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Evaluation of microstructural and corrosion resistance of as-cast Cu$_{45}$Mn$_{25}$Al$_{15}$Fe$_{5}$Cr$_{5}$Ni$_{5}$ high entropy alloy

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Abstract

Cu$_{45}$Mn$_{25}$Al$_{15}$Fe$_{5}$Cr$_{5}$Ni$_{5}$ high entropy alloy was prepared using casting route. Detailed microstructural analysis revealed the formation of dendritic structure in the as-cast sample. The results showed that the dendrite (DR) regions are riched with Cu and Mn, while the inter-dendrite (ID) regions are riched with Cr and Fe. Metallographic investigation was conducted using optical microscope and scanning electron microscope as well. Determination of phase analysis was carried out using x-ray diffraction. Corrosion properties were studied via Auto LAB PGSTAT 302N, supplied with Nova software. The investigated alloy demonstrates superior corrosion resistance with average corrosion rate 0.056 mm year$^{-1}$.

1. Introduction

High entropy alloys are considered as new set of metallic alloys that has defined since the first published work in 2004 [1–6]. The main idea behind the new concept of high entropy alloys relies on the influence of increasing configurational entropy of mixing on reducing the number of present phases and stabilizing a solid solution phase. A wide spectrum of high entropy alloys was developed with various chemical compositions during the past decade, emphasizing on two main categories of high entropy alloys: equiatomic and non-equiaxial alloys.

High entropy alloy is defined also as an alloy, which contains at least five principle elements in equal atomic percent [7, 8]. In addition, many reports demonstrate high entropy alloys as the presence of at least five major elements in a range of (5 up to 35) atomic percentage, the last definition represents the category of non-equiaxial high entropy alloys. Yao et al [9], developed a non-equiaxial, strong, and ductile FeMnNiCoCr high entropy alloy that is considered as a deviation from the classic Cantor alloy.

Cu containing high entropy alloys attracted attention due to its unique solidification path in terms of presence of liquid phase separation phenomenon [10–12]. The addition of Cu to FeMnCrNiCo alloy shows the formation of two fcc phases fcc1/fcc2 dual structure [10–17]. In addition, Tong et al [18], investigated the effect of Al on the mechanical properties of CoCrCuFeNi system. It has been found that increasing of Al content transforms the fcc crystal structure into bcc and increase the hardness from HV 133 to 655. Park et al [19], investigated the behavior of CoCrCuFeNi high entropy alloy upon recrystallization process. They indicated that the dual phase microstructure was stable even after annealing at 1100°C. Xu et al [20], elucidated the influence of mixing enthalpy as well as rapid solidification on the microstructure of AlxCoCrCuFeNi. It was shown that the microstructure evolved from fcc to bcc with increasing the content of Al. Rao et al [21], investigated the influence of Mn content on the microstructure formation of Fe$_{0.4}$Cr$_{0.4}$NiMn$_{0.4}$Cu.

There are quite similar high entropy alloys containing Cu that were examined in several corrosive mediums. Also, the segregation phenomenon and formation of dendritic structure influenced the corrosion resistance properties of this category of high entropy alloys. Therefore, the current work aims at developing a non-equiaxial Cu-rich alloying system, which is deviating from the equiaxial AlCrCuFeMnNi high entropy alloy. The microstructure and corrosion resistance of the casted alloy will be investigated.
2. Experimental

An alloy with nominal composition $\text{Cu}_{45}\text{Mn}_{25}\text{Al}_{15}\text{(Fe Cr Ni)}_{15}$ was prepared using high purity metals of 99.9% copper, aluminum, nickel, manganese, iron, and chromium. The charge was arc-melted under a high purity argon atmosphere, and re-melted three times to ensure homogeneity. Samples were cut from the solidified ingot for homogenization process. The homogenization process was conducted as follows: samples were heated up to 900 °C for 2 h with a heating rate of 10 °C min$^{-1}$ followed by water quenching. The chemical composition of the as-cast ingot was analyzed using Niton XL3T XRF mobile analyzer. Samples were cut using a wire cutting machine for optical microscopy, scanning electron microscope (SEM), and x-ray diffraction (XRD). Samples of 10 mg were prepared for differential scanning calorimetry (DSC) investigation using a heating/cooling rate of 10 °C min$^{-1}$. Table 1 shows the chemical composition of the as-cast ingot.

