



HIGH ENTROPY ALLOYS AND CORROSION RESISTANCE –A BIRD'S EYE VIEW

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The introduction of high entropy alloys (HEA) concept broke up the traditional rule that the main elements take up more than 50% atomic content. HEA means that alloys are composed of multi elements and each takes up a relatively high but less than 35% of atomic content. The properties of this innovative alloy are decided by the combined action of multi elements. HEA tends to form simple crystallization phase. By controlling the composition, it is possible to achieve high-hardness and high-abrasion performance at high temperature. Microstructure and properties of several HEAs prepared by various methods such as powder metallurgy laser cladding etc, are discussed. The corrosion resistance of HEAs is also discussed.

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Introduction

The past twenty years have witnessed the fast development of bulk metallic glasses (BMGs),¹⁻³ a relatively new type of metallic materials with non-crystalline or amorphous structure. Their unique mechanical and physiochemical properties have stimulated extensive research in the materials community.²⁻⁶ High entropy alloys (HEAs), or equiatomic multi-component alloys that are often in a single solid-solution form, were developed slightly later than the bulk metallic glasses and they even share many similar properties,⁷⁻¹⁰ but HEAs were given much less attention compared to BMGs. The concept of high-entropy bulk metallic glasses (HE-BMGs) which appeared very recently¹¹⁻¹³ provides an opportunity to compare and study the similarity and difference between these two types of multi-component alloys, particularly, from the alloy design perspective. A critical question relevant to the alloy design for multi-component alloys is: for a given composition with known constituent elements, can we predict which type of phases (amorphous phase, solid solution phase or inter metallic phase) will form? Alternatively, are we now capable of designing the multi-component alloys with the desired phase constitution.

Unfortunately, it is still too ambitious to answer the above two important questions. However, there do have some clues obtained over years of alloy development. For the alloy design of BMGs, the three empirical rules initiated by INOUE¹ have been proven useful: multi-component systems,

significant atomic size difference and negative heats of mixing among constituent elements. As traditionally the BMGs have only one or two principle elements, the uncertainty of the suitable composition for other alloying elements complicates the alloy design as there exist too many possibilities to be tried out. It is hence not surprised to see that currently many, if not most, alloy designs for BMGs are based on micro-alloying¹⁴⁻¹⁷ or substitution of similar elements^{18,19} for those mature BMG formers, which were also developed from try-and-error experiments. Along this line of thinking, the alloy design in the equiatomic HEAs could be relatively easier, as once the alloy elements are chosen their compositions are known. However, we now face the uncertainty of the resultant types of crystalline phases: fcc, bcc, mixed fcc and bcc phases.²⁰

In some multi-component alloys with a high mixing entropy (so in principle they can also be called HEAs even they do not form a single solid solution), intermetallic phases can form.²⁰ As the unique properties of HEAs mostly originate from the formation of the multi-component solid solution,^{7,10} we need to know the rules governing the formation of solid solution phases. Although the name of HEAs and the fact that the HEAs have large mixing entropy give the impression that the mixing entropy is the dominating factor controlling the formation of the solid solution phases, there exists no solid evidence supporting this argument. From the classical Hume-Rothery rule²¹ we know that to form a solid solution, the properties of constituent alloying elements need to be similar: they shall have similar atomic size and similar electro negativity.

However, the Hume-Rothery rule is apparently not applicable to the solid solution formation in HEAs. For example, it cannot explain why the equiatomic Co (hcp) – Cr(bcc) – Cu(fcc) – Fe(bcc) – Ni(fcc) alloy forms an fcc-typed solid solution, and how the addition of fcc-Al can eventually change the fcc-type CoCrCuFeNi to a bcc structure.²²

Microstructure and properties of high entropy alloys prepared by various methods are discussed.

Structure and properties of FeCoNiCrCu0.5Alx high-entropy alloy²⁵

Effects of Al content and heat treatment on the structure, hardness and electrochemical properties of FeCoNiCrCu0.5Alx high-entropy alloys were investigated. The phase structure of as-cast alloys evolves from FCC phase to BCC phase with the increase of Al content. The stable phase of FeCoNiCrCu0.5Alx high-entropy alloys will transform from FCC phase to FCC + BCC duplex phases when x value increases from 0.5 to 1.5. The hardness of BCC phase is higher than that of FCC phase, and the corrosion resistance of BCC phase is better than FCC phase in chlorine ion and acid medium. High hardness and good corrosion resistance can be obtained in as-cast FeCoNiCrCu0.5Al1.0 alloy.

