STUDY ON SINTERING PROCES PARAMETERS OF BULK HIGH-ENTEROPY ALLOY PREPARATION

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Abstract - Based on the preparation of FeAlCoCrNiTi0.5 bulk high-entropy alloy by mechanical alloying and inert atmosphere sintering, the influence of sintering temperature on the microstructure, morphology and mechanical properties of the alloy was studied. With the increase of sintering temperature, it was found by X-ray diffractometry that the main phase of the alloy changed from the body-centered cubic phase BCC1 to the body-centered cubic phase BCC2. Scanning electron microscopy can be used to observe that the microstructure of the section is denser and the gap has a tendency to become smaller. At the same time, using the response surface method to fit the curve, it can be seen that the comprehensive mechanical properties of the alloy also increase with the increase of temperature.

Keywords: High Entropy Alloy, Response Surface Methodology, Sintering Temperature, Mechanical Properties.

1. Introduction

High-entropy alloys (HEAs) play an important role in both theoretical and practical applications. They are alloys composed of 5 to 13 metals or non-metals, and the elements are mixed in an equimolar ratio or close to an equimolar ratio. The percentage of various elements in the alloy is between 5% and 35% [1-2]. In high-entropy alloys, the mixing of various components [3] tends to cause severe lattice distortion, hindering the diffusion effect [4], promoting the precipitation of nanoparticles in the alloy, and the composite effect [5] makes the different elements in the alloy interact with each other. The effect has an interactive effect on the properties of the alloy.

Mechanical alloying is a complex physicochemical process that undergoes repeated deformation, cold welding, and crushing of high-energy ball milling to achieve atomic level alloying between elements. It plays an important role in improving the performance and application of HEAs [6]. The preparation of HEAs by mechanical alloying can avoid the segregation of component components, which is easier to obtain amorphous or nanocrystalline structures than conventional methods [7-8]. When the HEA is prepared by mechanical alloying, the sintering temperature has a great influence on the performance of HEAs [9]. Therefore, this study used mechanical alloying to prepare high-entropy alloy powder, sintered FeAlCoCrNiTi0.5 bulk high-entropy alloy in the inert atmosphere, changed its sintering temperature, combined with response surface methodology to study the phase formation mechanism and hardness of the alloy. And then we expect to provide a theoretical basis for the subsequent development of such research.

2. Materials and Methods

In order to study the influence of sintering temperature on the microstructure and mechanical properties of high-entropy alloy FeAlCoCrNiTi0.5, FeAlCoCrNiTi0.5 alloy powder was prepared by the mechanical alloying method. The material composition is shown in *Table 1*. The powder is weighed with an electronic balance with an accuracy of 0.001 g, placed on a weighing paper, and the weighed metal powder is placed in a cleaned planetary ball mill (XQM-0.4L type, as shown in *Figure 1 (a)*) mixed to alloy. The ball-to-boil ratio is 10:1 during ball milling, the ball milling time is set to 24h, and the rotational speed is 400r/min. Before the ball milling, the vacuum stainless steel tank was vacuumed, and the vacuum stainless steel tank was filled with high-purity argon gas (≧99.0%, 0.5 MPa) as a protective atmosphere during ball milling.

Table 1. The composition of alloy powder materials

Element	Ture (g)
Fe	8.09
Al	3.90
Co	8.52
Cr	7.51
Ni	8.52
Ti	3.46

(a)Frequency conversion planetary ball mill

(b)Vacuum tube furnace
Figure 1: Main experimental instruments

After the alloying of the metal powder, 5g of the alloy powder was weighed, 0.2g of stearic acid was added as a binder, and the powder was compressed into tablets using a tableting machine (DY-30 type) at a pressure of 30kPa and held for 60 minutes to obtain a block.

The block was placed in ceramic tweezers, clamped with a ceramic sheet, and sent to a vacuum sintering furnace (as shown in *Figure 1 (b)*).

First, a certain argon gas was charged into the furnace, and then vacuumed by a vacuum machine, three times.

The air in the vacuum furnace was discharged, and then the argon gas was filled.

The pressure in the furnace did not exceed 0.02 kPa. The setting procedure was raised from room temperature to 650°C, 750°C, 850°C, 950°C for 2h, and the temperature was kept constant. Argon gas was used as a shielding gas to maintain a constant pressure of no more than 0.02 kPa.

