Effects of Mo Element on Microstructure and Mechanical Properties of CoCrFeMnNi High Entropy Alloys

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Abstract. In order to improve the mechanical properties of CoCrFeMnNi high entropy alloy, CoCrFeMnNiMox high entropy alloy were prepared by adding different content of Mo to re-alloying. The microstructure and phase composition were analyzed by OM, SEM, EDS and XRD, and the mechanical properties were tested by tensile test. The effects of Mo content on the phase composition and microstructure of CoCrFeMnNi high entropy alloy were investigated, and the mechanism of its influence on mechanical properties was studied. The results showed that with the increase of Mo element content, the crystalline morphology of CoCrFeMnNiMox high entropy alloy is change from dendrite crystals to cellular crystal, and the yield strength of the alloy is not change significantly. In the case of Mo content is less than 7%, Mo as substitutional atom is dissolves in the crystal structure of CoCrFeMnNi high entropy alloy substrate, which has function as solid solution strengthening, so that the strength of the alloy increases slightly, but the plasticity are not change significantly. In the case of Mo content is more than 7%, the ζ (CrMo) phase is precipitates in the alloy substrate, which has plays effect of second phase strengthening, so that strength of the alloy is increase significantly, and the plasticity is decreases obviously.

1. Introduction
High entropy alloy has many principal elements, which have many characteristics different from traditional alloys. The percentage elongation of CoCrFeMnNi high-entropy alloy can reach more than 57% at room temperature. [1] And it is reported that the percentage elongation at liquid nitrogen temperature is higher than 75%, [2] but its strength is relatively low, about 400MPa. [3] The second phase reinforcement is an enhanced method of the alloy, and the number, distribution and size of the second phase have a great influence on the properties of the material. [4, 5, 6, 7] Compared with Co, Cr, Fe, Mn and Ni, Mo has a large atomic radius. Some scholars have found that molybdenum is beneficial to the formation of hard and brittle intermetallic facies in AlCoCrFeNiMox and AlCrFeNiMox high entropy alloys. [8, 9] Kaisheng Ming and W.H. Liu et al. found in Cr15Fe20Co35Ni20Mo10 and CoCrFeNiMox high-entropy alloys that the amount, distribution and size of interphase of Mo-containing metals can be changed by heat treatment to improve the material properties. [10, 11] Therefore, an attempt is made to add Mo element to re-alloying the phase composition and microstructure of CoCrFeMnNi high entropy alloy in order to improve its comprehensive mechanical properties.

In this paper, a CoCrFeMnNiMox high entropy alloy was prepared by vacuum arc melting furnace, the influence of Mo element content on CoCrFeMnNi high entropy alloy phase structure and mechanical properties was analyzed, and the second phase formation mechanism of CoCrFeMnNi high entropy alloy after adding Mo was revealed. The strengthening mechanism of adding Mo element CoCrFeMnNi High entropy alloy was explored.
2. Experimental

2.1. Preparation of Experimental Materials
Metal materials Mn, Fe, Cr, Co, Ni and Mo with high purity (>99.9 wt.%) were used as starting materials. The mass fraction of each element of CoCrFeMnNi alloy composition is calculated according to the equal atomic ratio, and then the Mo elements with mass fraction of 1%, 3%, 5%, 7% and 10% are added respectively, using mass fraction ingredients. Under argon atmosphere, vacuum electric arc furnace is used for smelting, the vacuum degree is 3\times10^{-3} Pa. Repeated smelting at least 4 times to ensure the uniformity of alloy composition, the preparation of CoCrFeMnNiMox high entropy alloy ingot, for use in the experiment.

2.2. Material Analysis and Testing
The smelting CoCrFeMnNiMox high entropy alloy ingot is made by wire cutting to make the 10mm×10mm×3mm cube, and then the water sandpaper from 180# to 2000# is used to grind it up and down. The metallographic structure and microstructure were observed by optical microscope and SEM after polishing with diamond abrasive paste. EDS and XRD were used to analyze the element distribution and phase composition, the microhardness was tested by Vickers hardness tester, the tensile properties were tested by universal testing machine, and the tensile fracture was analyzed by SEM.