Microstructure and corrosion resistance of AlCrFeCuCo high entropy alloy²⁶

The AlCrFeCuCo high-entropy alloys were prepared by the laser cladding method. The microstructure and corrosion resistance property of AlCrFeCuCo high-entropy alloy were researched by scanning electron microscopy, X-ray diffraction and electrochemical workstation. The results show that, under the rapid solidification small microstructure gained, the morphology of AlCrFeCuCo high entropy alloy is simple, the phase mainly compose of FCC and BCC; elements segregated in the alloys; the alloy shows excellent corrosion resistance, along with the increase of the scanning speed, alloy corrosion resistance performance shows a enhancement in the first and then weakened trend. The corrosion resistance performance of AlCrFeCuCo high-entropy alloys in 1 mol L⁻¹ NaCl solution is better than in 0.5 mol L⁻¹ H₂SO₄ solution.

Corrosion behaviour of CuCrFeNiMn high entropy alloy system in 1 M sulfuric acid solution²⁷

Immersion tests and potentiodynamic polarization measurements were conducted in 1 M sulfuric acid solution (H₂SO₄) at ambient temperature (~25 °C) to investigate the corrosion behavior of CuCrFeNiMn alloy system. The results show that the alloys display a good general corrosion resistance that is mainly influenced by the Cu content and elemental segregation degree. The corrosion resistance degrades when increasing Cu content and elemental segregation degree. Among the tested alloys, the 2Mn₂ alloy with low Cu content and elemental segregation degree displays a better general corrosion resistance. On the contrary, the Cu₂CrFe₂NiMn₂ alloy with high Cu content and elemental segregation degree exhibits the worst general corrosion resistance.

Effect of nitrogen content and substrate bias on mechanical and corrosion properties of high-entropy films (AlCrSiTiZr)100-xNx²⁸

High-entropy alloy and nitride films of (AlCrSiTiZr)100-xNx containing large Zr atoms and small Si atoms were deposited on 6061 aluminum alloy and mild steel substrates

by DC reactive magnetron sputtering at various nitrogen flow ratio (R_N). The composition, crystalline structure, and film morphology were analyzed by electron probe X-ray micro analyzer (EPMA), X-ray diffractometer (XRD), transmission electron microscope (TEM), and scanning electron microscope (SEM), respectively. Also, their hardness and elastic modulus were studied by nano indentation. The corrosion behavior was studied by anodic polarization analysis in 0.1 M H₂SO₄ aqueous solution at room temperature. The properties of films deposited under substrate bias application were also studied. The tendency of the present composition to form amorphous or low-crystallinity structure is high because of its large difference in atomic size. Films demonstrate pure amorphous structures even as the nitrogen content reaches as high as 22.4 at. %.

All coatings can provide better corrosion resistance on both 6061 aluminum alloy and mild steel substrates. Under condition of no applied substrate bias, films of (AlCrSiTiZr)100-xNx deposited at R_N = 30 % give the best corrosion resistance. Substrate bias of -100V effectively improves the corrosion resistance of the amorphous film of (AlCrSiTiZr)100-xNx (R_N = 5 %). The factors that might influence the corrosion resistance have been reported.

Study on corrosion resistance of high-entropy alloys NiCoCrFeMnCuC in medium acid liquid²⁹

High-entropy alloy of NiCoCrFeMnCuC were made by vacuum non-consumable arc furnace. The crystal structure of NiCoCrFeMnCuC was analyzed by XRD. The corrosion resistance of NiCoCrFeMnCuC in 10 % HNO₃ - 3 % HF, 10 % H₂SO₄, 5 % HCl and 10 % HF was investigated, respectively with weight loss experiment. The results show that main inter metallics of the alloy are CoCx, FeNi₃ and Fe₃Mn₇. The NiCoCrFeMnCuC has simple crystal structures with face-centered cubic crystal structure FCC and Quartet and has excellent corrosion resistance in some medium acid liquids.

Microstructural evolution and corrosion behaviour of directionally solidified FeCoNiCrAl high entropy alloy³⁰

The FeCoNiCrAl alloys have many potential applications in the fields of structural materials, but few attempts were made to characterize the directional solidification of high entropy alloys. Recently, the micro structure and corrosion behavior of FeCoNiCrAl high entropy alloys have been investigated under directional solidification. The results show that with increasing solidification rate, the interface morphology of the alloy evolves from planar to cellular and dendritic. The electrochemical experiment results demonstrate that the corrosion products of both non-directionally and directionally solidified FeCoNiCrAl alloys appear as rectangular blocks in phases which Cr and Fe are enriched, while Al and Ni are depleted, suggesting that Al and Ni are dissolved into the NaCl solution. Comparison of the potentiodynamic polarization behaviors between the two differently solidified FeCoNiCrAl high entropy alloys in a 3.5 % NaCl solution shows that the corrosion resistance of directionally solidified FeCoNiCrAl alloy is superior to that of the non-directionally solidified FeCoNiCrAl alloy.