The potentiodynamic polarization measurements were conducted in a typical three electrode cell containing 3.5% NaCl solution at room temperature (25 °C). This process was utilizing a computerized potentiostat (Auto LAB PGSTAT 302N) in addition to Nova software for data acquisition and analysis. The measurements were performed at scanning rate of 1 mV s$^{-1}$ in a range of $-400$ up to $600$ mV. The corrosion potential ($E_{corr}$) and corrosion current density ($I_{corr}$) were extracted from the polarization curves by Tafel extrapolation method.

![Figure 1. (a) Optical micrograph of the as-cast sample, (b) SEM micrograph of the as-cast sample, and (c) SEM higher magnification showing the Cu-Mn rich precipitates.](image)

| Table 1. Nominal & actual chemical composition of the as-cast ingot. |
|------------------|---|---|---|---|---|---|
| Element (% at)   | Cu | Mn | Al |Ni | Fe | Cr |
| Nominal composition | 45 | 25 | 15 | 5 | 5 | 5 |
| Actual composition | 44.02 | 26.01 | 12.89 | 6.19 | 5.58 | 5.31 |

The potentiodynamic polarization measurements were conducted in a typical three electrode cell containing 3.5% NaCl solution at room temperature (25 °C). This process was utilizing a computerized potentiostat (Auto LAB PGSTAT 302N) in addition to Nova software for data acquisition and analysis. The measurements were performed at scanning rate of 1 mV s$^{-1}$ in a range of $-400$ up to $600$ mV. The corrosion potential ($E_{corr}$) and corrosion current density ($I_{corr}$) were extracted from the polarization curves by Tafel extrapolation method.
3. Results and discussion

3.1. Microstructure & XRD analysis

Figure 1 represents the microstructure of the as-cast sample, indicating the formation of a dendritic structure. It can be seen also the formation of very fine Cu-Mn rich precipitates in the dendritic region (DR). Ren et al [22, 23], showed a similar microstructure in two different high entropy alloys Cu$_2$Cr$_2$FeNi$_2$Mn and Cu$_2$CrFe$_2$NiMn$_2$, where the DR regions are riched with Cu and Mn and the inter-dendritic regions (ID) are riched with Fe and Cr. Figure 2 depicts the XRD pattern of the as-cast sample. It conveys the existence of two bcc phases associated with both DR and ID. Soare et al [24] reported a similar result, suggesting that one of the two bcc structures is ordered and the other is disordered. In addition, the peaks of bcc1 phase are quite similar to L2$_1$ superlattice structure of Heusler AlCu$_2$Mn alloy; however, no superlattices peaks were observed.

![Figure 2. The XRD pattern of the as-cast sample.](image)

![Figure 3. Heating and cooling DSC curve of the as-cast sample.](image)
This might sound logic, as the Cu-Mn rich DR composition may be considered as a deviation from the stoichiometric Al$_{25}$Cu$_{50}$Mn$_{25}$ Heusler alloy.

The lattice parameter of the two bcc phases is 2.94 Å and 2.88 Å, respectively. In addition, the XRD peaks of bcc1 is wider than that of bcc2, which suggest a finer crystallite size for bcc1 phase compared to bcc2 phase.

### 3.2. Thermal analysis

Figure 3 demonstrates both heating and cooling DSC curves with heating/cooling rate of 10 °C min$^{-1}$. The sample is characterized by two distinct endothermic peaks on heating at 943 °C and 972 °C associated with melting of the inter-dendritic regions. This result may be due to uneven distribution of Cr, Fe, Al, and Cu in the ID regions as shown in table 2 and figure 4. Nevertheless, on cooling, the sample shows only one exothermic peak associated with the solidification of the ID. Furthermore, the heating curve of DSC reveals that very fine Cu-Mn precipitates dissolve at temperatures higher than 820 °C, which probably formed by spinodal decomposition on cooling [27]. While on cooling the precipitates do not form, which suggests the cooling rate is high enough to prevent their formation.