3. Results and Discussions

3.1. Microstructure of CoCrFeMnNiMox High Entropy Alloy
Fig. 1 shows the optical image and SEM morphology of CoCrFeMnNiMo high-entropy alloy with different Mo contents. As can be seen from the optical diagram, the microstructure of CoCrFeMnNi high-entropy alloy is typical dendrite crystals. With the increase of Mo content, the primary dendrite gradually becomes coarser and longer. As Mo content is more than 3%, the primary dendrite shows obvious directional growth and the secondary dendrite becomes shorter. As Mo content is 7%, the alloy microstructure was cellular crystal. As Mo element content is more than 10%, the alloy microstructure is cellular crystal. This indicates that Mo element obviously affects the crystal growth morphology of CoCrFeMnNiMo high-entropy alloy. With the increase of Mo content, the crystal morphology of CoCrFeMnNiMo high-entropy alloy changes from dendritic to cellular crystal. It can be seen from the SEM diagram that with the addition of Mo elements, the second phase substances appear in the grain boundary of CoCrFeMnNiMo high-entropy alloy. As the content of Mo elements is 7%, the second phase of the alloy grain boundary is blocky. At 10%, the second phase is continuously distributed at the grain boundary. This indicates that the increase of Mo element content will promote the formation of the second phase in the alloy, and the morphology and distribution of the second phase will change accordingly.
Figure 1. Optical image and SEM morphology of CoCrFeMnNiMo high-entropy alloy with different Mo contents (a: Mo1%, b: Mo3%, c: Mo5%, d: Mo7%, e: Mo10%)

3.2. Phase Constitution of CoCrFeMnNiMox High Entropy Alloy

XRD patterns shown in Fig.1 reveal the CoCrFeMnNiMox high-entropy alloy with different Mo contents. It was found that the composition phase of CoCrFeMnNiMox high-entropy alloys is single FCC phase structure, and no second phase was precipitated. Local analysis between the maps of 41 ° ~ 46 °, it can be seen that the addition of Mo element, the diffraction peak shifts to the left, as the content of Mo increases, the diffraction peak shift increases, this is because the atomic radius of Mo is relatively large, the lattice constant of the alloy becomes larger. According to the Bragg diffraction formula, the position of the diffraction peak shifts to a small angle, indicating that Mo with larger...
The atomic radius will form a substitutional solid solution as they occupy the solid solution lattice sites, leading to an appreciable increase of the lattice distortion.

![X-ray diffraction pattern of CoCrFeMnNiMox series high-entropy alloy](image)

**Figure 2.** X-ray diffraction pattern of CoCrFeMnNiMox series high-entropy alloy

Table 1 shows the results of energy spectrum analysis of CoCrFeMnNiMox high-entropy alloys with different Mo contents. It can be found that as the Mo content is less than 5%, there is no significant difference in the distribution of Mo elements in the crystal and grain boundaries, and there is no significant difference in the distribution of the elements of the principal elements. This indicates that the Mo element is dissolved in the matrix and the second phase is not formed. As the content of Mo is more than 7%, the content of Mo in the grain boundary is significantly larger than that in the crystal. Meanwhile, the content of Cr in the grain boundary is significantly higher than other. The principal element, which indicates that the bulk and continuous phase at the grain boundary is the nascent second phase, and the nascent corresponding to the δ (CrMo) phase is analyzed according to the composition ratio.

