Research on Microstructures and Properties of CoNiCr and CoNiCu Medium-entropy Alloys

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Abstract: CoNiCr and CoNiCu medium-entropy alloys (MEAs) were prepared by powder metallurgy with Co, Ni, Cr, Cu powders milled for 5h and 30h, and the effects of different milling time and different elements on the microstructures and properties of MEAs were studied. Through microstructures characterization (by scanning electron microscope and energy dispersive spectrum analysis, X-ray diffraction analysis) and mechanical properties (compressive performance, hardness, wear resistance) testing, the following conclusions are drawn: First, with the increase of the milling time, the density of the sintered samples is increased. Second, the microstructure of CoNiCr MEA is composed of Ni-rich FCC solid solution, Cr-rich BCC solid solution and CoNiCr intermetallic compound, while the microstructure of CoNiCu MEA is mainly composed of FCC solid solution with uniform Co, Ni, and Cu, and Co-rich FCC solid solution. Third, as the agglomeration of powder is weakened and the density of sintered sample is increased, the hardness of CoNiX (X=Cr/Cu)-30h is higher (about 20HV) than that of CoNiX (X=Cr/Cu)-5h, and long-term ball milling effectively improves the wear resistance, moldability and compressive strength of CoNiCr MEA, while the moldability and compressive strength of CoNiCu MEA are reduced, and the wear resistance of CoNiCu MEA is slightly improved. Finally, the hardness and wear resistance of CoNiCr MEA are better than that of CoNiCu MEA, the hardness is increased by about 70HV, and the wear resistance is increased by about 20-40 times, but the compressive performance of CoNiCu MEA is better than that of CoNiCr MEA.

1. Introduction
Since the concept of high-entropy alloys (HEAs) first proposed by Yeh JW et al. [1] in 2004, HEAs have been widely concerned and studied by scholars, and become one of the hot research topics due to their excellent performance, such as high strength and hardness, good work hardening, wear resistance, corrosion resistance and thermal stability[1~7].

According to Boltzmann's hypothesis on the relationship of entropy and system complexity[8],
combined with the formula of statistical thermodynamics, the overall mixed entropy value of the system when the molar concentrations of various principal elements are equal can be obtained by the formula as following: \[ S = R \ln N \] (Where N is the number of principal elements in the alloy, and R is the molar gas constant of the ideal gas), and according to the calculation results, all alloys are classified according to the values of the mixing entropy\[1,9\]: low-entropy alloys (LEAs, mixing entropy< 5.762 J•mol\(^{-1}•K^{-1}\)), they usually include a single principal element, such as steel and aluminum alloys; medium-entropy alloys (MEAs, mixing entropy: 5.762~13.382 J•mol\(^{-1}•K^{-1}\)), they usually include 2~4 principal elements; high-entropy alloys (HEAs, mixing entropy>13.382 J•mol\(^{-1}•K^{-1}\)), they usually include 5 or more (generally no more than 13 \[1\]) principal elements, and the proportion of every element does not exceed 35%, for example Cantor alloy, which is prepared from 5 principal elements with equal molar ratio, and has an obvious single-phase microstructure with face-centered cubic (FCC) structure solid solution \[10\].

The development of MEAs is based on the research and exploration of HEAs\[11\]. Compared with HEAs, the microstructures of MEAs are simpler, and the design concept proposed provides a new idea for the development of new alloys with good strength, hardness, plasticity and toughness\[12\]. In 2016, Bernd Gludovatz et al.\[13\] studied CoCrNi MEA and found that the alloy is composed of a single-phase FCC solid solution, and its strength and toughness exceed all HEAs and most multiphase alloys. Liu et al.\[14\] studied the Fe-Co-Ni-Cr-Mn HEAs and found that the stacking fault energy in the alloys depends on the stacking fault energy of each component, and low stacking fault energy can refine the deformation twins, and it is beneficial to obtain more excellent mechanical properties, especially the mechanical properties at low temperature, and obtain larger deformation and higher tensile strength.

The purpose of this research is to use powder metallurgy to prepare CoNiCr and CoNiCu MEAs, and analyze the effects of Cu and Cr elements on the microstructures and properties of Co-Ni-X MEAs. It is hoped to provide some references for the research of MEAs.