### 3.3. EDX analysis

Figure 4 illustrates the elemental mapping of all the constituting elements for both the as-cast and homogenized samples, respectively. The main feature of the as-cast sample is the uneven distribution of Cr and Fe in the ID. It is obvious that there are two distinct ID rich and depleted regions from Cr and Fe. In addition, the deviation in
Ni and Mn content in ID regions is relatively small. It can be seen also that an increase of Al content is associated with increasing the content of both Cr and Fe. Furthermore, the DR region is rich in Al, Mn, and Cu, while depleted in Fe and Cr.

The segregation phenomenon in this type of high entropy alloys may be attributed to the positive binary enthalpy of mixing between the pairs Cu–Cr and Cu–Fe. Table 3 shows the binary enthalpy of mixing values based on Miedema semi-empirical model. In addition, the enthalpy of formation for Cu–Cr with atomic ratio 1:1 is 18.530117 kJ mol$^{-1}$, $\Delta H$(Cu in Cr) is 49.286705 kJ mol$^{-1}$, and $\Delta H$(Cr in Cu) is 49.793041 kJ mol$^{-1}$ [29]. As a result of positive enthalpy of mixing, segregation phenomenon will be promoted leading to the formation of ID rich in Cr and Fe.

The possible explanation of the inhomogeneous distribution of Cr and Fe in ID of as-cast sample may be due to the occurrence of liquid phase separation (LPS) in the ID regions after the growth of primary DR, which is confirmed by Munitz [30]. For the Al$_2$CrCuFeNi$_2$ alloy, constitutional LPS occurred in the ID liquid, as the ID liquid decomposed into Cr–Fe-rich Liquid$_1$ and a Cu-rich Liquid$_2$. It may be also attributed to the influence of sluggish diffusion in multi-component alloys. Tsai et al [31], clarified that sluggish diffusion core effect is due to the fluctuation in lattice potential energy (LPE), which is a consequence of the change in total interaction energy from one lattice site to another. Thus, the migration of any atom relies on the bond interaction energy (BIE), which depends on the binary enthalpy of mixing between each possible pair of unlike atoms. For instance, considering the diffusion of Cr atom in the bcc crystal to a vacancy in (1/2, 1/2, 1/2) position. Considering the fact that there are eight neighbors to this vacancy, it is most probably that Cr atoms will be surrounded by Cu or Ni and Mn content in ID regions is relatively small. It can be seen also that an increase of Al content is associated with increasing the content of both Cr and Fe. Furthermore, the DR region is rich in Al, Mn, and Cu, while depleted in Fe and Cr.

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Table 2. EDX analysis of the as-cast phases.

| Element (%) at (%) | Cu | Mn | Al | Ni | Fe | Cr |
|-------------------|----|----|----|----|----|----|
| ID (rich in Fe & Cr) | 27.13 | 22.41 | 23.38 | 12.24 | 7.43 | 7.40 |
| ID (depleted in Fe & Cr) | 49.13 | 21.09 | 11.69 | 15.87 | 1.56 | 0.66 |
| DR | 49.84 | 26.84 | 14.51 | 7.19 | 1.26 | 0.36 |
| Cu rich precipitates | 55.82 | 26.52 | 9.88 | 6.25 | 0.98 | 0.56 |

Table 3. Mixing enthalpies of atomic pairs in (kJ mol$^{-1}$) [28].

| Elements | Cr | Fe | Mn | Ni | Al |
|----------|----|----|----|----|----|
| Cu | 12 | 13 | 4 | 4 | $-1$ |
| Cr | $-1$ | $-1$ | 2 | 7 | $-10$ |
| Fe | $0$ | $-2$ | $-11$ | |
| Mn | $-8$ | $-19$ | |
| Ni | $-22$ | |

Figure 5. (a) Cathodic polarization measurement of the as-cast alloy, (b) Nyquist plot of the as-cast alloy.
As Mn. As, table 4 shows the binary enthalpy of mixing between Cr-Cu and Cr-Mn is positive, leading to Cr atoms segregation alongside with Fe atoms. In addition, Almazouzi et al. [32, 33], indicated that Do(Ni in Cu) > Do(Mn in Cu) > Do(Cr in Cu) > Do(Fe in Cu), where Do is the maximal diffusion coefficient (at infinite temperature). As a consequence, as the temperature falls down upon solidification of ID regions, Cr and Fe atoms tend to segregate.