**Table 1.** Energy spectrum analysis of CoCrFeMnNiMox high-entropy alloy in different Mo contents

| Mo content | position | Co   | Cr   | Fe   | Mn   | Ni   | Mo  |
|------------|----------|------|------|------|------|------|-----|
| No         | 1        | 19.404 | 19.404 | 19.404 | 19.404 | 19.404 | 2.98 |
|            | 2        | 18.85  | 17.81 | 17.15 | 23.11 | 22.17 | 0.91 |
| 1%         | 1        | 18.57  | 17.71 | 17.05 | 22.91 | 22.07 | 1.51 |
|            | 2        | 16.52  | 17.49 | 14.64 | 26.92 | 23.59 | 0.84 |
| 3%         | 1        | 18.75  | 17.71 | 17.05 | 22.91 | 22.07 | 1.51 |
|            | 2        | 16.52  | 17.29 | 14.64 | 26.82 | 23.29 | 1.44 |
| 5%         | 1        | 19.20  | 19.97 | 19.31 | 18.72 | 19.6  | 3.19 |
|            | 2        | 16.67  | 17.75 | 14.48 | 25.94 | 22.37 | 2.79 |
| 7%         | 1        | 19.94  | 20.83 | 18.93 | 16.73 | 18.52 | 5.05 |
|            | 2        | 14.01  | 24.28 | 13.24 | 18.02 | 12.83 | 17.61 |
| 10%        | 1        | 17.74  | 20.59 | 17.46 | 18.66 | 18.26 | 7.29 |
|            | 2        | 14.97  | 23.98 | 12.84 | 19.23 | 10.67 | 18.31 |

3.3. **Tensile Properties of CoCrFeMnNiMox High Entropy Alloy**

Fig. 3 shows the stress-strain curves of CoCrFeMnNiMox high-entropy alloys with different Mo contents. It can be seen that the yield strength of the alloy does not change significantly with the increase of Mo element content. As Mo content is less than 5%, there is no significant change in strength, while as Mo content is more than 5%, strength increases slightly and plasticity decreases significantly. This is mainly because as the content of Mo is less than 5%, Mo mainly exists in the alloy crystal structure in the form of substituting atoms, which leads to an appreciable increase of the
lattice distortion and plays a role of solid solution strengthening, thus leading to an increase in strength, but no significant change in plasticity. As the Mo content is more than 5%, the second phase of δ (CrMo) is formed in the alloy on the basis of solid solution strengthening, which plays the role of the second phase strengthening, slightly increasing the strength and significantly reducing the plasticity.

![Stress-strain curves of CoCrFeMnNiMox series high-entropy alloys](image)

**Figure 3.** Stress-strain curves of CoCrFeMnNiMox series high-entropy alloys

Fig.4 is the tensile fracture morphology of CoCrFeMnNiMox high-entropy alloy with different Mo content. It can be seen from the low-power morphology that the fracture sites of different Mo content have obvious necking and plastic deformation. As can be seen from the high-power morphological diagram, As the Mo content is less than 5%, the number of micro-polypores in the microstructure of the fracture is relatively large, and the fracture presents dimple morphology, indicating ductile fracture. As Mo content is more than 5%, the fracture presents dimple morphology, which is still a ductile fracture. However, the number of micropores in the fracture morphology decreases, and the dimple gradually becomes shallow and flat. Therefore, its percentage elongation and plasticity decrease.

![Fracture morphology of CoCrFeMnNiMox series](image)
4. Conclusions

(1) With the increase of Mo content, the crystal morphology of CoCrFeMnNiMo high-entropy alloy changed from dendritic to cellular crystal. As the Mo element content is less than 3%, the crystal form is dendritic; as the Mo element content is 7%, the alloy microstructure is cellular dendrites; as the Mo element content is more than 10%, the alloy microstructure is cell crystal.

(2) The yield strength of the alloy did not change significantly with the increase of Mo content. As Mo element is less than 5%, Mo mainly exists in the alloy crystal structure in the form of substituting atoms in the atomic state, which increases the lattice distortion and plays the role of solid solution strengthening, thus leading to the increase of strength without obvious change in plasticity. As the content of Mo element is more than 5%, the second phase of δ (CrMo) is formed in the alloy on the basis of solid solution strengthening, which enhances the strength and significantly reduces the plasticity.

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6. References
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