2. Experimental materials and methods
CoNiCr and CoNiCu MEAs were prepared with four kinds of powder such as Co, Cr, Ni and Cu powder (purity > 99%, 300 mesh) by powder metallurgy. The raw powder was milled by QM-3SP4 ball grinder under argon atmosphere protection, and the ball milling process was as follows: the milling time was 5h or 30 h, and the milling speed was 150 r/min. CoNiCr and CoNiCu block MEAs were prepared by SMVB80 vacuum hot pressing sintering machine under the following condition: sintering temperature was 950 °C, and pressure was 30 MPa and holding time was 6 min. The size of the block samples were 16mm×16mm×90mm, and the error was controlled within ±0.3mm.

D/Max2500V X-ray diffractometer (XRD) was used to analyze the phases of the MEAs, the scanning speed was 8°/min, and the 2θ was 20°-100°. The density of the MEAs was measured by the Archimedes drainage method. The microstructures of the MEAs were analyzed by a scanning electron microscope (SEM) (Hitachi S-3400N) and the attached energy spectrometer (EDS). The hardness and compressive performance were tested on the HVS-1000 microhardness tester and the Instron 8801 universal testing machine respectively, and the characteristics of compressive fractures were analyzed. A high-speed reciprocating friction and wear tester (HSR-2M) was used to measure the friction coefficient and wear resistance of the MEAs.

3. Experimental results and analysis

3.1 Microstructure
Fig.1a shows the XRD patterns of CoNiCr MEA, and it shows that the phase composition of CoNiCr MEA is three main phases: a solid solution phase with body-centered cubic structure (BCC), a solid solution phase with FCC structure and CoNiCr intermetallic compound (the PDF card number: #21-1271); the phase composition of CoNiCu MEA is two main phases: FCC1 solid solution phase and FCC2 solid solution phase (as Fig.1b).
The aggregates are more harmful to the sintered samples, because the internal connections of the aggregates are connected by atomic force or surface tension, and inside the aggregates there are a lot of voids and gas which have a bad influence on the formation of sintered samples, and uniform microstructures and high-density organization cannot be formed [15]. The two kinds of powder of MEAs obtained by ball milling in this experiment are soft aggregates which have less internal stresses and more loose structures compared with hard aggregates, and are easier to disperse in the sintering process and have better sintering performance.

![Fig.1 XRD diffraction patterns of MEAs](image)

Table 1 shows the density values of the MEAs. According to the SEM images (as Fig.2 and Fig.3), the density values of CoNiCr and CoNiCu increase with the increase of ball milling time. Because with the increase of ball milling time, the density of aggregates in MEA powder decreases, and the voids and inclusions in sintering powder decrease.

| Block samples | Actual density (g·cm⁻³) | Theoretical density (g·cm⁻³) | K(%)   |
|---------------|--------------------------|-----------------------------|--------|
| CoNiCr-5h     | 7.9                      | 8.3                         | 94.7   |
| CoNiCr-30h    | 8.2                      | 8.3                         | 98.8   |
| CoNiCu-5h     | 8.7                      | 8.9                         | 97.8   |
| CoNiCu-30h    | 8.8                      | 8.9                         | 98.5   |

Note: K=Actual density/ Theoretical density
Fig. 2 SEM images of CoNiCr raw material powder by ball milling for different time (a) 5h; (b) 10h; (c) 20h; (d) 30h

Fig. 3 SEM images of CoNiCu raw material powder by ball milling for different time (a) 5h; (b) 10h; (c) 20h; (d) 30h
Fig. 4 SEM images of MEAs (a) CoNiCr-5h; (b) CoNiCr-30h; (c) CoNiCu-5h; (d) CoNiCu-30h

Fig. 4 shows the SEM images of the block samples. It can be observed that the pore content of the sintered alloys is different because the four kinds of MEAs powder have gone through different ball milling time. With the increase of ball milling time, the porosity of CoNiCr MEA shows a downward trend (as shown in Fig. 4(a), (b)). It is consistent with the above-mentioned trend that the soft aggregates decrease with the increase of ball milling time. The black second phase of CoNiCu MEA presents a relatively dispersed state; but with the ball milling time increasing, the number of pore defects tends to increase (as shown in Fig. 4(c), (d)).