The concept of design is deviating from the equiatomic composition, in other words exploring non-equiatomically portioned compositions. Many reports showed that stabilizing a single solid solution is not strongly related to maximizing the entropy of mixing [34–38]. This means that the entropy curve has a weak maximum and no steep changes, except for the case of very small concentrations [39]. Here, Cu_{45}Mn_{25}Al_{15}Fe_{5}Cr_{5}Ni_{5} possesses ideal entropy of mixing 1.44R which is closely approaching the criteria of 1.5R, where R is the universal gas constant. For example, restricting the content Ni in the proposed alloy minimizes the possibility of formation of Al-Ni intermetallic. It should be taken into account that the Al-Ni(B2) compounds are thermodynamically stable at elevated temperature [10], while the Cu-Mn rich phase has a lower melting point nearly in the range of 1050 °C [12]. As a result, there will be two competing phases during solidification; however, controlling the Ni content in conjunction with increasing the entropy of mixing will promote the formation of a solid solution instead of intermetallic compounds.

3.4. Corrosion behavior

3.4.1. Potentiodynamic polarization measurements

Figures 5(a) and (b) shows the cathodic polarization and potentiostatic impedance behaviors of the as-cast alloy in 3.5% NaCl at room temperature (25 °C). The as-cast sample demonstrates a superior electrochemical resistance as well as low corrosion current density. The polarization resistance (Rp) is related to corrosion current density (i_{corr}) by the following equation [40]:

\[ i_{corr} = \frac{\beta_a \beta_c}{2.3(\beta_a + \beta_c)} \frac{1}{R_p} \]  \hspace{1cm} (1)

Where \( \beta_a \) and \( \beta_c \) are Tafel slopes (cathodic and anodic).

The electrochemical parameters resulted from the electrochemical polarization tests of the as-cast alloy are listed in table 4. Furthermore, table 5 some values of corrosion parameters to compare them with the studied
alloy. It can be seen that the current alloy outperforms most of them, demonstrating superior corrosion resistance. Generally, higher corrosion potential and lower corrosion current density indicates superior corrosion resistance.

Figure 7. EDX analysis of the corroded surface showing three different spectrums.

| Alloy                  | $E_{\text{corr}}$ (V) | $i_{\text{corr}}$ (μA cm$^{-2}$) | References |
|-----------------------|-----------------------|----------------------------------|------------|
| As-cast (Cu$_{45}$Mn$_{25}$Al$_{15}$Fe$_{5}$Ni$_{5}$Cr$_{5}$) | $-$0.308              | 5.18                             | Current study |
| AlFeNiCoCuCr (as-cast) | $-$0.237              | 216.32                           | [24]        |
| AlFeNiCoCuCr (remelted)| $-$0.215              | 130.11                           | [24]        |
| AlFeNiCoCuCr (annealed)| $-$0.189              | 98.93                            | [24]        |
| AlCrCuFeMnNi (as-cast) | $-$0.282              | 3.9                              | [24]        |
| AlCrCuFeMnNi (re-melted)| $-$0.265              | 3.6                              | [24]        |
| 304L                  | $-$0.415              | 4.7                              | [24]        |
| FeCoNiCrCu0.5          | $-$0.49               | 0.72                             | [41]        |
| FeCoNiCrCu             | $-$0.53               | 1.23                             | [41]        |
| AlCoCrFeNi             | $-$0.17               | 0.073                            | [42]        |
| Al$_2$CrFeCoCuTi       | $-$0.51               | 68                               | [43]        |
| Al$_2$CrFeCoCuTiNi0.5  | $-$0.43               | 32                               | [43]        |
| Al$_2$CrFeCoCuTiNi1    | $-$0.22               | 13                               | [43]        |
| Al$_2$CrFeCoCuTiNi1.5  | $-$0.48               | 64                               | [43]        |
| Al$_2$CrFeCoCuTiNi2    | $-$0.50               | 67                               | [43]        |