The property research on high-entropy alloy Al_xFeCoNiCuCr coating by laser cladding³¹

High-entropy alloys have been found to have novel microstructures and unique properties. The main method of manufacturing is vacuum arc remelting. As in situ cladding laser cladding has capability of achieving a controllable dilution ratio, fabricating high-entropy alloy by laser cladding is of great significance and potential for extensive use. Recently, a novel Al_xFeCoNiCuCr high-entropy alloy system was manufactured as the thin layer of the substrate by laser cladding; also high temperature hardness, abrasion performance, corrosion nature of the Al_xFeCoNiCuCr high-entropy alloy were tested under the different ratio of aluminum. It is observed that higher aluminum clad exhibit higher hardness, better abrasion resistance and corrosion resistance

Electro-spark deposition of multi-element high entropy alloy coating³²

A multi-element high entropy alloy coating AlCoCrFeNi was fabricated on AISI 1045 carbon steel substrates using electro-spark deposition. The surface morphology of the as-deposited coating was examined and the phase of the coating was identified. In addition, the hardness and the corrosion properties of the coating were evaluated. An SEM examination showed that a metallurgically bonded coating of thickness up to 100 μm can be produced on carbon steel substrates. The results of an EDX analysis suggest that the coating has the same chemical composition as the high entropy alloy without apparent dilution of content. The XRD results indicate that the coating has a simple BCC structure and no inter metallic phase was detected. The micro hardness of the coating was some two times higher than that of the substrate material. With regard to corrosion properties, the corrosion current density and the corrosion potential of the as-deposited coating were three orders of magnitude lower and 140 mV higher than those of the substrate material, respectively. Moreover, the polarization curve of the coating exhibits a passive region, indicating that the corrosion resistance of the coating is superior to that of the substrate material.

Effect of aging treatment on microstructure and properties of high-entropy Cu_{0.5}CoCrFeNi alloy³³

The microstructure and properties of Cu_{0.5}CoCrFeNi high-entropy alloys with as-cast structure and heat treated structures were investigated. The as-cast alloy specimens were firstly heated at 1050 °C for a holding time of 1 h. Serial aging heat treatment processes were performed at 350 °C, 500 °C, 650 °C, 800 °C, 950 °C, 1100 °C, 1250 °C and 1350 °C with a holding time of 24 h at each temperature. The microstructures, chemical composition, and precipitate phase of alloys with as-cast and various aging heat treated specimens characterized analyses were performed by scanning electron microscopy (SEM), X-ray diffraction (XRD) and transmission electron microscopy (TEM). The results show that FCC phase structures remain unchanged after aging the Cu_{0.5}CoCrFeNi alloy of the as-cast specimens that had been heated to 1350 °C. The microstructure of the alloy specimens consisted of FCC matrix, Cu-rich phase, and Cr-rich phase. This Cr-rich phase precipitates to FCC matrix after being aged at 1100-1350 °C.

The hardness of the Cu_{0.5}CoCrFeNi alloy was unchanged for the specimens after various heat treatments. The corrosion resistance of the specimens was evaluated by potentiodynamic polarization in immersion tests. The as-cast specimen and those that had undergone aging heat treatments from 350 to 950 °C were seriously corroded in 3.5 % NaCl solution due to segregation of the Cu-rich phase precipitate formed in the FCC matrix. Cl⁻ ions preferentially attacked the Cu-rich phase which was a sensitive zone exhibiting an appreciable potential difference with the consequent galvanic action. The specimens that were heat treated at 1100-1350 °C showed the best corrosion properties, because the Cu-rich phase was dissolved into the FCC matrix at elevated temperatures.

Microstructure and electrochemical properties of Al-FeCuCoNiCrTi_x high entropy alloys³⁴

Microstructure of AlFeCuCoNiCrTi_x (atom weight, x=0.5, 1.0, 1.5) high entropy alloys was observed, and electrochemical behavior of the high entropy alloy was examined and compared with that of commercial 304 stainless steel in 0.5 mol H₂SO₄ solution and 1 mol NaCl solution. The results reveal that the AlFeCuCoNiCrTi_x (atom weight, x = 0.5, 1.0, 1.5) high entropy alloys is mainly composed of fcc structure and bcc structure. Polarization curves show that compared with that of 304 stainless steel, the alloys exhibits lower corrosion rate in 0.5 mol H₂SO₄ solution, however the pitting corrosion resistance is superior to that of 304 stainless steel in 1 mol NaCl solution

Corrosion behaviour of 6061Al - 15vol. Pct. SiC composite and its base alloy in a mixture of 1:1 hydrochloric and sulphuric acid medium³⁵

