



# HIGH ENTROPY ALLOYS PROPERTIES AND ITS APPLICATIONS – AN OVERVIEW

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High entropy alloys are more corrosion resistance than 316L stainless steel HEA are used as implantation material Because its unique properties and better corrosion resistances behaviors. The improved corrosion behavior could be attributed to the different chemical composition as well as the formation of a unique high entropy atomic structure with a maximum degree of disorder. It is also possible to achieve high-hardness and high-abrasion performance at high temperature, microstructure and properties of several HEA. High entropy alloys are prepared by various methods such as powder metallurgy laser cladding etc, are discussed. The corrosion resistance of HEAs and its applications also discussed.

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## Methods of preparation of HEA's

High entropy alloys are made by several methods. They can be prepared in vacuum arc induction melting furnace,<sup>1</sup> equivalent thermal entropy method,<sup>4</sup> powder metallurgy method,<sup>5</sup> and simple casting method.<sup>15</sup>

## Properties of High Entropy Alloys

High entropy alloys have unique properties and applications. Ca<sub>20</sub>Mg<sub>20</sub>Zn<sub>20</sub>Sr<sub>20</sub>Yb<sub>20</sub> has biomedical application.<sup>2</sup> It promotes bone formation.

HEA's have high corrosion resistance. For example Al<sub>0.5</sub>FeCoCrNiCu has high corrosion resistance. Its resistance is better than that of 304 stainless steel in 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution and 1 mol L<sup>-1</sup> NaCl solution.<sup>3</sup> Corrosion resistance of CrFeNiCuMoCo increases and its corrosion current density decreases.<sup>5</sup> AlCoCrFeNiTi<sub>0.5</sub> alloy has good corrosion resistance in 3.5 % NaCl solution.<sup>6</sup> Tempering treatment of this alloy improves its corrosion resistance. Iron alloys have high strength and ductility. They have high resistance to oxidation and corrosion. They can be considered for structural metallic materials.<sup>15</sup>

The properties of high entropy alloys have been investigated by various techniques such as polarisation study<sup>3,10,13</sup> and AC impedance spectra.<sup>16,19</sup>

The surface morphology has been analyzed by methods such as SEM, EDS, X-rays diffraction,<sup>5,8,17</sup> selected area diffraction<sup>14</sup> and differential scanning calorimetry.<sup>14</sup> The surface of high entropy alloys has fcc phase and bcc phase.<sup>1,3,13,14</sup> Addition of one element to the mixture sometimes changes the phase. For examples when Al is added the phase of AlFeCoNiCrTi alloy changes from fcc to bcc phase.<sup>13</sup>

The composition of high entropy alloys, the methods of preparation of alloys, their properties, uses, methods of studying the HEA's, and the surface morphology of HEA's are summarised in Table 1.

## Introduction

HEAs are loosely defined as solid solution alloys that contain more than five principal elements in equal or near equal atomic percent (at. %). The concept of high entropy introduces a new path of developing advanced materials with unique properties, which cannot be achieved by the conventional micro-alloying approach based on only one dominant element. Up to date, many HEAs with promising properties have been reported, e.g., high wear-resistant HEAs, Co<sub>1.5</sub>CrFeNi<sub>1.5</sub>Ti and Al<sub>0.2</sub>Co<sub>1.5</sub>CrFeNi<sub>1.5</sub>Ti alloys; high-strength body-centered-cubic (BCC) AlCoCrFeNi HEAs at room temperature, and NbMoTaV HEA at elevated temperatures. Furthermore, the general corrosion resistance of the Cu<sub>0.5</sub>NiAlCoCrFeSi HEA is much better than that of the conventional 304-stainless steel. In general, commercial alloy systems are based on one principal element and the total quantum of solute atoms is not large in many cases. In contrast, high-entropy alloys are equiatomic multi component alloys. These alloys form simple solid solutions due to the large configurational entropy. If these multi-metallic cocktails are made in nano crystalline state, they are expected to have high strength coupled with reasonable formability. Nanocrystalline high entropy alloys can be made easily by high energy ball milling.

