Heat-treatment (Annealing) Effect on the Mechanical and Electrochemical Performance of a Synthesized AlCrFeMnNiV Equi-atomic High Entropy Alloy (HEA) via Arc-melting and Casting Technologies

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Abstract
In this work, an equi-atomic AlCrFeMnNiV HEA was synthesized by means of arc-melting and casting processes. The casted alloy ingots were heat-treated (annealed) at temperatures of 400, 600 and 800 ºC, for 2 h. The effect of the heat-treatment temperature on the HEA microstructural evolution, compressive strength and corrosion behavior was investigated. Heat-treatment temperatures of 400 and 600 ºC resulted in increased micro-hardness properties that, at 800 ºC, were drastically reduced, although a good combination between strength and ductility was observed. HEA showed an extreme decrease in the current density (J (A/cm^2)), after the heat-treatment, with a lower potential (V). The heat-treated HEA demonstrated a good corrosion rate in acidic conditions, as compared to that of nickel (Ni) based, titanium (Ti) alloys and stainless steel (SS) super alloys.

Keywords: HEA, AlCrFeMnNiV, arc-melting, casting, heat-treatment (annealing), compression and corrosion.

Introduction

As human beings have improved their ability to fabricate materials, alloys have evolved from simple to complex compositions, improving functions and performances, and promoting the advancements of civilization. The stability of materials at great heat is one of the most exotic characteristics that are required for manufacturing high temperature applications. These components are required to have high thermo-mechanical fatigue endurance, creep strength and corrosion resistance. Failure of conventional market materials, such as Ni-based, Ti and SS alloys, due to oxidation, wear, thermo-mechanical failure and corrosion at high temperatures, gives room for the design and properties optimization of new alloys

[1-4]. HEAs development has generated a huge interest for many industrial applications, due to their extensive properties. With a series of elements in great proportions, they consist of five or more principal substances [5-8]. Conventional materials, such as Ti6Al4V, SS and Ni-based super alloys, have shown poor heat mechanical properties, namely, hardness, fracture toughness and compressive strength, due to changes in their hotness, thermal expansion and phases [9-14]. Sigrum [15] stated that the AlCrFeNiMn HEA behavior, in a geothermal power plant, revealed poor resistance, with high corrosion rates of 3.25 mm/year. From literature, it is clear that the incorporation of reinforcement elements in the HEA can result in outstanding corrosion properties [16-19]. It was also stated that HEAs synthesized via casting techniques show superior V for high-temperature engineering applications, due to their properties. However, the complex temperature distribution developed during the casting process results in significant obstacles to the fabrication of materials with good mechanical properties governed by a final microstructure, due to defects that arise. Hence, post-procedures, such as annealing, are promising techniques for the improvement of the as-cast HEAs mechanical properties [6, 20-23]. Heat-treatment is a breaking edge manufacturing procedure, with the possibility of changing the perception of design and manufacturing as a whole. It is well suited for building components in the aerospace and automotive industries, which usually require a high level of accuracy and customization of the parts [24]. In contrast to the conventional casting techniques used to fabricate HEAs ingots, in which numerous remelts are advised for chemical homogeneity, the heat-treatment gives the opportunity to produce HEAs in a single-melt process, with the freedom to synthesize bulk components for aerospace applications [25]. The aim of this study is to develop novel AlCrFeMnNiV HEAs using the heat-treatment technology. The major properties assessed on this research are corrosion, hardness and compressive strength resistance.