According to the energy spectrum analysis of the MEAs (as shown in Fig. 5), the microstructure of CoNiCr-5h MEA is composed of gray matrix (area 1 in Fig. 5), black phase (area 2 in Fig. 5) and white second phase (area 3 in Fig. 5). Combined with the XRD analysis results of Fig. 1, the matrix is Ni-rich FCC solid solution, the black phase is Cr-rich BCC solid solution and the white second phase is CoNi intermetallic compound. Similarly, the microstructure of the CoNiCu-30h MEA is mainly composed of gray matrix (area 1 in Fig. 6) and black second phase (area 2 in Fig. 6), with a small number of oxides. Combined with the XRD analysis results of Fig. 1, the matrix is FCC1 solid solution with uniform Co, Ni, and Cu composition. The black second phase is Co-rich FCC2 solid solution. The area 3 in Fig. 6 is composed of FCC1, FCC2 and oxides. It is speculated that oxides result from residual acid or poor seal condition during corrosion.

Combined with the comprehensive analysis of XRD, SEM, EDS and density, the influence of different ball milling time on the sintering of CoNiCr and CoNiCu MEAs can draw the following conclusions: ① with the increase of ball milling time, the agglomeration phenomenon reduces, and the size of powder particle decreases, and the sintering density increases and the porosity reduces. ② compared with adding Cr, the powder adding Cu tends to less aggregates, and CoNiCu block MEA has higher density and lower porosity, however, the EDS analysis of the sintered samples shows that CoNiCr block samples are more uniform and have better solid solution effect.

| Elements (at%) | 1   | 2   | 3    |
|---------------|-----|-----|------|
| Ni            | 50.45 | 0   | 9.74 |
| Cr            | 26.49 | 65.11 | 34.35 |
| Co            | 22.85 | 34.89 | 55.91 |

Fig. 5 Results of EDS of CoNiCr-5h block sample
3.2 Hardness
According to the nine hardness data measured for each sample, the average hardness of CoNiCr and CoNiCu block MEAs were calculated (as shown in Fig.7). Through comparison, it is found that the hardness of CoNiX(X=Cr/Cu)-30h is higher (about 20HV) than that of CoNiX(X=Cr/Cu)-5h. It can be concluded that the addition of Cr has a better effect on the hardness of the CoNiX MEAs than the addition of Cu. The hardness of the alloys with Cr is approximately 70HV higher than that of the alloys with Cu under the same ball milling time. The reason is possible that CoNiCr alloy is composed of FCC and intermetallic compound, while CoNiCu alloy is composed of two kinds of FCC structure phases, and intermetallic compound, so more FCC structure and less second phase may decrease the hardness of the alloy.

| MEAs          | Average hardness /HV | Standard deviation |
|---------------|-----------------------|--------------------|
| CoNiCr-5h     | 269.23                | 38.45              |
| CoNiCr-30h    | 299.83                | 63.07              |
| CoNiCu-5h     | 199.88                | 41.72              |
| CoNiCu-30h    | 221.73                | 21.93              |

3.3 Compressive performance
According to the compressive stress-strain curves of the four samples (as shown in Fig.8), it can be clearly seen that the CoNiCu MEA has an increase of about 20% in compression ratio compared to the CoNiCr MEA, but the compressive strength is not significantly improved. The compressive curve of CoNiCr MEA belongs to the typical compressive curve of brittle materials. At the same time, according to the comparison of this two MEAs, the compressive strength and compression ratio of CoNiCr MEA increase with the increase of ball milling time, while those of the CoNiCu MEA decrease with the increase of ball milling time. Analyzing the reason from the microscopic morphologies of the sintered samples, it is inferred that the BCC structure of the CoNiCr MEA decreases with the increase of the ball milling time, and the volume fraction of the matrix phase of the FCC structure increases, which leads to the improvement of the compression ratio. While the porosity in CoNiCu increases with the increases of ball milling time, it results in decreasing compressive performance.
According to the compression fractures (as Fig.9), it can be clearly seen that the compression fracture of the CoNiCr-5h shows obvious intergranular fracture and grain shape. The reason may be that the poor sinterability of raw materials powder that was ball-milled only 5 hours results in low density and poor grain boundary bonding force. Therefore, when MEAs are subjected to external load, fracture tends to occur at the grain boundary. The compression fractures of the CoNiCr-30h show obviously cleavage fracture, and the compression fractures of CoNiCu-5h and CoNiCu-30h have obvious dimples and cleavage steps, which is quasi-cleavage fracture.

