Microstructures and properties of CoCrFeNiX (X=Mn, Cu) high entropy alloys

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Abstract: CoCrFeNiX (X=Mn, Cu) high entropy alloys (HEAs) were prepared by powder metallurgy. The effects of milling time and milling speed on the microstructures and properties of CoCrFeNiX (X=Mn, Cu) HEAs were studied. The results show that at high rotational speed, the particle size of the HEA powders is refined and is tended to be uniform, and obvious solid solution phenomenon occurs; the microstructure of CoCrFeNiMn HEA is mainly composed of BCC solid solution, FCC solid solution and CoNiCr intermetallic compound; with the increase of ball milling time, Cr-rich phase and CoNiCr compound decrease. The microstructure of CoCrFeNiCu HEA is mainly composed of BCC solid solution and FCC solid solution; with the increase of ball milling time, Ni-rich FCC solid solution is gradually replaced by Co-rich and Ni-rich FCC solid solution. CoCrFeNiMn and CoCrFeNiCu HEAs have higher compressive strength, compression ratio and hardness, and they are 1300 Mpa and 1100 Mpa, 34% and 33%, 400 HV and 350 HV, respectively; The friction coefficient curve of CoCrFeNiMn HEA is more stable than that of CoCrFeNiCu HEA.

1. Introduction
The traditional alloys commonly used in modern times are those with a single metal element as the principal component. Certain properties of conventional alloys are improved by the addition of little other metals or nonmetallic elements. In 1994, different from the designing concept of traditional alloys, Professor Jien-Wei Yeh prepared a new system of alloys by mixing several metals with equal molar ratio and named them high entropy alloys (HEAs) in 2004[1~3].

HEA is composed of 5~13 different metal elements with equal molar ratio or approximate equal molar ratio, and the proportion of each element in the alloy is 5%~35%[4~7]. HEAs can be designed to meet the production and usage requirements according to the physical and chemical properties of the
elements. They make the alloys have better physical or chemical properties. There are many methods to prepare HEAs, and the most common methods are vacuum melting, powder metallurgy and magnetic levitation melting[8~11]. The powder metallurgy method can prepare HEAs below the melting point of metals, and it is usually the first choice for the preparation of refractory metals.

Nowadays, the multi-component alloys derived from the new system have attracted extensive attention. As a relatively new alloy system, there are many problems worth exploring, such as the rules of phase transformation, the role of atomic size, mixing entropy and mixing enthalpy in formation of solid solutions in HEAs, the stability of HEAs at high temperature. In this paper, CoCrFeNiX (X=Mn, Cu) HEAs were prepared by powder metallurgy method, and the effects of milling time and milling speed on the microstructures and properties of the HEAs were investigated.

2. Materials and Methods

2.1 Alloy composition

The composition and milling time of the samples are CoCrFeNiMn-5h, CoCrFeNiMn-30h, CoCrFeNiCu-5h, CoCrFeNiCu-30h. The raw materials are 99.9% purity powder. The powder weight and theoretical density values of the HEAs are shown in Table 1.

Table 1 Powder weight and theoretical density of CoCrFeNiX (X=Mn, Cu) HEAs

| Samples            | Fe (g) | Ni (g) | Co (g) | Cr (g) | Mn (g) | Cu(g) | Total weight(g) | Theoretical density(g·cm⁻³) |
|--------------------|--------|--------|--------|--------|--------|-------|-----------------|----------------------------|
| CoCrFeNiMn        | 43.82  | 46.05  | 46.23  | 40.08  | 43.1   | 0     | 220             | 8.014                      |
| CoCrFeNiCu        | 42.51  | 44.68  | 44.86  | 39.58  | 0      | 48.37 | 220             | 8.324                      |

2.2 Experimental scheme

Six kinds of metal powder (Fe, Ni, Co, Cr, Mn and Cu powder, diameter < 48 μm) were selected. The powder samples were mechanically alloyed by planetary ball mill (QM-3SP4). The rotation speed was 150 r/min. The microstructures of powder samples after 5, 10, 20, 30 hours of ball milling were analyzed respectively. The powder samples were sintered by vacuum hot pressing sintering machine (SMVB80) at the condition of 950°C and 100 KN and retained 9 min for obtaining CoCrFeNiMn-5h, CoCrFeNiMn-30h, CoCrFeNiCu-5h and CoCrFeNiCu-30h HEA bulks. The actual density values of the bulk samples were determined by Archimedes drainage method. Scanning electron microscope (Hitachi S-3400N) with energy dispersive spectrometer was used to analyze the microstructures of powder samples and bulks. The phases were characterized by X-ray diffractometer (XRD) (Bruker D8 DISCOVER) with scanning speed of 8°/min and 2θ of 20°-100°. The hardness and compressive property of the bulk samples were tested by nanoindentation hardness tester (NVM-1000A) and universal testing machine (Instron 8801). The friction coefficient and wear resistance of the HEAs were measured by a high-speed reciprocating friction and wear tester (HSR-2M), and the wear morphologies were analyzed. Corrosion resistance of the HEAs were tested by electrochemical workstation (CHI660E).

