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Comparative Study of High Entropy Alloys-AlCoCrFeNi, AlCoFeNi and CoCrFeNi with 304SS

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Abstract* – High Entropy Alloys (HEA) are defined as alloys with four or more principal elements. Each principal element should have a concentration between 5 and 35%. Besides principal elements, HEAs can contain minor elements, each below 5%. HEAs differentiate with conventional alloys in that they have at least four principal elements, instead of one or two in the latter. It is a breakthrough to the alloy design in the traditional physical metallurgy, and it opens a new arena for explorations of new materials and new properties. Many research works are going on these fields. This work is to compare the properties of HEAs- AlCoCrFeNi, AlCoFeNi and CoCrFeNi with 304 Stainless steel. 304 SS is one of the widely used stainless steel with high corrosion resistance. Properties like density, hardness, corrosion resistance are compared. Microstructure and composition Analysis is also performed for the comparative study.

Index Terms—**Corrosion resistance, Composition analysis, Hardness, High Entropy Alloys (HEA), Microstructure, 304 SS (Stainless Steel)**

I. INTRODUCTION

Metals in actual commercial use are almost exclusively alloys, and not pure metals. It is possible to obtain an infinite variety of physical properties by varying the metallic composition of an alloy. Alloys are normally harder than their components, less ductile and may have a much lower conductivity, whereas the highly purified single crystal of a metal is very soft and malleable, with high electrical conductivity. This is why pure metals are used only for specific applications. The alloy is usually more corrosion resistant and less affected by atmospheric conditions. The conductivity of an alloy varies with the degree of order of the alloy and the hardness varies with the particular heat treatment.

Alloys are widely used in industries as their physical and chemical properties can be easily varied to suit the exact individual requirement. One can achieve this by preparing alloys of different metals. The alloying elements are added to improve one or more of the following properties: (a) tensile strength, hardness and toughness (b) corrosive and oxidation resistance, (c) machinability, (d) elasticity (e) hardenability (f) creep strength and (g) fatigue resistance etc.

A. High Entropy Alloys (HEAs)

HEAs are defined as alloys with four or more principal elements. Each principal element should have a concentration between 5 and 35%. Besides principal elements, HEAs can contain minor elements, each below 5%. HEAs differentiate with conventional alloys in that they have at least four principal elements, instead of one or two in the latter. It is a breakthrough to the alloy design in the traditional physical metallurgy, and it opens a new arena for explorations of new materials and new properties.

Research indicates that HEAs are also considerably lighter, with a higher degree of fracture resistance, tensile strength, as well as corrosion and oxidation resistance than conventional alloys. These alloys are currently the focus of significant attention in materials science and engineering because they have potentially desirable properties. HEAs have been described in the literatures that have better strength-to-weight ratios, fracture toughness, tensile strength, high-temperature strength, thermal stability, and corrosion resistance than similar conventional alloys.

B. Corrosion

Corrosion is the process in which a material is oxidized by the environment and loses electrons in its result. Therefore, corrosion resistance is the capability to hold that binding energy of metal and withstand the deterioration and chemical breakdown that occurs during surface exposure to such an environment. AISI type-304 stainless steel (304SS) is the most popular alloy used by the chemical industry, in food processing plants and breweries, cryogenic vessels, gutters, downspouts, flashings, etc. These alloys are corrosive resistant and easily machinable. In marine industry these are used in fabrication of interior cabins and other areas. Some literatures are mentioning about the corrosive nature of 304 SS in marine atmosphere. High Entropy Alloys (HEA) are a new class of alloys where more researches are going on. The chemical compositions of 304 SS and the proposed HEA can be quite similar in that both can be made of Fe, Cr, Ni, and Cu, being different only in their relative proportions. Although substantial information is now available on the electrochemical behavior of stainless steels in numerous corrosive environments, the corrosion behavior of the HEA is relatively unknown. Therefore, it is of interest to determine the corrosion behavior of the HEA in comparison with conventional ferrous alloys, such as 304 SS.

II. EXPERIMENTAL SETUP

A. *Casting of Alloys*

Vacuum induction melting (VIM) have been stimulated by the need to produce superalloys containing reactive elements within an evacuated atmosphere. The process is relatively flexible, featuring the independent control of time, temperature, pressure, and mass transport through melt stirring. VIM offers more control over alloy composition and homogeneity than other vacuum melting processes.

The first alloy AlCoCrFeNi was prepared from commercially pure powdered elements (Al, Co, Ni: 99.9 wt.%; Cr, Fe: 99.5 , 99.6 wt.%). The raw elements of 20 at. wt. % of each was alloyed in a 120ml cylindrical Alumina (Al_2O_3) crucible in the vacuum induction melting furnace. The Alumina crucible with 100 gm raw elements were heated to 1800 ºC and held at maximum temperature for 1 hour 30 minutes. The alloying process is done step by step with increasing the temperature. The furnace chamber was first evacuated to 6×10^{-2} Pa and then backfilled with high purity argon gas to reach 0.06 MPa. An IRTM-2CK infrared pyrometer was employed to monitor the temperature with an absolute accuracy of 62 °C. After heating, the furnace is kept off slowly by decreasing the temperature without releasing the argon in the chamber. The crucible with alloy is allowed to anneal within the furnace containing argon so that no oxidation occurs till it reaches the atmospheric temperature.

