplored. This overall survey assays the state of the HEA mechanical properties.. There are many literature surveys that dealt with HEAs, however, studies of the microstructure and mechanical properties of these alloys are relatively few. This review provide and discuss the effect of microstructure , corrosion , and mechanical properties of HEAs, especially about the electrodeposition of these alloys.

Key words: **High Entropy Alloy, Electro deposition, Corrosion, Mechanical Properties**

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1-Introduction

High-entropy alloys contain a several basic elements added in equal or nearly equal molar ratios that have tendency to produce single phases. In the previous period, the field of HEAs metallurgy have attracted wide attention despite being a new study. The structure of the families (HEAs) havehexagonal close packed, body centered cubic, and face centered cubic. According to an innovative material development approach, the HEAs denote a new metallic materials category consisting of five or more metal components that do not have a major element, unlike traditional alloys [1]. The HEAs greatestamazing feature is their excellentmechanical properties, and their capability to simply achieve a stabilityamong strength and toughness.

One of the common methods for preparing high-entropy alloys is the melt casting method, and it is commonlypresentedvia physical techniques. In addition, the coating of these alloys can be produced through different deposition wayslike laser cladding[2][3][4]. Electrodeposition is one of the simplest methods used in the formation of high entropy alloys to produce thin films deposited on complex engineering substrates. This method is characterized by its low cost and does not require complicated equipment and is used at low temperatures and available raw materials as well as low energy consumption. In addition to what was mentioned, the coating produced by electrodeposition can be easily controlled by controlling the deposition conditions and this allows the production of coating with thickness and good properties[5].

2. Electrodeposition of High Entropy Alloy

Electrodeposition of most common metallic alloys, over the years, are from sulphate, chloride, fluorborate, sulphamate, or non-aqueous baths. From the economic perspective, sulphate and chloride baths are the best choices for the electrodeposition process. Recently, electrodeposition of high entropy alloy coatings from chloride bath containing different additives have been reported by the authors .

Soarea et al studied the electrochemical deposition of Al-Cr-Fe-Mn-Ni and Al-Cr-Cu-Fe-Mn-Ni HEA thin-films were carried out at 298 K. The coating of high entropy alloys was studied by depositing them on copper samples in an electrolyte containing the chlorides of the constituent elements of HEA. The researcher used a platinum electrode as an anode with a voltage between -1.5 and 2.7 for a different period of time (30, 60 and 90 minutes). Then the formed high-entropy alloy film was thermally treated by annealing in an inert atmosphere for two hours at a temperature of 473-873 K[6].

Through the results, the researcher concluded that changing the parameters of the electric deposition makes it possible to control the surface morphology, and he found that the microstructure consists of spherical, and clusters with different particle sizes between (500nm-4µm). On the other hand, the high entropy alloys AlCrFeMnNi and AlCrCuFeMnNi are amorphous when detected by XRD. Film adhesion provided higher values for AlCrCuFeMnNi alloy as compared to the other alloys[6].

Aliyu and Srivastavaprepared the high enetropy alloys such as (MnCrFeCoNi , AlCrFeCoNiCu, and AlFeCoNiCu) with addition different amounts of graphene oxide by electrodeposition coating and studied the microstructure and corrosion behavior relationship in electro-deposited. The HEA and HEA-GO resistance of corrosion determinedin 3.5%of sodium chlorides solution shown that addition of GO leads toraisethe coating corrosion resistance. The microstructure-characterizations performed byTEMtest revealed that addition of graphene.The segregation resulting from galvanic coupling leads to an attack of local corrosion and is eliminated by homogenization, whether in structure or composition, which increases the corrosion resistance of the composite coating of HEAs with graphene[7][8][9].Also, the preparing of thin films ofCo-Cr-Fe-Mn-Ni-HEAsvia the pulse electro-deposition way by [10] in an solutionaccording to an N,N-dimethylformamide—CH3CN organic system containing chlorides cations of elements that constituent the HEAs at 2500 and 5000 Hz frequencies in addition to50% and 60%duty cycles [10].

3-Microstructure of HEAs

HEAs with microstructures contains a multicomponent solid solution have the potential for wide-scale engineeringuses as a result of their exceptionalfunctional and mechanical properties[11] which isan alloys of solid solution containing five maincomponents or more where added as equal or near-equal molar ratio [12].

The HEAs case appears as an exception to the rules of Hume-Rothery.In alloying systems, Hume Rothry generalized a set of rules for substitutive solid solutions, one of those rules being that the solvent and the solute have identical crystal structure, similar valence state, the same electrical potential, and the difference in atomic size between them is less than 15%. [13]

HECoCrCuFeNi alloy was a Face center cubic which consist of Cu and Ni are FCC metals but a Cr is a BCC metal. Fe and Co suffers to allotropic change from BCC-FCC-to BCC and FCC to HCP respectively. Moreover, Chrome has much lesser electro-negativity as the other elements rest in the alloy too [12].