## Composition of High Entropy Alloys

High Entropy Alloys (HEA) are made of many metals mixed in desired Proportions. Usually the HEA's are made of Al, Fe, Co, Ni, Cr, Mg, Zn, K, and Cu. HEA's consisting of AlFeCoNiCr,<sup>1</sup> CaMgZn,<sup>2</sup> AlFeCoCrNiCu,<sup>3</sup> FeCoNiCrCu,<sup>7,8</sup> and FeCrNiAlLa.<sup>14</sup>

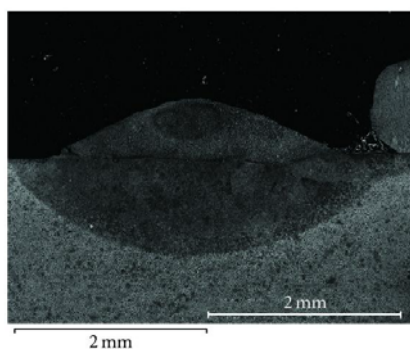
**Table 1.** Preparation methods and properties of high entropy alloys

HEA	Preparation method/Properties	Method and Spectroscopy	Finding/Application	Ref
Al <sub>x</sub> FeCoNiCr(B)	High entropy alloys were prepared in a vacuum arc induction melting furnace.	Electrochemical investigation	The microstructure is a simple solid solution structure, and the fraction of FCC crystal structure decreased with increasing of Al content. Chromium tends to segregate at the inter-dendrite grain boundary	1
Ca <sub>65</sub> Mg <sub>15</sub> Zn <sub>20</sub>	A Ca <sub>20</sub> Mg <sub>20</sub> Zn <sub>20</sub> Sr <sub>20</sub> Yb <sub>20</sub> high-entropy bulk metallic glass was fabricated with unique properties of high-entropy alloys.	In vitro tests, in vivo animal test	The mechanical properties and corrosion behavior were enhanced. The in vitro tests showed that the Ca <sub>20</sub> Mg <sub>20</sub> Zn <sub>20</sub> Sr <sub>20</sub> Yb <sub>20</sub> high-entropy bulk metallic glass could stimulate the proliferation and differentiation of cultured osteoblasts. The in vivo animal tests showed that this high-entropy bulk metallic glass did not show any obvious degradation after 4 weeks of implantation, and they can promote osteogenesis and new bone formation after 2 weeks of implantation	2
Al <sub>x</sub> FeCoCrNiCu (x=0.25, 0.5, 1)	HEA is gradually changed from a single FCC to FCC phase and BCC phase with the addition of Al. With the addition of Al from x=0.25 to 1.0, the hardness of the alloys increase from 165 to 485 HV correspondingly	Polarization curves	The polarization curves show that alloys has the better corrosion resistance than 304 stainless steel in 0.5 mol L <sup>-1</sup> H <sub>2</sub> SO <sub>4</sub> solution and 1mol L <sup>-1</sup> NaCl solution, and meanwhile Al <sub>0.5</sub> FeCoCrNiCu high-entropy alloy has the best comprehensive corrosion resistance.	3
K4169	The Cell Automaton technology was adopted to coupled simulate the grain structure formation process of K4169 superalloy blade with its temperature fields using continuous nucleation model and kinetic model of dendrite tip growth	Equivalent thermal entropy method	In order to control the grain structure of K4169 superalloy blade which affects its mechanical performance and ability of resistance to corroding in high temperature state, the transient temperature field distributions were analyzed. The relationships between temperature and time of every point on vertical section and cross section during phase change heat transference process of K4169 superalloy were obtained.	4
CrFeNiCuMoCo	Powder metallurgy method	SEM/EDS, XRD micro-Vicker hardness test, electro-chemical methods	The morphology of the CrFeNiCuMoCo HEA is simple, the phase mainly composes of FCC and BCC; Mo and Cu are segregated in the alloy; the alloy shows excellent corrosion resistance, the corrosion current density decreases by an order of magnitude compared with 304 stainless steel	5
AlCoCrFeNiTi 0.5	The AlCoCrFeNiTi 0.5 high-entropy alloys fabricated by cold crucible levitation melting (CCLM)	Electrochemical methods	The alloy exhibits a superior resistance to tempering and softening property. The tempering treatment improves corrosion properties in a 3.5 % NaCl solution, and the alloy tempered at 700 °C exhibits the best corrosion property among the experimental alloys.	6