3.4 Friction and wear performance

According to the friction and wear test data of MEAs (as Table 2 and Fig.10), it can be clearly seen that the friction coefficient of CoNiCu MEA is more stable than that of CoNiCr MEA, and the fluctuation range is smaller. Meanwhile, the friction coefficient of CoNiCu MEA is higher than that of CoNiCr MEA. According to the data of wear scar depth, wear scar width, wear loss and specific wear rate (as Fig.11 and Table 2), the wear resistance of CoNiCr MEA and CoNiCu MEA is improved with the increase of ball milling time. The reason may be that, in CoNiCr MEA, the decreasing number of black BCC phase with the increase of ball milling time results in more uniform internal composition and structure of the alloy, which reduces the weakening effect of the phase boundary with weak binding force on the frictional properties. With the increase of ball milling time, the distribution of the
second phase of the CoNiCu MEA tends to be uniform, which improves the evenness of the composition and microstructure of the alloy, and enhances the wear resistance to a certain extent. Compared with the addition of Cu, the addition of Cr makes the friction performance of the CoNiX MEAs more excellent. The wear resistance of CoNiCr MEA is about 20–40 times that of CoNiCu MEA. This is because the microstructure of CoNiCr MEA is composed of FCC solid solution, BCC solid solution and CoNiCr intermetallic compound, while the microstructure of CoNiCu MEA is composed of FCC solid solution and BCC solid solution. The dispersed intermetallic compounds improve the hardness and wear resistance of the MEAs.

Table 2 Wear test data of MEAs

| MEAs     | Width of wear marks (mm) | Depth of wear marks (µm) | Wear loss (mm³) | Specific wear rate (×10⁻⁵ mm³/N·m) |
|----------|--------------------------|--------------------------|----------------|-----------------------------------|
| CoNiCr-5h| 0.879                    | 15.694                   | 0.083          | 4.611                             |
| CoNiCr-30h| 0.781                   | 11.299                   | 0.047          | 2.611                             |
| CoNiCu-5h| 1.925                    | 150.863                  | 1.881          | 104.500                           |
| CoNiCu-30h| 1.916                   | 148.726                  | 1.849          | 102.722                           |

Fig. 10 Friction coefficients of MEAs

Fig. 11 Contours of wear marks of MEAs

4. Conclusion

CoNiCr and CoNiCu MEAs were prepared by powder metallurgy with Co, Ni, Cr and Cu powder milled for 5h and 30h, and the effects of different milling time and different elements on the microstructures and properties of MEAs were studied, and the following conclusions are drawn:

(1) As the milling time increases, the agglomeration of metal powder weakens, and the density values of the sintered MEAs increase.

(2) The microstructure of CoNiCr MEA composed of Ni-rich FCC solid solution, Cr-rich BCC solid solution and CoNiCr intermetallic compound; while the microstructure of CoNiCu MEA is mainly composed of FCC solid solution with uniform composition of Co, Ni and Cu, and Co-rich FCC solid solution.

(3) Due to the weakening of powder agglomeration and the increasing density of sintered samples, the hardness of CoNiX (X=Cr/Cu)-30h is higher (about 20HV) than that of CoNiX (X=Cr/Cu)-5h, and long-term ball milling effectively improves the wear resistance, moldability and compressive strength of CoNiCr MEA, while the moldability and compressive strength of CoNiCu MEA are reduced, and the wear resistance of CoNiCu MEA is slightly improved.

(4) The addition of Cr and Cu has different effects on the properties of CoNiX MEAs. CoNiCr
MEA have high hardness and better wear resistance than CoNiCu MEA (hardness increased by about 70HV, wear resistance increased by about 20-40 times), while CoNiCu MEA has better compressive property than CoNiCr MEA (compression rate increased by about 1.5%).

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