3. Results & Discussion

3.1 Density and microstructure

Every bulk sample was processed into a sample of 5 mm × 15 mm × 25 mm, and the actual density was measured by the drainage method. The calculation results were based on formulas (1) and (2). Table 2 is the actual density and theoretical density values of CoCrFeNiX (X=Mn, Cu) HEAs bulk samples. It can be seen from Table 2 that with the extension of milling time, the density decreases. The reason for this phenomenon may be that after long-term low-speed milling, the powder particles are still in the stage of deformation and agglomeration, and there is no cold welding and re-breaking, which deteriorates the powders pressing performance.

$$\rho_s = \frac{m_1 \times \rho_1}{m_1 - m_2}$$  

(1)
where \( \rho_s \) is actual density of alloy; \( m_1 \) is quality of alloys in air; \( m_2 \) is mass of alloys suspended in water; \( \rho_1 \) is density of water; \( \rho_1 = 0.9958 \text{ g/cm}^3 \); \( K \) is relative density of alloy; \( \rho_0 \) is theoretical density of alloy.

Table 2 Density of CoCrFeNiX (X=Mn, Cu) HEAs bulk samples.

| Bulk samples       | Actual density (g·cm\(^{-3}\)) | Theoretical density (g·cm\(^{-3}\)) | Relative density (%) |
|--------------------|---------------------------------|-------------------------------------|----------------------|
| CoCrFeNiMn-5h      | 7.860                           | 8.014                               | 98.08                |
| CoCrFeNiMn-30h     | 7.716                           | 8.014                               | 96.28                |
| CoCrFeNiCu-5h      | 8.170                           | 8.324                               | 98.15                |
| CoCrFeNiCu-30h     | 8.098                           | 8.324                               | 97.28                |

Fig.1 and Fig.2 show the XRD patterns of CoCrFeNiX (X=Mn, Cu) HEAs powder samples and bulk samples respectively. It is obvious that with the increase of milling speed, the diffraction peaks of several elemental elements become wider and their heights become lower or even disappear. This indicates that the solid solution occurs at high rotation speed. The microstructures of CoCrFeNiX (X=Mn, Cu) HEAs bulk samples are mainly composed of solid solution with body-centered cubic structure (BCC) and solid solution with face-centered cubic structure (FCC), and a small amount of CoNiCr intermetallic compound. With the extension of milling time, the diffraction peaks of BCC solid solution and intermetallic compound decrease, which may mean that the extension of milling time will make the chemical compositions of the powder more uniform, and the atomic diffusion process during sintering is more sufficient, which tends to form uniform solid solution.
(e), with the increase of milling speed, it is obvious that the particle size of the powder is homogenized, and all of them are in the range of 10~15μm. This shows that under the condition of high speed, the powder has undergone a cold welding-breaking process.

Fig.3 SEM morphologies of CoCrFeNiMn HEA powder samples
(a) 150 r/min, 5 h; (b) 150 r/min, 10 h; (c) 150 r/min, 20 h; (d) 150 r/min, 30 h; (e) 250 r/min, 30 h

Fig.4 SEM morphologies of CoCrFeNiCu HEA powder samples
(a) 150 r/min, 5 h; (b) 150 r/min, 10 h; (c) 150 r/min, 20 h; (d) 150 r/min, 30 h