Methodology

An equi-atomic AlCrFeMnNiV HEA was prepared using high grade powders of Al, Cr, Fe, Mn, Ni and V (vanadium). They were put into a tubular mixer, for 8 h, to ensure an even HEA distribution. The mixture was compacted using a tablet machine, and the blocks were arc-melted in a furnace. During this process, high purity argon gas was utilized, in order to achieve a more inert environment in the furnace, while the Cu crucibles were flipped over, to attain chemical homogeneity. The as-cast ingots (diameter of 20 mm and height of 10 mm) were sectioned. The annealing technique took place at 400, 600 and 800 ºC, for 2 h, at air. The microstructural evolution and phase composition of the as-cast HEA and of the annealed HEA were studied using a scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS), and X-ray diffraction (XRD), respectively. The micro-hardness properties of both HEAs were studied using the Emco Test Durascan tester coupled with Ecos workflow ultramodern software. An applied force of 500 kg, at five randomly selected points on the surface, which were indented for 15 s of dwelling time, was used, and the mean value was reported. The samples were also tested for compression strength, using an Instron 1342 machine, at a test rate of 2 mm/min. The samples cross section was 8 x 8 mm^2, and the height was 10 mm. HEAs corrosion resistance was studied in aerated 0.5 M H_2SO_4 and in a 3.65% NaCl solution, at room temperature, using the AutoLab Potentiostat (PGSTAT20) device.

Results and discussion

SEM/EDS results

Fig. 1 presents SEM images of as-cast (Fig. 1a) and heat-treated (Figs. 1 b-d) AlCrMnFeNiV HEAs. In Fig. 2, it is also clear that an even distribution of elements throughout the fabricated alloys has been achieved. This has the advantage of solid solution phases formation being possible. The as-cast (Fig. 1a) sample shows well-defined boundaries, with individual grains composed of a substructure made of a dendritic core rich in Ni (29.66%) and Fe (16.32%), and inter dendritic regions (ID). The heat-treated alloy shows clear micro pores (Fig. 1c), at 600 ºC. It is also clear that, by increasing the temperature to 800 ºC, grain boundaries became poorly defined. In a study by Masemola et al. [26], the authors stated that HEA well-defined grain boundaries are mostly formed at high heat-treatment temperatures. However, by introducing V in an AlCrMnFeNi high entropy system, the results are the opposite.

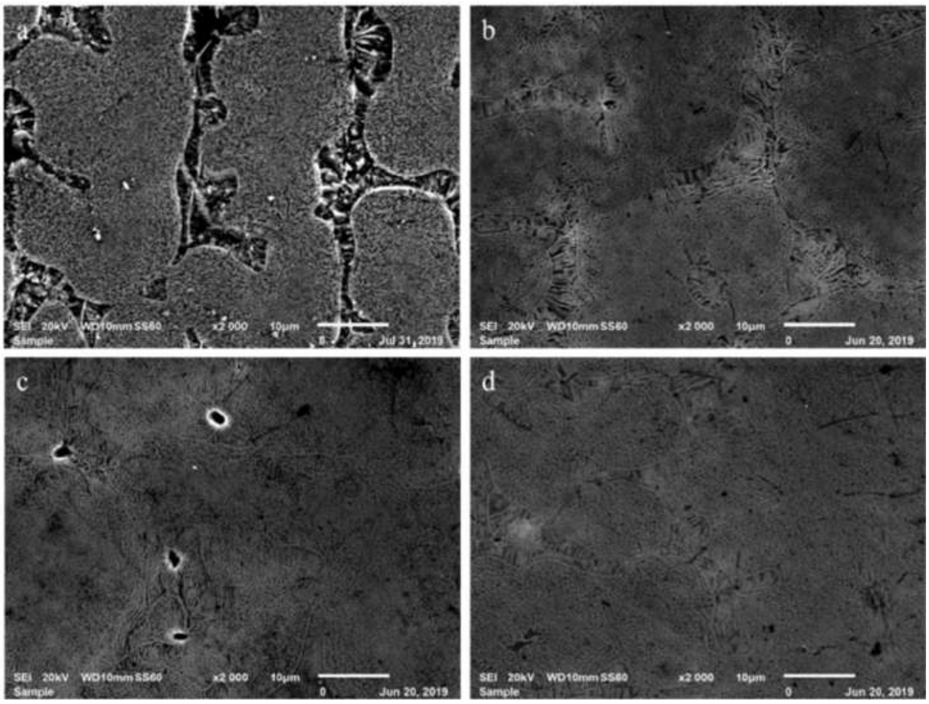
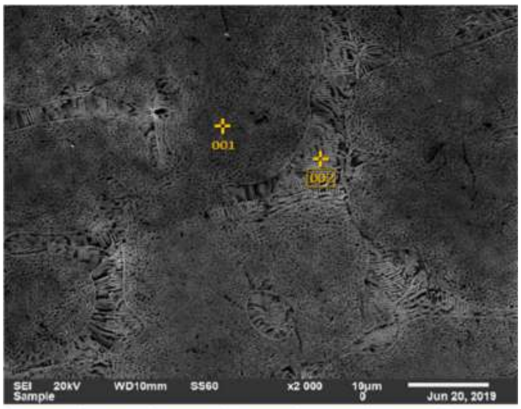


