The Effect of Mn Content on the Microstructure and Properties of CoCrCu$_{0.1}$Fe$_{0.15}$Mo$_{1.5}$Mn$_{x}$Ni Near Equiatomic Alloys

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The effect of Mn content on the microstructure and properties of a newly-designed CoCrCu$_{0.1}$Fe$_{0.15}$Mo$_{1.5}$Mn$_{x}$Ni (where $x$ is atomic ratio, $x = 0.05, 0.12$ and $0.3$) near equiatomic alloys are investigated in this study. Typical dendrites and interdendritic structures are observed. According to EDS, the primary dendrites are enriched with Co and Mo, while at the interdendritic region Cr-rich and (Co, Fe, Ni)-rich structures are obtained. The X-ray diffraction patterns of the CoCrCu$_{0.1}$Fe$_{0.15}$Mo$_{1.5}$Mn$_{x}$Ni alloys indicate that all the alloys exhibit simple BCC, FCC solid solution phase and $\mu$ phase. The volume fraction of FCC phase increases when Mn element was added, confirming that Mn is a FCC-forming element. Notely, the hardness of the alloys dropped from HV 715 to HV 392 when the Mn content changed from 0.05 to 0.3. The wear resistance declines as the Mn content increases. The optimal wear resistance was obtained in CoCrCu$_{0.1}$Fe$_{0.15}$Mo$_{1.5}$Mn$_{0.05}$Ni near equi-atomic alloys.

Keywords: microstructure, near equiatomic alloys, phase structure, hardness, wear resistance

1. Introduction

High-entropy alloys (HEAs), defined as alloys composed of at least five major metallic elements each having an atomic percentage between 5% and 35%, have been extensively developed. HEAs are usually formed into solid solution, but they include other phases in their wide-sense. Previous studies have indicated that HEAs have high strength, high hardness, prominent resistance to tempering softening, superior abrasion resistance, oxidation resistance and good corrosion resistance. Therefore, the high-entropy alloys will be favored which meet different requirements of properties under different conditions by adjusting alloy compositions.

Single FCC structure was obtained in equiatomic CoCr-FeMnNi$^{2}$ alloy. It is investigated that Cr and Fe are segregated into the dendrite spines and Mn enriches in the interdendritic region. Moreover, the mechanical properties of CoCrFeMnNi alloy were investigated at temperature in the range of 77–263 K, tensile test showed that the yield and ultimate strengths of this high-entropy alloy increase as the temperature is decreased. Replacing one or other of the components with other transition metals leads to two phase or polygrain structure and hardness and plasticity of AlCoCrCuFeNi alloy. Additionally, it is found that Mo addition is intended to promote the strength and hardness of AlCoCrCuFeNi alloy. As Fe content is increased the microstructure change from “dendritic” to “polygrain” in AlCoCrFe$_{x}$Mn$_{0.5}$Ni alloy, at the same time the hardness and wear resistance decline. Cu element intends to segregate at the grain boundary, and the soft Cu-rich region also lowers the wear resistance. Based on the above-mentioned researches, a newly designed CoCrCu$_{0.1}$Fe$_{0.15}$-Mo$_{1.5}$Mn$_{x}$Ni near equiatomic alloy system is prepared in this study, in which the molar ratios of Cu and Fe are limited to 0.1 and 0.15, and that of Mo is increased to 1.5. Additionally, the effect of Mn content on the microstructure and properties of CoCrCu$_{0.1}$Fe$_{0.15}$Mo$_{1.5}$Mn$_{x}$Ni near equiatomic alloys are investigated.