The second alloy AlCoFeNi was prepared in the same way as the first alloy prepared. Here the raw powdered elements of 25 at. Wt. % of each was alloyed because the number of elements in the alloy reduced to four. Here in this composition the presence of Cr was avoided. The rest of the process was same for this alloy as the first alloy.

The third alloy CoCrFeNi was prepared in the same way as the first and second alloy were prepared. Here the raw powdered elements of 25 at. Wt. % of each was alloyed because here also the number of elements in the alloy reduced to four. Here in this composition the presence of Al was avoided. The rest of the process was same for this alloy as the first and second alloy.

B. *Testing of Alloys*

After casting of three alloys each alloy samples were under gone certain tests and analysis. Microstructure and composition analysis were conducted on Joel 6900 Scanning electron microscope (SEM) with Energy Dispersive X ray Spectroscopy (EDAX). The ability to identify and quantify changes in the microstructure of metal alloys is valuable in metal cutting and shaping applications. The mechanisms of microstructure changes in alloys under various treatments, which cause them to behave differently, are not yet fully understood. The changes are currently evaluated in a semi-quantitative manner by visual inspection of images of the microstructure.

Density tests were conducted on three samples using Archimedes's principle. Since density is mass per unit volume, the density of a metal can be calculated by submerging it in a known amount of water and measuring how much the water rises. This rise is the volume of the metal. Its mass can be measured using a scale. The unit for density is g/cm^3.

Hardness is a characteristic of a material, not a fundamental physical property. It is defined as the resistance to indentation, and it is determined by measuring the permanent depth of the indentation. More simply by using a fixed force (load) and a given indenter, the smaller the indentation, the harder the material. Indentation hardness value is obtained by measuring the depth or the area of the indentation using one of over 12 different test methods. Hardness test were conducted on Vickers hardness testing machine. The Vickers hardness test method**,** also referred to as a micro hardness test method, is mostly used for small parts, thin sections, or case depth work. The Vickers method is based on an optical measurement system.

Immersion corrosion evaluations using G31 provide a straightforward and simple method of determining the rate of corrosion in aqueous solutions. It is most appropriate for determine the corrosivity of liquids in static applications, but may also be used as an evaluation tool for many other applications Immersion test of three alloys in 5% NaCl solution were conducted for understanding the corrosion properties.

III. RESULT AND DISCUSSION

A. *Microstructure and Composition Analysis*

The chemical compositions of specimens are listed in Table I. The optical micrographs of these alloys are shown in Fig. 1.

Table -I: Composition analysis (EDAX) results of three alloys (wt. %)

	Al	Co	Cr	Fe	Ni
AlCoCrFeNi	8.65	21.34	19.56	26.22	24.23
AlCoFeNi	12.45	29.005		29.265	29.28
CoCrFeNi		25.93	23.28	24.76	26.03

Figure-1 shows the SEM images of the as-cast AlCoCrFeNi high entropy alloy. These images are back scattered electron images which shows some white droplets and shades on the surface. These patterns show the distribution of materials. Small white droplets are precipitate formation of Al-Ni and dark area shows the Co-Cr-Fe matrix.

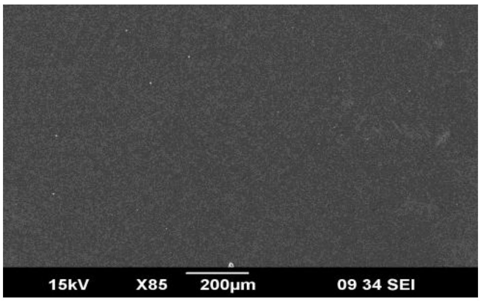

Fig. 1: Microstructure of as-cast AlCoCrFeNi

Figure- 2 shows the SEM images of the as-cast AlCoFeNi high entropy alloy. Here in this image it is clearly visible the dendrite formation. From Edax analysis it will be clear about the composition at dendrite and interdendrite regions.

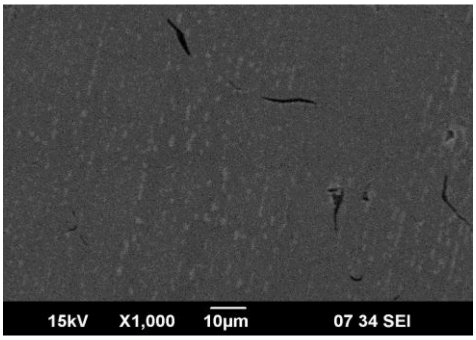

Fig. 2: Microstructure of as-cast AlCoFeNi

Figure 3. shows the SEM images of the as-cast CoCrFeNi high entropy alloy. Here in these images more white shades are visible with the formation of dendrite structures. White shades are the Cr precipitate formation and Co-Fe-Ni forms the dark matrix.