Figure 1. SEM microstructures of **(a)** as-cast and **(b)** heat-treated alloys, at 400, **(c)** 600 and **(d)** 800 ºC.



	Al	Cr	Fe	Mn	Ni	V
Point 1	7.04	20.29	22.14	15.41	17.58	17.54
Point 2	12.6	12.85	16.32	15.76	29.66	12.81

Figure 2. SEM image and EDS chemical composition (%) of alloys annealed at 400 ºC.

The synthesized alloys chemical compositions were determined by EDS (Fig. 3). The differences in compositions, specified as point 001 and 002 regions, are responsible for the diverse morphologies that resulted in different micro-hardness and compressive strength properties. In the point 1, the ID microstructure consisted mainly of Fe-Cr, being considered as an ordered Fe-rich phase (FCC) [26] that mostly results in lower mechanical properties.

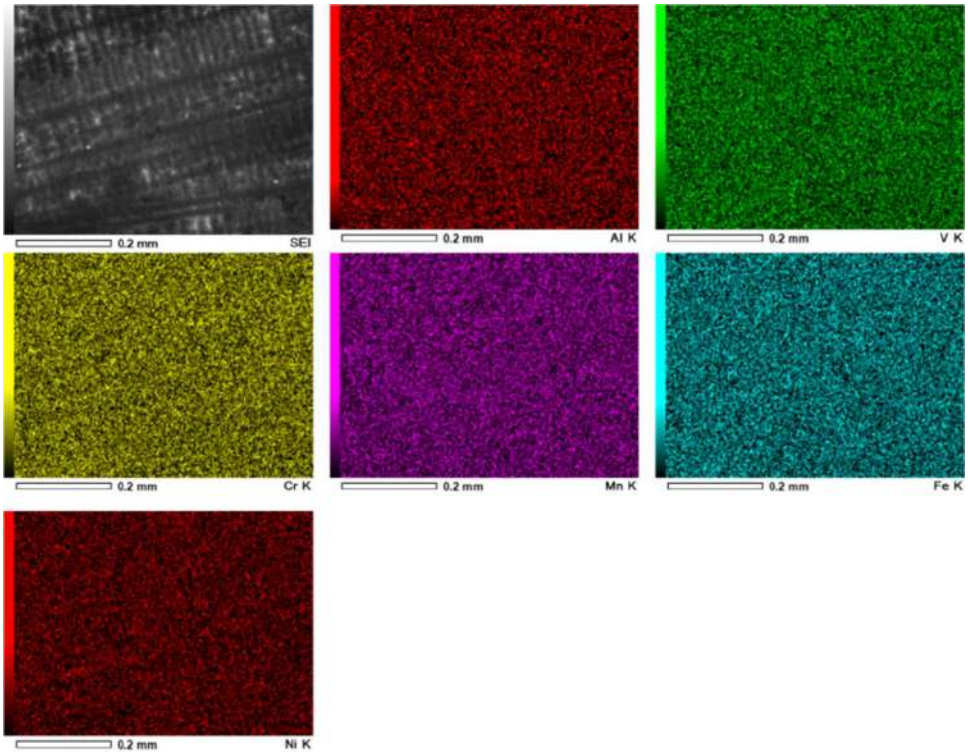


Figure 3. EDS map of the synthesized alloys.