Fig.5 and Table 3 show the microstructures and energy spectrum analysis results of CoCrFeNiX (X=Mn, Cu) HEAs bulk samples. It can be found that there are many obviously organizational partitions. According to the XRD analysis results, the Ni-rich phase at 1 in Fig.5 is a solid solution with FCC structure; the Cr-rich phase at 2 in Fig.5 (a) and 1 in Fig.5 (b) is a solid solution with BCC structure; the Cr-poor phase and Fe-poor phase at 2 in Fig.5 (b) are solid solution with FCC structure, and the gray-black particles at 3 in Fig.5 (b) include CoNiCr compound and the BCC solid solution with Cr-rich. It can be seen that with the increase of milling time, the Cr-rich phase and CoNiCr compound of
CoCrFeNiMn HEA decrease. The Ni-rich phase at 1 in Fig. 5 (c) is FCC3 solid solution with FCC structure. The Cu-rich phase at 2 in Fig. 5 (c) and 3 in Fig. 5 (d) is FCC2 solid solution with FCC structure. The Cr-rich phase at 3 in Fig. 5(c) and 2 in Fig. 5 (d) is BCC solid solution. The Co-rich phase and Cr-rich phase at 1 in Fig. 5 (c) and 2 in Fig. 5 (d) are FCC1 solid solution with FCC structure. With the increase of milling time, the BCC solid solution phase and Cu-rich FCC2 solid solution phase continue to remain in CoCrFeNiCu HEA. The Ni-rich FCC3 solid solution phase is gradually replaced by the Co-rich and Ni-rich FCC1 solid solution phase. The CoCrFeNi (X=Mn, Cu) HEAs do not form a uniform single FCC phase like CoCrFeNiMn as-cast HEA[12], nor do they form a uniform FCC1 + FCC2 dual phases like CoCrFeNiCu as-cast HEA[13]. This may be due to the difficulty of atomic diffusion movement, although the solid solubility between different elements of the HEAs is improved due to the high entropy effect, the energy barrier needed to overcome by atomic synergistic diffusion is higher than that of traditional alloys.

Table 3 EDS analysis results of CoCrFeNiX (X=Mn, Cu) HEAs bulk samples (at%).

| Samples and regions | Co    | Cr    | Fe    | Mn    | Ni    | Si    | Cu    |
|---------------------|-------|-------|-------|-------|-------|-------|-------|
| CoCrFeNiMn-5h, Fig. 5 (a) 1 | 13.81 | 9.23  | 3.87  | 29.11 | 43.99 |       |       |
| CoCrFeNiMn-5h, Fig. 5 (a) 2 | 25.93 | 43    | 2.5   | 20.67 | 6.72  | 1.19  |       |
| CoCrFeNiMn-30h, Fig. 5 (b) 1 | 20.25 | 51.30 | 2.91  | 19.18 | 6.36  |       |       |
| CoCrFeNiMn-30h, Fig. 5 (b) 2 | 16.88 | 8.69  | 2.79  | 38.26 | 33.37 |       |       |
| CoCrFeNiMn-30h, Fig. 5 (b) 3 | 9.04  | 67.21 | 4.30  | 11.72 | 7.37  |       |       |
| CoCrFeNiCu-5h, Fig. 5 (c) 1 | 6.34  | 8.2   | 16.47 | 62.01 | 6.98  |       |       |
| CoCrFeNiCu-5h, Fig. 5 (c) 2 | 3.28  | 3.11  | 1.22  | 2.84  | 89.55 |       |       |
| CoCrFeNiCu-5h, Fig. 5 (c) 3 | 1.82  | 92.5  | 2.38  | 2.62  | 0.68  |       |       |
| CoCrFeNiCu-30h, Fig. 5 (d) 1 | 29.35 | 31.1  | 17.64 | 17.29 | 4.62  |       |       |
| CoCrFeNiCu-30h, Fig. 5 (d) 2 | 2    | 94.69 | 1.56  | 1.06  | 0.68  |       |       |
| CoCrFeNiCu-30h, Fig. 5 (d) 3 | 4.77  | 2.75  | 2.94  | 8.59  | 80.95 |       |       |
3.2 Hardness and compressive property

The hardness values of CoCrFeNiX (X=Mn, Cu) HEAs bulk samples are shown in Table 4. The hardness values of the two HEAs are similar, indicating that the ball milling time has little effect on the average hardness of the HEAs. From the data of each point, the hardness range values of CoCrFeNiMn HEA are 237 HV and 347 HV, respectively, while those of CoCrFeNiCu HEA are 139 HV and 268 HV. The hardness of two kinds of HEA with different milling time fluctuates greatly. The reason is probably that the appearance of two phases and intermetallic compounds in the CoCrFeNiMn HEA. For CoCrFeNiCu HEA, it may be due to the appearance of multiple phases.