Microstructure and mechanical properties have been evaluated for various HEA systems. Recently, Tong et al. studied the microstructure-characterizations of Al*x*-Co-Cr-Cu-Fe-Ni HEA-system with multi-principal components. A bcc single structure was get for Al-contents greaterof*x*-2.8. The influence of high entropy and sluggish diffusion improve the solid solution phases creationand submicron structure with multi-principal components rather than intermetallic-compounds[14].Lin and Tsai investigate the microstructure, hardness, and corrosion properties of as-castAl0.5CoCrFeNi alloy as well as Al0.5CoCrFeNi alloys aged at temperatures of 350C, 500C, 650C, 800 C, and 950C for 24 h.[15].

Aliyu, and Srivastava studied the corrosion and microstructure properties of Mn-Cr-Fe-Co-Ni, AlFeCoNiCu, and AlCrFeCoNiCu, HEA-GO composite-coatings. The TEM results of the microstructure showed that the homogeneity in the microstructure or in the structure when graphene was added led to an increase in the corrosion resistance of the alloy by removing the local corrosion attack caused by galvanic coupling. The addition of graphene to the high entropy alloys formed granular particles and tended to be softer with increasing graphene percentage. As graphene led to the formation of a mixture of BCC and FCC phases, and by increasing it, the percentage of FCC phase formation increased[7][9][16].

4-Mechanical properties of HEA

Studies of HEAs mechanical properties cover (hardness, elastic modulus, yield strength, ultimate strength, elongation, fatigue, and creep) compared with traditional alloys, these alloys have better performance. In addition, the Alx-Co-Cr-Cu-Fe-Ni system is the first widely studied alloy. [14][17]. The system hardness increases as X increased whichimputed to the lattice distortion increment since Al is the largest atom between the alloy elements[18][19].

The HE alloy of CrCoNi-based series have unique physical and mechanical properties where the toughness of fracture was superior of Cantor alloy that large than200 MPa and the tensile strength was 1GPa (fig.1) as reported by Gludovatzet al, also, this alloywas radiation damage resistant[20][21].The Cantor alloy unique toughness is attributed to 100% of the ductile-failure due to the association of micro-cavities and this was concluded by Gludovatz et al. [22].