Micro-hardness results

The micro-hardness values of the as-cast and heat-treated AlCrMnFeNiV HEA samples are presented in Fig. 4. An improvement in hardness can be noticed on samples that were exposed to 400 and 600 ºC, in a furnace, for 2 h. An increase in the heat-treatment temperature to 800 ºC resulted in a drastic decrease in the HEA micro-hardness properties. Several authors [27-29] mentioned that HEAs can lead to the development of solid solution phases in a microstructure, which could result in good micro-hardness properties, for potential advanced engineering applications. The heat-treatment processing of materials is also known for either the refinement or enlargement of the grains structure. The heat-treatment at temperatures below and above 600 ºC resulted in a micro-hardness of 556.8 and 590 HV, respectively. At 800 ºC, the micro-hardness was 540 HV. This is mostly attributed to the enlargement of grains, or to the phase transformation during the heat-treatment. However, the resulting grains of the 800 ºC heat-treated sample appear to be smaller. Hence, the phase transformation could be the reason behind the micro-hardness decrease in the heat-treated alloy. Generally, the heat-treated HEAs show better micro-hardness properties than those of other competitive materials, such as Ti alloys and SS [30-32].

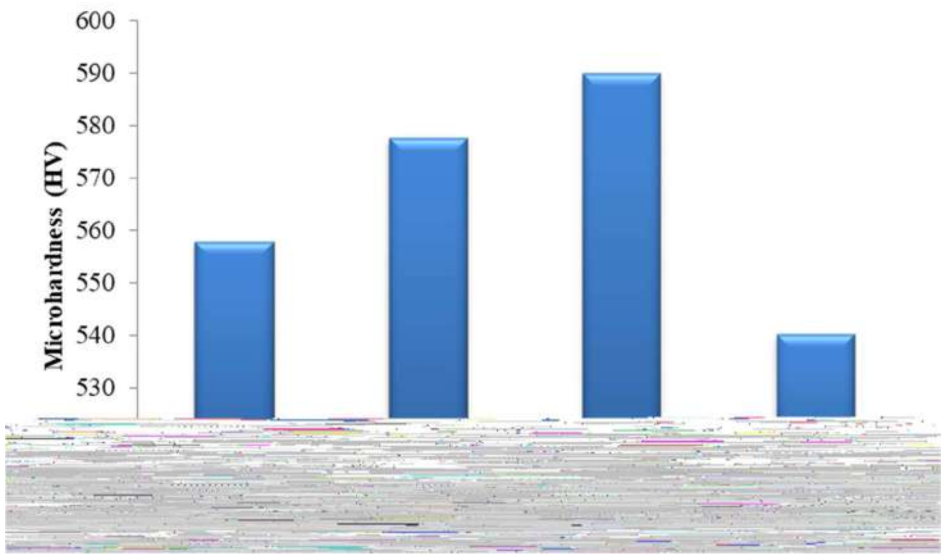


Figure 4. Micro-hardness properties of the as-cast and heat-treated HEA samples.

Compressive strength results

Fig. 5 shows the compression curves of the equi-atomic AlCrMnFeNiV HEAs, as-cast, and heat-treated, at 600 and 800 ºC. From the ultimate compressive strength (UCS), the as-cast HEA recorded 1776 MPa, with a strain of 13.7%. After the heat-treatment, at 600 ºC, there was a significant increase in strength and elongation, to 1999.65 MPa and 24%, respectively. The greater strength could be attributed to related high micro-hardness properties of the as-cast HEA. The annealing at more than 600 ºC triggered a major alteration in the HEA mechanical properties.