Table 4 Hardness of CoCrFeNiX (X=Mn, Cu) HEAs bulk samples (HV).

| Samples            | 1         | 2         | 3         | 4         | 5         | 6         | 7         | 8         | Averages |
|--------------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|----------|
| CoCrFeNiMn-5h     | 399.15    | 554.62    | 318.10    | 358.19    | 405.07    | 369.12    | 317.95    | 515.02    | 455.37   |
| CoCrFeNiMn-30h    | 357.83    | 277.09    | 346.88    | 304.96    | 392.73    | 497.09    | 347.23    | 327.39    | 624.01   |
| CoCrFeNiCu-5h     | 318.25    | 346.88    | 332.10    | 266.04    | 358.19    | 405.07    | 399.36    | 346.71    | 300.53   |
| CoCrFeNiCu-30h    | 462.85    | 357.83    | 246.55    | 514.40    | 463.12    | 380.36    | 256.29    | 462.59    | 352.21   |

Fig.6 shows the engineering stress-strain curves for compression of CoCrFeNiX (X=Mn, Cu) HEAs bulk samples. The compressibility of the two HEAs is close to 35%, and the highest compressive strength is about 1300 MPa. But the compressive property of the sample-30h is worse than that of the one-5h. It is possible because that the density of the sinter of CoCrFeNiMn-30h is only 96%, which is less than that of CoCrFeNiMn-5h. In conclusion, the compactness of the structure will influence the compressive properties of the HEAs.

Fig.7 Compressive fracture morphologies of CoCrFeNiMn HEA bulk samples. (a) CoCrFeNiMn-5h. (b) CoCrFeNiMn-30h.
The compressive fracture morphologies of CoCrFeNiX (X=Mn, Cu) HEAs bulk samples are shown in Fig.7 and Fig.8. There are cleavage steps, dimples and particles, which indicates that the fracture of the HEAs is a mixture of brittle fracture and ductile fracture.

### 3.3 Friction and wear performance

The friction coefficient curves of CoCrFeNiX (X=Mn, Cu) HEAs bulk samples are shown in Fig.9. At the beginning, the friction coefficients of CoCrFeNiMn-5h and CoCrFeNiMn-30h are low due to the existence of oxide film. As the friction proceeds, the oxide film gradually breaks and the friction enters the stable stage. The friction curves of the two alloys are similar in the stable friction stage, but they both fluctuate slightly in the experimental process. This may be due to the existence of hard spots on the surface, which enlarges the shear strength and causes the friction coefficient \( \mu \) increasing sharply. Under the progress of friction, the debris gradually gather to both ends of the wear pit and gradually return to the stable friction stage. Both of them are relatively stable in the early and middle stages of friction. But in the later stage of friction, CoCrFeNiCu-5h sample has larger fluctuation, while CoCrFeNiCu-30h sample has less fluctuation.

The morphologies of CoCrFeNiX (X=Mn, Cu) HEAs bulk samples after friction and wear are shown in Fig.10 and Fig.11. The existence of granule proves that it has abrasive wear. Because of the inherent sintering pore defects in powder metallurgy and the hard phase contained in the alloys, the alloy must suffer from uneven stress in the friction process, and result in fatigue cracks on the material surface. With the development of friction process, these fatigue cracks gradually expand, and cause surface spalling and fatigue wear.
4. Conclusions

In this paper, CoCrFeNiX (X=Mn, Cu) HEAs were prepared by powder metallurgy. The effects of milling time and milling speed on the microstructures and properties of CoCrFeNiX (X=Mn, Cu) HEAs were investigated. CoCrFeNiX (X=Mn, Cu) -5h and CoCrFeNiX (X=Mn, Cu) -30h HEAs bulk samples with the powder which has been milled under the milling speed of 150 r/min and milling time of 5 h or 30 h have been analyzed in particular. The results show that:

1. At high rotational speed, the particle size of the HEA powder is refined and is tended to be uniform, and obvious solid solution phenomenon occurs.

2. The microstructure of CoCrFeNiMn-5h HEA is composed of BCC solid solution (Cr-rich), FCC solid solution (Ni-rich) and a small amount of CoCrNi intermetallic compound. The microstructure of CoCrFeNiMn-30h HEA is composed of BCC solid solution (Cr-rich), FCC solid solution (Cr, Fe-poor) and a small amount of CoNiCr intermetallic compound; with the increase of milling time, Cr rich phase and CoNiCr compound decrease.

3. The microstructure of CoCrFeNiCu-5h HEA is composed of FCC solid solution (Cu-rich), FCC solid solution (Ni-rich) and BCC solid solution (Cr-rich). The microstructure of CoCrFeNiCu-30h HEA is composed of FCC solid solution (Cu-rich), FCC solid solution (Co, Cr-rich) and BCC solid solution (Cr-rich).

4. CoCrFeNiMn and CoCrFeNiCu HEAs have higher compressive strength, compression ratio and hardness, and they are 1300 Mpa and 1100 Mpa, 34% and 33%, 400 HV and 350 HV, respectively.

5. The friction coefficient curve of CoCrFeNiMn HEA is more stable than that of CoCrFeNiCu HEA.
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