Table 5. Electrochemical parameters of as-cast alloy compared to some alloys reported in literature in 3.5% NaCl solution.
The corrosion rate can be determined from the following equation [44]:

\[
\text{Corrosion rate (mm year}^{-1}\text{)} = \frac{3.27 \times 10^{-3} \times i_{\text{corr}}}{\rho \times E.W}
\] (2)

Where \( \rho \) is the density of the alloy and E.W is the equivalent weight of the alloy.

Figure 6 shows the corroded zone and the de-corroded zone, where the ID zones are characterized with corrosion pitting. This observation can be attributed to the existence of both rich and depleted zones with Cr inside the ID regions. So, the formation of Cu and Cr rich and depleted zones will be responsible for the occurrence of galvanic corrosion. The higher degree of elemental segregation and non-uniformity of the microstructure will result in increasing the probability of galvanic corrosion. Generally, the elemental segregation that influences corrosion rate could be estimated from the following equation:

\[
S_{\text{R}} = \frac{C_{\text{DR}}}{C_{\text{ID}}-1}
\] (3)

Figure 7 illustrates an EDX analysis of the corroded surface in order to comprehend the microstructure response to the corrosive medium. Primarily, the ID regions where corrosion pitting was observed, is characterized with Cl\textsuperscript{−} ions penetration. In sea water, Cl\textsuperscript{−} ions penetrate and attack the passive layer in its weak points. Here, the weak points are the spots with higher concentration of Cu atoms that combine with dissolved oxygen forming metastable oxide layer, then decompose readily. This decomposition manifests itself with corrosion pitting as well as higher concentration of Cl\textsuperscript{−} ions, indicating lower degree of Cl\textsuperscript{−} adsorption/penetration. The chemical analysis of the DR regions demonstrates nearly no sign of Cl\textsuperscript{−} adsorption/penetration, confirming the explanation that the elemental segregation inside ID region is the responsible for galvanic corrosion.

3.4.2. Immersion test

The corrosion rate of the investigated alloy in 3.5% NaCl as a result of 672 h immersion test can be deducted by the following equation [24]:

\[
\text{Corrosion rate (mm year}^{-1}\text{)} = \frac{8.76 \times 10^4 \times W}{t \times A \times D}
\] (4)

Where \( W \) is the total weight loss in gm, \( t \) is the exposure time in hrs, \( D \) stands for density in gm/cm\textsuperscript{3}, and \( A \) is the exposed area in cm\textsuperscript{2}. Table 6 provides the calculated corrosion rate after 672 h immersion in 3.5% NaCl. It can be seen that the weight loss is 0.0286 gm, which is considered too low.
Table 6. Weight loss and corrosion rate of the as-cast alloy.

| Condition | Pre-corrosion mass (g) | Corroded mass (g) | Corrosion rate (mm year⁻¹) |
|-----------|-------------------------|-------------------|---------------------------|
| As-cast   | 6.4182                  | 6.3987            | 0.056                     |

Figure 8 depicts the change of weight loss versus the exposure time, where the weight loss plunged during the first 150 h of the test. This observation suggests the formation protective passive layer after nearly 150 h. Furthermore, during the last 500 h of the test, the weight loss is nearly constant with a slight deviation.

4. Conclusion

In summary, Cu₄₅Mn₂₅Al₁₅Fe₅Cr₅Ni₅ showed a dendritic structure on solidification as well as the formation of very fine Cu-Mn rich precipitates embedded in the DR regions. The results of DSC demonstrated that ID regions melt at a temperature range of 940 °C to 970 °C. In addition, the investigated alloy shows also outstanding corrosion resistance properties; as it demonstrates lower current density in potentiodynamic polarization test as well as low average corrosion rate upon immersion test. The current results pave the way for economic and corrosion resistant high entropy alloy.

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