Generally, the high strength of the samples is attributed to the as-cast HEA phase formation. The FCC is identified as a stable solid solution phase, and characterized by the balanced elasticity and poor high temperature properties. However, the softness contributes to an increase in the HEA ductility. As the heat-treatment temperature increased to 800 ºC, the yield strength was reduced to ≈1871 MPa, with an elongation of 22%. The heat-treatment temperature to 800 ºC pulled down the alloy yield strength and ductility. The decrease in strength could be ascribed to a lower observed micro-hardness, as a result of the phase transformation after the HEA heat-treatment.

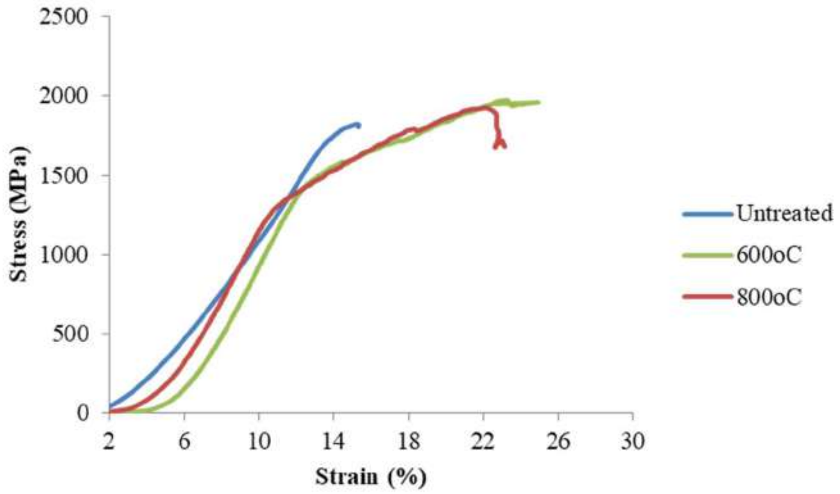


Figure 5. Compressive strength results of the as-cast and heat-treated HEAs.

Electrochemical behavior

Fig. 6 shows the linear polarization curves of the as-cast, achieved via arc melting, and of the heat-treated HEAs, respectively.

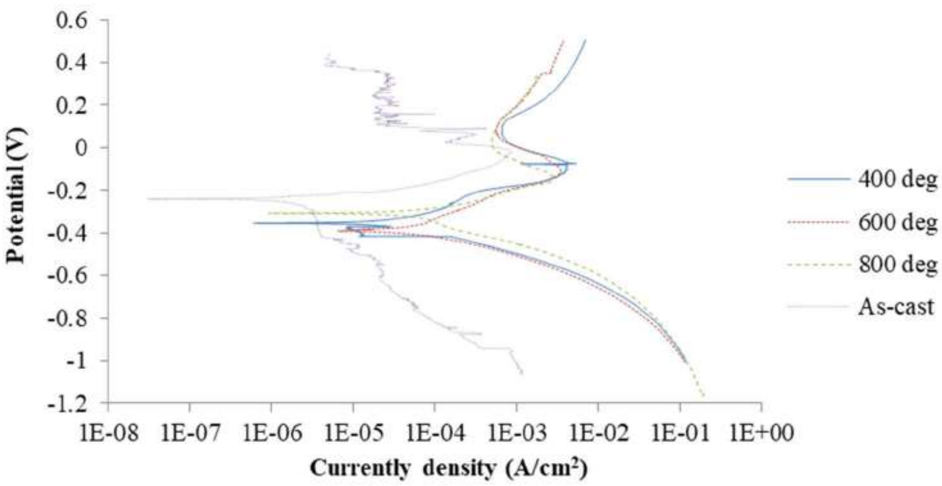


Figure 6. Linear polarization curves for as-cast and heat-treated samples in 0.5 M H_2SO_4.