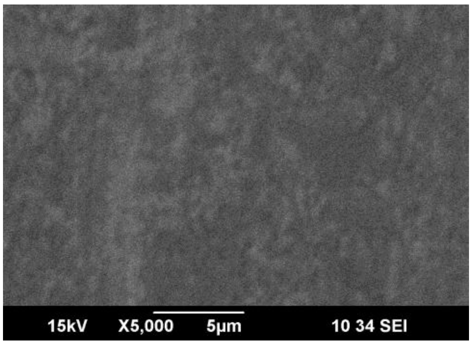

Fig. 3: Microstructure of as-cast CoCrFeNi

B. Density Test

The density is calculated using the archemedie's principle:

$$\rho = W_{air} / (W_{air} - W_{water}) \quad (1)$$

Where,
W_{air} = Weight of the alloy in air
W_{water} = Weight of the alloy in water
ρ = Density of the alloy

Table -II: Density of four alloys

Alloy	AlCoCrFeNi	AlCoFeNi	CoCrFeNi	304 SS
Density(g/cc)	6.7	6.54	7.54	8

Comparing the results of HEAs with 304 SS it is clear that SS is having high density. Though HEAs are having more number of elements they are less dense.

C. Hardness test

The hardness of the alloys are taken in as cast condition using Vicker's Hardness testing machine under 50 kgf for 15 sec ,the result is given below in the table III.

Table -III: Hardness of four alloys

Alloy	AlCoCrFeNi	AlCoFeNi	CoCrFeNi	304 SS
Hardness(HV)	530	350	442	129

The alloy AlCoCrFeNi is exhibiting high hardness value. This may due to the crystal structure. From the design analysis it was predicted that this alloy forms a mixture of FCC and BCC. The third alloy CoCrFeNi also have better hardness value. Third alloy also have crystal structure mixture of FCC and BCC.

D. Corrosion test

Immersion test was done under 5% Nacl solution for 15 days and the weight loss and corrosion rate of the alloys were obtained. The below shown table gives the details of the corrosion test conducted on three alloy samples. Average weight losses after corrosion test were obtained.

Table -IV: Average weight loss of four alloys after immersion test

Alloy	**Average weight loss (gm)**
AlCoCrFeNi	0.0008
AlCoFeNi	0.0015
CoCrFeNi	0.0002

The Corrosion rate for each alloy where calculated and tabulated below. From the table it is clear that Corrosion rate for CoCrFeNi alloys where higher than other two alloys.

Table -V: Corrosion rate of three casted alloys

Alloy	**K value (constant)**	**Weight loss in grams(W)**	**Area (cm^2)**	**Time (T)**	**Density (g/cc)**	**Corrosion Rate (mm/yr)**
AlCoCrFeNi	87600	0.0008	1	360	6.7	0.0290
AlCoFeNi	87600	0.0015	1	360	6.54	0.0558

CoCrFe Ni	87600	0.0002	1	360	7.53	0.0064

The figure 4 shows the comparison of corrosion rate between alloys. The amount of Cr content increases the corrosion resistance. So the alloy combination CoCrFeNi shows the better resistance to corrosion than other alloys. First alloy AlCoCrFeNi also resistance to corrosion in a better way due to the presence of Cr content. 304 SS contains 17.99 at. wt.% of Cr. Corrosion rate of this alloy is 0.03048 mm/year. Comparing with other three alloys first and third alloy are having less corrosion rate.

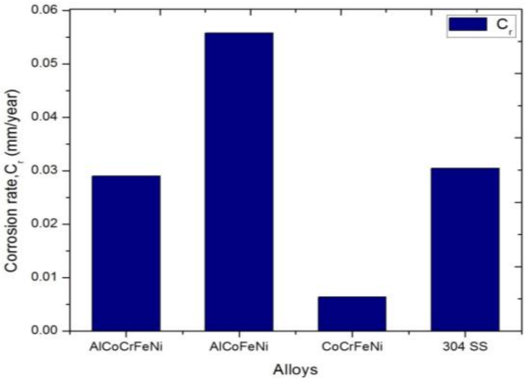

Fig -4: Comparison of Corrosion rate of four alloys

IV. CONCLUSIONS

High entropy alloys (HEAs) are a newly developed family of multi-component alloys composed of several major alloying elements, such as copper, nickel, aluminum, cobalt, chromium, iron, silicon, titanium, etc. As per the tests conducted AlCoCrFeNi alloy comprises amorphous structure with FCC + BCC phases and CoCrFeNi alloy also have FCC + BCC structure. Both these alloys exhibiting low corrosion rate compared to 304 SS. Variation in the Cr amount significantly affect the corrosion rate and density of the alloy. CoCrFeNi alloy having density 7.53g/cm^3 exhibiting a high hardness value of 442 HV and corrosion rate of 0.0064 mm/year. Further more tests like tensile test, compressive test etc. must be conducted to more about HEAs.

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