Silicon carbide particulate - reinforced aluminum (SiCp-Al) composites possess a unique combination of high specific strength, high elastic modulus, good wear resistance and good thermal stability than the corresponding non-reinforced matrix alloy systems. These composites are potential structural material for aerospace and automotive applications. The corrosion characteristics of 6061Al/SiCp composite and the base alloy were experimentally assessed. The corrosion test was carried out at different temperatures in 1:1 mixture of hydrochloric acid and sulphuric acid at a concentration range of 0.01 to 1 N for each of the acid, as corrosion media using Tafel extrapolation technique and Electrochemical impedance spectroscopy (EIS). The results obtained from Tafel extrapolation technique and Electrochemical impedance spectroscopy was in good agreement. The results showed an increase in the corrosion rate with increases in temperature as well as the increase in the concentration of the corrosion media. The thermodynamic parameters like energy of activation were calculated using Arrhenius theory equation and, enthalpy of activation and entropy of activation were calculated using transition state theory equation.

Enhancing pitting corrosion resistance of Al_xCrFe1.5MnNi_{0.5} high-entropy alloys by anodic treatment in sulfuric acid³⁶

High-entropy alloys are a newly developed family of multi-component alloys that comprise various major alloying elements. Each element in the alloy system is

present in between 5 and 35 at %. The crystal structures and physical properties of high-entropy alloys differ completely from those of conventional alloys. The electrochemical impedance spectra (EIS) of the $\text{Al}_x\text{CrFe1.5MnNi0.5}$ ($x = 0, 0.3, 0.5$) alloys, obtained in 0.1 M HCl solution, clearly revealed that the corrosion resistance values were determined to increase from 21 to 34 $\Omega \text{ cm}^2$ as the aluminium content increased from 0 to 0.5 mol, and were markedly lower than that of 304 stainless steel (243 $\Omega \text{ cm}^2$). At passive potential, the corresponding current declined with the anodizing time accounting, causing passivity by the growth of the multi-component anodized film in H_2SO_4 solution. X-ray photoelectron spectroscopy (XPS) analyses revealed that the surface of anodized $\text{Al}_{0.3}\text{CrFe1.5MnNi0.5}$ alloy formed aluminum and chromium oxide film which was the main passivating compound on the alloy. This anodic treatment increased the corrosion resistance in the EIS measurements of the CrFe1.5MnNi0.5 and $\text{Al}_{0.3}\text{CrFe1.5MnNi0.5}$ alloys by two orders of magnitude. Accordingly, the anodic treatment of the $\text{Al}_x\text{CrFe1.5MnNi0.5}$ alloys optimized their surface structures and minimized their susceptibility to pitting corrosion.

Effect of the aluminium content of $\text{Al}_x\text{CrFe1.5MnNi0.5}$ high-entropy alloys on the corrosion behaviour in aqueous environments³⁷

High-entropy alloys (HEAs) are a newly developed family of multi-component alloys. The potentiodynamic polarization and electrochemical impedance spectroscopy of the $\text{Al}_x\text{CrFe1.5MnNi0.5}$ alloys, obtained in H_2SO_4 and NaCl solutions, clearly revealed that the corrosion resistance increases as the concentration of aluminium decreases.

The $\text{Al}_x\text{CrFe1.5MnNi0.5}$ alloys exhibited a wide passive region, which extended > 1000 mV in acidic environments. The Nyquist plots of the Al-containing alloys had two capacitive loops, which represented the electrical double layer and the adsorptive layer. SEM micrographs revealed that the general and pitting corrosion susceptibility of the HEAs increased as the amount of aluminium in the alloy increased.

Effect of boron on the corrosion properties of $\text{Al}_{0.5}\text{CoCrCuFeNiB}_x$ high entropy alloys in 1 N sulfuric acid³⁸

High entropy alloys are a newly developed family of multi-component alloys composed of several major alloying elements, such as copper, nickel, aluminum, cobalt, chromium, iron, etc. Each element in the alloy system is between 5 at % and 35 at %. High entropy alloy has a lot of advantages regarding its mechanical, magnetic and electrochemical properties. Lee et al have discussed the corrosion resistance of $\text{Al}_{0.5}\text{CoCrCuFeNiB}_x$ alloys with various amounts of boron addition. Surface morphology and EDS analysis confirmed that the addition of boron produced Cr and Fe borides. Therefore the content of Cr in the region besides borides precipitates was very scanty. The anodic polarization curves and electrochemical impedance spectra of $\text{Al}_{0.5}\text{CoCrCuFeNiB}_x$ alloys, obtained in 1 N H_2SO_4 aqueous solution, clearly indicated that the general corrosion resistance decreases as the amounts of boron increases.

Conclusion

High entropy alloys (HEAs), (equiatomic multicomponent alloy) are in a single solid –solution form. They have unique mechanical and physicochemical properties. 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 XRD. Corrosion resistance has been evaluated by polarization study and Electrochemical Impedance spectra.

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