The influence of the annealing on the alloy sample was investigated, and it displayed an improvement in the corrosion resistance property; despite having a dissimilar polarization behaviour in the J and V, it showed some differences in the magnitude of the passive region and passive J, as compared to those of the as-cast HEA. The as-cast HEA corrosion performance was negatively affected in 0.5 M H_2SO_4. This is evident on the V negative shift. However, the general good performance of the synthesized HEAs could be attributed to the thin film protective layer resulting in high cathodic protection. Most of the synthetized high entropy alloys tend to form a passive oxide layer, when exposed to acidic environments. These results are aligned with findings [33, 34] which showed that the AlCoCrFeNi high entropy alloy displayed superior properties in a H_2SO_4 acidic solution.

Fig. 7 shows the linear polarization curves of as-cast and heat-treated AlCrFeMnNiV HEAs in 3.5% NaCl. The heat-treatment temperature effect was evaluated. Many authors stated that HEAs alloys are very resistant to corrosion in marine and acidic environments. Generally, both as-cast and heat-treated HEAs show better corrosion resistance than other conventional materials, such as Ti alloys and SS [11, 35]. The as-cast alloy polarization curves show that, during the corrosion test, it developed an oxide protective layer which prevented current injection into the sample, so that a low J and a high V are evident. The heat-treated samples anodic branch shows that the formed oxide was unstable. Therefore, they have lower corrosion resistance than the as-cast alloys. On the other hand, the passive J shows a dissimilar trend. However, there was a negative shift of J in the as-cast material, compared to the heat-treated samples.

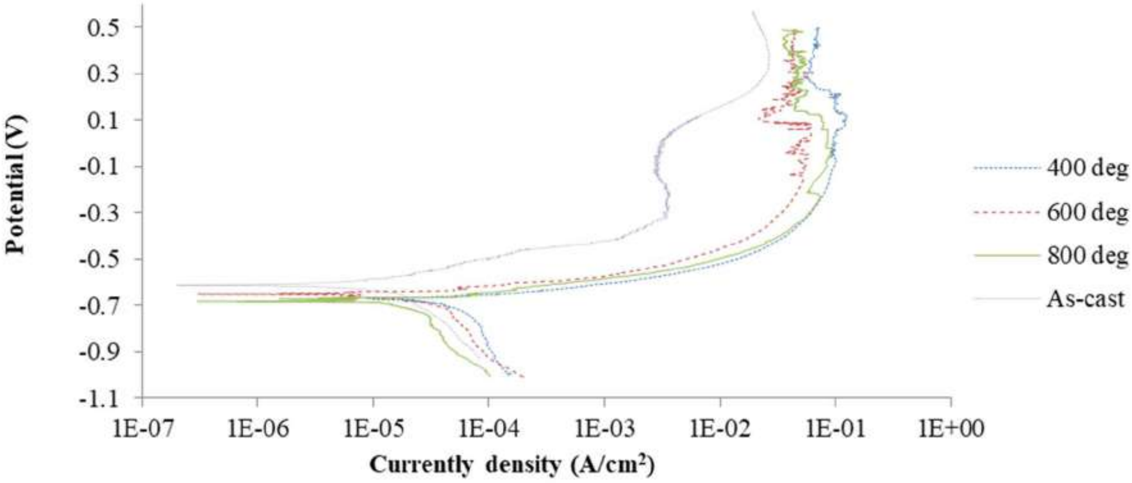


Figure 7. Linear polarization curves for as-cast and heat-treated samples in 3.5% NaCl.

Conclusions

AlCrFeMnNiV HEA was successfully synthetized by means of arc-melting and casting. The effect of the heat-treatment temperature on the micro-structural evolution, micro-hardness, compressive strength and corrosion behaviour of the developed HEAs was investigated.

- EDS analysis confirms the presence of the elements used to develop the alloy, and the SEM images display no cracks or initiation of stress.
- Maximum micro-hardness of 590 $HV_{0.1}$ was achieved at a heat-treatment temperature of 600 ºC, which also resulted in a compressive strength and an elongation of 1999.65 MPa and 24%, respectively.
- The heat-treated AlCrFeMnNiV HEA showed outstanding corrosion resistance properties in both H_2SO_4 and NaCl.

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