2. Experimental Procedure

Approximately 50 g ingots of CoCrCu$_{0.1}$Fe$_{0.15}$Mo$_{1.5}$Mn$_{x}$Ni (subscript value is molar ratio, $x = 0, 0.05, 0.12, 0.3$) near equiatomic alloys were prepared by the high temperature electric arc furnace melting. The samples were sectioned and polished for microstructural and compositional characterization using scanning electron microscope (SEM, JEOL-5410) and X-ray energy dispersive spectrometry (EDS), X-ray diffractometer (XRD, Rigaku ME510-FM2) at a scanning speed of 6°/min and a scanning range from 30° to 80° using a copper target and an applied voltage and current of 30 KV and 20 mA respectively. Hardness testing was tested by Vickers micro-hardness tester model UHT-1 with 50 g load. Wear behavior of the alloys were investigated by ball-on-disk sliding using the UMT-2 friction and wear testing machine which taken Al$_{2}$O$_{3}$ ceramic ball as dual material with its diameter equal to 9.38 mm. The specifications of specimens (15 mm × 15 mm × 5 mm) were prepared and fixed in the center of the disk. The radius of wear track was kept constant at 5 mm. The sliding speed and sliding time were 400 r/min and 20 min, respectively, with a normal load of 20 N. The worn surface was also investigated using SEM. The wear rate is defined as follows:

$$ W_r = \frac{C \cdot S}{F \cdot L} $$

where $W_r$ is the wear rate, mm$^3$ N$^{-1}$ mm$^{-1}$, $C$ is perimeter of wear crack, mm; $S$ is wear track area, mm$^2$; $L$ is the sliding distance and $F$ is the load.
3. Results and Discussion

3.1 Microstructure of CoCrCu0.1Fe0.15Mo1.5MnNi near equiatomic alloys

Three structures are found in CoCrCu0.1Fe0.15Mo1.5MnNi (x = 0.05, 0.12, 0.3) near equiatomic alloys, labeled as A, B and C in Fig. 1. According to Table 1, the composition of primary dendrites (zone A) is detected to be enrich with Co and Mo elements. Conversely, region C in the interdendritic region is rich in Cr element, while Co, Fe and Ni elements are segregated in region B. Notely, Cr content increases dramatically in region C with the increasing of Mn content. Surprisingly, Cu element is almost non-existent in region A. The mixing enthalpies between Cu and most other elements in alloys are positive, which usually leads to the repulsion atoms. The mixing enthalpies between Cu and (separately) Co, Cr, Fe, Mo, Mn and Ni are +6, +12, +13, +19, +4 and +4 kJ/mol, respectively.16)

3.2 Constituent phase and hardness

The X-ray diffraction patterns of CoCrCu0.1Fe0.15Mo1.5MnNi (x = 0.05, 0.12, 0.3) alloys are shown in Fig. 2. It is found that all alloys exhibit simple BCC, FCC solid solution phase and $\mu$ phase. The $\mu$ phase has been shown to exist in the binary Co-Mo and Fe-Mo phase diagrams, as well as in the ternary system of these three elements.17 Also, it is found that the relative intensity of FCC phase is stronger when Mn content is up to 0.3. On the contrary, the intensities of BCC and $\mu$ phase Bragg peaks get weaker and weaker with the increase of Mn content. When comparing EDS results with XRD results, it is noted that the region A is $\mu$ phase, region B is FCC and region C is BCC.
In order to understand the volume fraction of BCC, FCC and \( \mu \) phase on the hardness of the alloys, the volume fractions of BCC, FCC and \( \mu \) phase are calculated by the following formula: \(^{18)}\)

\[
W_p = \frac{P}{\Sigma P_i} \times 100\% \tag{2}
\]

Where \( W_p \) is the volume fraction of the phase, \( P \) is the peak intensity of a given phase in the XRD pattern, \( i \) is the number of the phase, and \( \Sigma P_i \) is the total peak intensity of all phases in the XRD pattern. Table 2 shows the volume fraction of BCC, FCC and \( \mu \) phase and the hardness of CoCrCu\( _{0.1} \)-Fe\( _{0.15} \)Mo\( _{1.5} \)Mn\( _x \)Ni alloys. It indicates that the volume fraction of FCC phase increases with the increase of Mn content. It proves that Mn is a FCC-forming element.

Moreover, the value of hardness presents a remarkable decreasing trend. When Mn content changes from 0.05 to 0.3, the hardness of the alloys dropped from HV 715 to HV 392. Obviously, it is related to the relative volume of BCC, FCC and \( \mu \) phase. It can be found that the alloys with less volume fraction of BCC and \( \mu \) phase have a low hardness level. On the contrary, the alloys with more volume fraction of BCC and \( \mu \) phase have a higher hardness. In particular, the alloy with the highest amount of BCC and \( \mu \) phase has the highest hardness of 714.68 HV.