FeCoNiCrCu	Corrosion resistance of directionally solidified alloy is superior to that of the as-cast FeCoNiCrCu alloy	Potentiodynamic polarization	The results showed that only diffraction peak corresponding to a FCC crystal structure was observed in the directionally solidified FeCoNiCrCu alloy. With increasing solidification rate, the interface morphology would grow in planar, cellular and dendrite.	7
FeCoNiCrCu0.5	The as-cast and annealed alloys were severely corroded in 3.5 % NaCl solution with precipitation of the Cu-rich phase in the matrix. The potential of this phase differed considerably from that of the matrix. The Cl <sup>-</sup> ions preferentially attacked this susceptible area.	X-ray diffraction, SEM, TEM.	This study examined the microstructure and electrochemical corrosion behaviour of high-entropy FeCoNiCrCu0.5 alloys annealed at various temperatures.	8
FeCoNiCrCu	The alloy was prepared by arc melting technique, when the coating is made without Si, Mn and Mo additions, the microstructure is mainly composed of columnar and equiaxed grains with uniformly distributed alloying elements	Arc melting, laser cladding	The influences of Si (1.2 mol %), Mn (1.2 mol %) and Mo (2.8 mol.%) additions on the microstructure, properties and coating quality of laser cladded FeCoNiCrCu high-entropy alloy coating have been investigated.	9
Co1.5CrFeNi1.5Ti0.5Mox	The corrosion resistance of the Mo-free alloy was superior to that of the Mo-containing alloy	Potentiodynamic polarization	Electrochemical properties of the Co1.5CrFeNi1.5Ti0.5Mox high-entropy alloys in three aqueous environments which simulate acidic, marine, and basic environments at ambient temperature (~25°C) were studied.	10
AlFeCoNiCrTiVx	The alloy system had better corrosion resistance than 304 stainless steel in 0.5 mol L <sup>-1</sup> H <sub>2</sub> SO <sub>4</sub> solution and 1 mol L <sup>-1</sup> NaCl solution, and the AlFeCoNiCrTiV 0.5 alloy had the best comprehensive corrosion resistance.	Polarization curves	The microstructure and electrochemical properties of equiatomic and high entropy AlFeCoNiCrTiV <sub>x</sub> (x, molar ratio, x=0.5, 1, 1.5, 2) alloys were investigated in 0.5 mol L <sup>-1</sup> H <sub>2</sub> SO <sub>4</sub> solution and 1 mol L <sup>-1</sup> NaCl solution, and compared with 304 stainless steel.	11
Bulk and thin film intermetallic alloys	Connected with the entropy gain, the degree of order depends on temperature and thereby the stability of the designed beneficial materials properties is affected. By monitoring changes in the degree of atomic order an access to atom migration is gained, which is complementary to the usual diffusion experiments, where the degree of order is not changed on average.	Thermal treatment	Due to their excellent corrosion resistance and their advantageous mechanical and in many cases also magnetic properties, intermetallic alloys are among the most important materials of the 21st century. Most of their outstanding qualities are linked to long-range order, the fact that unlike atoms are preferred as neighbours, which then segregate to different sublattices.	12