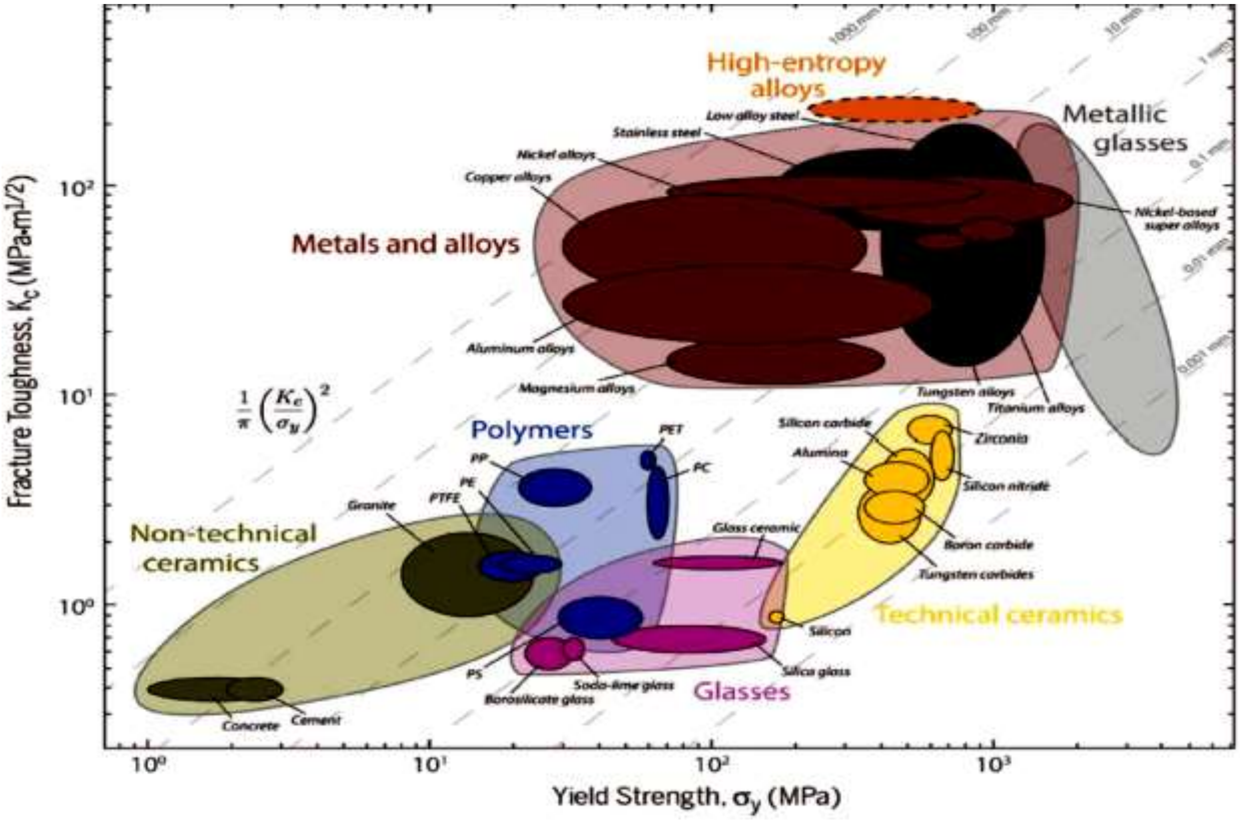

Fig. 1. fracture toughness *versus* yield strength plot of the structural materials

The HEAs Vickers hardness is dependupon the structureof crystal toughly, so it mayvariety from 100 HV[17] to 1200 HV [12]for the FCCto the BCC-HEAs respectively. The FeCoNiCrMn HEA has been establish to showductility,good stability thermodynamically[24], and exceptional toughness of fracture[20]. High-entropy alloy (FeCoNiCrMn) tensile properties investigated by Otto et al. this alloy of fine grain size has ultimate and yield strengths equal to 630 and 450 MPa respectively and 60% elongation but the the ultimate, yelid strength, and elongation were equal to 450, 125 MPa , and 80% respectively.

The first researcher to study the HEAsfatigue behavior in 2012 is Hemphill et al for annealed Al0.5CoCrCuFeNi alloy, where the researcher found that the fatigue behavior is much better than it is in traditional alloys (titanium alloys, steel, etc.) where it ranges from 540 to 950 MPa and the potential The use of these alloys in applications where fatigue is an influencing factor, when the surface is free of defects[19].

5-Corrosion Properties of HEA

Corrosion is defined as a chemical or electrochemical reaction between materials and the surrounding environment, which affects the work of those materials and increases their failure[25].Lately, the HEAs corrosion behaviorin aqueous-solutions has been stated. **Shih et al.,**discovered that resistances of corrosion of HEAs (AlxCrFe1.5MnNi0.5 (x=0, 0.3, 0.5 at.%)) in solutions of H_2SO_4 and NaCl improveswhendecreases the Al-concentration from (0 to 0.5 at.%)[26].

Rodriguez et al., , studied the Co-Cr-Fe-Mn-Ni HEAs corrosion behavior in NaCl+CO_2 solution showing that the Chrome-content effects an essentialcharacter on the HEAs corrosion rate. In addition, this alloy studied in NaCl solution by[27] and it was exposed that the segregation of elementsdisplayshurtful influence on the resistance of corrosion of the HE-Alloy coating[28].

Luo et al compared the low carbon stainless steel 304 and the high entropy alloy

CoCrFeMnNi in terms of corrosion behavior in sulfuric acid solution. The results showed that specectin has good corrosion resistance by forming protective films, but the clear difference is that the high entropy alloy did not suffer from selective dissolution of metal elements during loading. We conclude from this that the alloys are similar in the corrosion mechanism.[22].

In addition to the chemical inertness, the impermeability of graphene to the corrosion-forming media causes corrosion. Therefore, Aliyu et al. added graphene to the coating of high-entropy alloys and to show its effect on corrosion resistance. The researchers found that graphene increases corrosion resistance and the microstructure becomes granular with finer texture.The results showed that the corrosion voltage potential for the coating of high-entropy alloys with graphene tends to the noble values compared to coatings of high-entropy alloys without graphene, and this indicates an increase in the corrosion resistance due to a decrease in the dissolution of the anode due to the addition of grapheme as shown in Fig.2.[16]

The corrosion behavior of chloride-containing solutions of high-entropy alloy coatings (AlCrFeCoNiCu) was studied by electrodeposition after adding graphene. The researchers found through this study the extent of the effect of graphene on the corrosion behavior, as the corrosion resistance increases per the rise in the graphene content by converting the value of Ecorr to a noble area and decreasing the value of icorr. The reason for this is due to the homogeneity in the microstructure after the addition of GO[7].