### 3.3 Wear behavior

#### 3.3.1 Wear resistance

The effect of Mn content on the wear rate of CoCrCu\( _{0.1} \)-Fe\( _{0.15} \)Mo\( _{1.5} \)Mn\( _x \)Ni alloys is shown in Fig. 3. The wear rate increases as the manganese content increases. Also, it can be seen that the wear rate of CoCrCu\( _{0.1} \)-Fe\( _{0.15} \)Mo\( _{1.5} \)Mn\( _x \)Ni alloys is sensitively related to their hardness in transition from BCC and \( \mu \) phase to FCC phase. It is in agreement with Khruschov’s conclusion, that is, the wear resistance of materials is in general proportional to their Vickers’ hardness. \(^{19)}\) It is revealed that the alloy has the optimal wear resistance when the value of manganese is up to 0.05. As discussed earlier, BCC and \( \mu \) phase have higher mechanical strength than FCC phase. It is reasonable that wear resistance becomes better with increasing amount of BCC and \( \mu \) phase.

#### 3.3.2 Worn surface

The morphologies of wear surface are obtained and shown in Fig. 4. Obvious differences in wear surface morphology are seen as a function of manganese content. With the

![Fig. 3 The wear rate of CoCrCu\( _{0.1} \)-Fe\( _{0.15} \)Mo\( _{1.5} \)Mn\( _x \)Ni alloys.](image)

![Fig. 4 Microstructure of worn surface of CoCrCu\( _{0.1} \)-Fe\( _{0.15} \)Mo\( _{1.5} \)Mn\( _x \)Ni (\( x = 0.05, 0.12, 0.3 \)) alloys.](image)
increasing manganese content, the wear surface and wear mechanism are different. For \( x = 0.05 \) alloy, the worn surface is relatively flat with shallow grooves, which are caused by plastic deformation. It indicates that the wear mechanism is abrasive wear. For CoCrCu\(_0.1\)Fe\(_{0.15}\)Mo\(_1.5\)Mn\(_{0.12}\)Ni alloy, the surface is deeply grooved with the advent of local peeling pit simultaneously. Abrasive wear is still dominant although adhesive wear occurs in some region. An increase in manganese content to 0.3 results in a rougher worn surface. Surprisingly, the zone of peeling pit is markedly bigger than that of CoCrCu\(_0.1\)Fe\(_{0.15}\)Mo\(_1.5\)Mn\(_{0.12}\)Ni alloy, which confirms that FCC phases are ineffective to improve the wear resistance. It is revealed that the optimal wear resistance obtained in CoCrCu\(_0.1\)Fe\(_{0.15}\)Mo\(_1.5\)Mn\(_{0.05}\)Ni alloys.

4. Conclusion

The effect of Mn content on the microstructure and properties of CoCrCu\(_0.1\)Fe\(_{0.15}\)Mo\(_1.5\)Mn\(_{X}\)Ni (\( x = 0.05, 0.12, 0.3 \)) near equiatomic alloys were studied. The following conclusions were made:

(1) Typical dendrites and interdendritic structures are observed. The primary dendrites enrich with Co and Mo element, while at the interdendritic region Cr-rich and (Co, Fe, Ni)-rich structures are obtained, respectively.

(2) All alloys exhibit simple BCC and FCC solid solution phases, as well as \( \mu \) phase.

(3) The volume fraction of FCC phase increases with the increase of Mn content. As a FCC-forming element, when Mn content changes from 0.05 to 0.3 the hardness of the alloys dropped from HV 715 to HV 392.

(4) The wear resistance declines as the Mn content increases. The optimal wear resistance obtained in CoCrCu\(_0.1\)Fe\(_{0.15}\)Mo\(_1.5\)Mn\(_{0.05}\)Ni alloys. The wear mechanism changes from abrasive wear to adhesive wear with the increase of Mn content.

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