Al <sub>x</sub> FeCoNiCrTi	By using of the strategy of equiatomic ratio and high entropy of mixing. The composition of the alloy system is gradually changed from FCC phase and BCC phase to a single BCC phase with the addition of Al.	Polarization curves	The alloy has better corrosion resistance than 304 stainless steel and AlFeCuCoNiCrTi <sub>x</sub> high-entropy alloys in 0.5 M H <sub>2</sub> SO <sub>4</sub> and 1 M NaCl solutions, and that the AlFeCoNiCrTi alloy has the best comprehensive corrosion resistance.	13
FeCrNiAlLa alloy, with high (> 40 %) chromium content.	Surface layer ( $\leq 1 \mu\text{m}$ thickness) of the mechanically polished specimen of the alloy Fe <sub>44</sub> Cr <sub>1</sub> Ni <sub>4</sub> Al <sub>0.3</sub> La consists of the amorphous Beilby layer and that its adjacent matrix layer, crushed due to the plastic deformation, formed an entropy "excited" functional system, which at the temperature of 1200 °C in laboratory atmosphere permits the formation of an oxide surface layer with a micro-wrinkles modulated structure of uniform thickness, in the form of mixture of nanocrystallites (100 ÷ 500nm) made of oxides of atoms constituting the basic metallic matrix. Beneath this layer a thin alumina scale is observed to form. Increasing the oxidation temperature causes the regrowth of nanocrystallites and also the recrystallization processes, accompanied by solid-phase reactions between oxide nanoparticles.	SEM, Auger electron spectrometry fast electron diffraction (FED) in the "on reflection" regime and wavelength dispersive spectrometry	The Al <sub>2</sub> O <sub>3</sub> layer is characterized by high adherence with metallic substrate and provides protective features against both high temperature (1200 °C) oxidation of the matrix and resistance to abrasion. By the pretreatment at 1200 °C of the investigated alloy's surface modified specimens, there forms a low thickness (several microns) scale which has ultra fine graininess ( $\sim 1 \mu$ ) with no porosity and blocked grain boundaries short-circuit diffusion paths. This gives to the scale the ability to protect the metallic matrix against high temperature gas (and other aggressive environment) corrosion.	14
Based (Fe) alloy	The iron alloy was prepared by a simple casting method, to obtain a hierarchical structure, with better mechanical performance. The alloy was composed of milli-scale lathy, micro-scale dendritic phases, nanoscale crystalline particles, and a glassy matrix, with short-range order of a length scale less than 1 nm.	Simple casting method	It was observed that the alloy showed significant high strength and ductility, high resistance to oxidation and corrosion that were superior in comparison to most of the high-strength iron alloys. It was also found that these properties of the alloy made it a potential candidate, to emerge as a structural material that may serve as a design consideration for the development of structural metallic materials.	16

Al <sub>0.5</sub> CoCrCuFeNiB <sub>x</sub> alloys	High entropy alloys are a newly developed family of multi component alloys that consist of various major alloying elements, including copper, nickel, aluminum, cobalt, chromium, iron, and others. Each element in the alloy system is present at between 5 and 35 atom %.	Anodic polarization curves electrochemical impedance spectra	This investigation discusses the corrosion resistance of the Al <sub>0.5</sub> CoCrCuFeNiB <sub>x</sub> alloys with various amounts of added boron. Surface morphological and chemical analyses verified that the addition of boron produced Cr, Fe, and Co borides. Therefore, the fraction of Cr outside borides precipitates was scant.	16
High entropy alloys	(HEAs) are a newly developed family of multi-component glassy alloys composed of several major alloying elements, such as copper, nickel, aluminum, cobalt, chromium, iron, silicon, titanium, etc.. The dendritic phase was composed mainly of a non-crystalline phase with a little body centered cubic (BCC) structure whereas the interdendritic phase had an amorphous structure containing small amounts of nano-scale precipitates.	XRD, selected area diffraction (SAD), and DSC analysis, Anodic polarization curves	Tests in 1 N sulfuric acid containing different concentrations of chloride ions showed that the HEA has least resistance to general corrosion at a chloride ion concentration of 0.5 M (close to the concentration in seawater). The lack of hysteresis in cyclic polarization tests confirmed that the HEA-like 304S-is not susceptible to pitting corrosion in chloride-free 1 N H <sub>2</sub> SO <sub>4</sub> .	17
MB-50 alloy	The high corrosion resistance of the alloy, caused by very low solubility of its components in mercury is demonstrated.	Thermal cycling	Corrosion resistance of an MB-50 alloy in mercury is studied at 473 and 573 K under conditions of thermal cycling.	18



**Figure 1.** Macroscopic images of SEM of Al<sub>x</sub>FeNiCuCr high entropy alloys

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### Conclusion

High entropy alloys (HEAs), (equiatomic multicomponent alloy) are in a single solid –solution form. They have unique mechanical and corrosion resistances properties. Hence they are used as implantation materials. They have fcc or bcc structure. These structures are inter convertible on addition of some foreign substances. The microstructure, hardness, corrosion resistance and compression resistance have made these HEAs unique. They can be prepared by various methods such as powder metallurgy and laser cladding. Their microstructures have been investigated by SEM, TEM and RD. Corrosion resistance has been evaluated by polarization study and Electrochemical Impedance spectra.

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