Based on the abovesearch, the behavior of corrosion has a very related to the inert films properties. For example, the Cu addition influenced on the HEAs corrosion behavior, Hsu et al. studied the FeCoNiCrCux alloy behavior of the corrosion in 3.5 % of sodium chloride solution [29]. After the 30 day of immersion test, the appearance of the surface of the as cast Fe-Co-Ni-Cr-Cux discovered that the maincorrosion forms were pitting and localized. The In high entropy alloys (FeCoNiCrCu0.5 and FeCoNiCrCu) localized corrosion appears due to the separation of copper along the interdendrites.

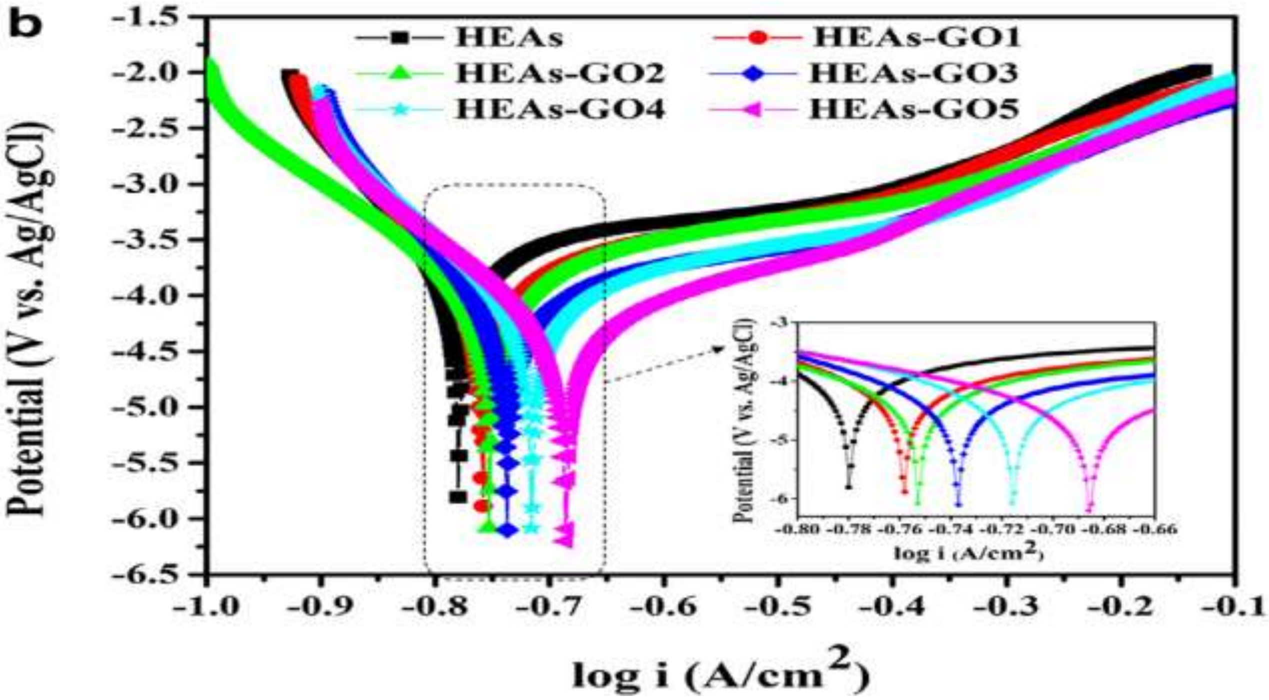

Fig 2 : The Tafel curves in the potential range of − 0.80 to − 0.66 V.

Because of the force of binding was weaker with other components for example iron, cobalt, nickel, and chrome, copper be apt to separate as clusters, making Cu rich inter-dendrites and grain-boundaries through the solidification period [30]**.** Consequently, the copper rich, Cr consumed inter-dendrites act as the anode together with the cathodic Cu-consumed, Cr rich dendrites, creating the corrosion of the galvanic at the inter-dendrites . This leads to the narrowing of the inert region by increasing the copper content. As a result, the researcher concluded that increasing the copper content reduces corrosion resistance[29].

6- Conclusion

Recently, HEAs have fascinatedraisingconsiderationsfor their exceptional compositions, microstructures, and adjustable properties. From this review, we conclude that:

1. The chemical composition and surface morphology of the prepared HE alloys can be controlled through the variation of the deposition potential.
2. Homogeneous microstructure which reduced galvanic coupling and enhanced the corrosion resistance of the HEA-GO composite coatings.
3. Single-phase alloys have also been stated to be more strong to radiation damage, as compared to the pure elements, as a result ofimportingreduction in the dislocations mobility.
4. The equi-atomic HEAsdisplay good ability of creating passive layer, but no apparent selective dissolution of metalliccomponentshappenedthrough the surface passivation.

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