After sintering, after the furnace was cooled to room temperature, the sample was taken out and placed in a desiccant for storage.

The phase structure of the high-entropy alloy was analyzed by XRD, and the surface hardness of the sample was measured using a microhardness tester.

The friction and wear properties of the samples were tested using a material surface performance tester.

Finally, the microstructure of the section was examined by SEM.

3. Results and Discussion

- ***Phase analysis***

Figure 2 shows the X-ray diffraction spectrum of high-entropy alloy AlFeCoCrNiTi0.5 at different sintering temperatures. Through analysis, we can know that the high-entropy alloy AlFeCoCrNiTi0.5 is mainly composed of two body-centered cubic phases, BCC1 phase and BCC2 phase, and no other complicated intermetallic compounds have been found. This is also in line with the core effect of high-entropy alloys, namely the high entropy effect. It refers to the thermodynamically hindered formation of complex phases. Because of the traditional metallurgical laws, multi-element metals tend to form a variety of compounds and segregation phases due to the different interactions between the elements, and the resulting structure is not only complicated but difficult to analyze and brittle. However, the high entropy effect can inhibit the formation of various intermetallic compounds, making the high-entropy alloy exhibit a simple body-centered cubic structure or a face-centered cubic structure [10].

At the same time, since the Ti atoms and Al atoms in the alloy differ greatly from other atomic sizes, the atomic radius difference is greater than 15%. an asymmetrical gap is formed, which causes the degree of lattice distortion to be more serious. The distorted lattice increases the scattering of X-rays, so the other peaks except the main peak in the figure are lower.

It can also be seen from the above figure that when the sintering temperature is 650°C, the content of the BCC1 phase in the high-entropy alloy is dominant, much larger than the content of BCC2. As the temperature rises to 750°C, the BCC1 phase is still the main phase in the alloy, but the intensity ratio of the peak in the diffraction pattern shows that the content of BCC1 is decreased, and the content of BCC2 is gradually increasing. Continue to increase the sintering temperature and found that the presence of the ω phase can be detected not only in the XRD detection range. The comparison shows that the ω phase belongs to a close-packed hexagonal structure, and its diffraction peak coincides with the diffraction peak of AlTi3. When the sintering temperature is raised to 950°C, the diffraction peak of the BCC1 phase has not been detected in the detection accuracy range of XRD. *Table 1* gives the volume fraction of each phase at different sintering temperatures. It can be seen from the data in the table that increasing the sintering temperature will promote the transformation of the main phase BCC1 to BCC2. After reaching a certain temperature, the BCC1 phase will all be converted into BCC2 phase and ω phase.

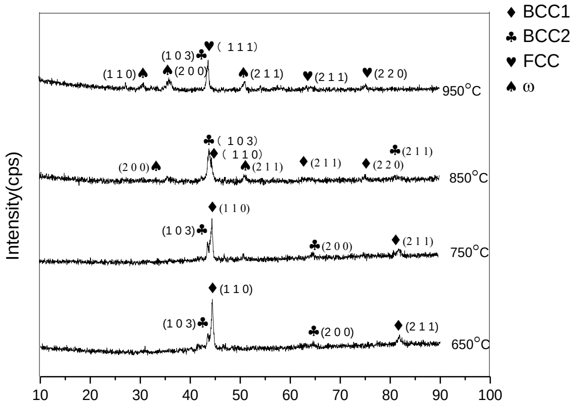

Figure 2: XRD Image of AlCoCrFeNiTi0.5 at Different Sintering Temperatures

Table 2. Percentage of the volume fraction of the main phase for the different sintering temperature

V.fraction	V_{bbc1} (%)	V_{bbc2} (%)
650(2h)	63.61	36.39
750(2h)	61.08	38.92
850(2h)	51.74	48.25
950(2h)	0	100

Table 3. The cell parameters of high entropy alloys at different sintering temperatures

Sintering temperature(°C)	BCC1 (Å)	BCC2 (Å)	ω-phase (Å)
650(2h)	2.8843	6.5756	-
750(2h)	2.8791	6.5296	-
850(2h)	2.8649	6.5028	2.4634/4.0236
950(2h)	-	6.5605	2.3440/3.8284

- ***Micromorphology analysis***

In this study, the fracture morphology of high-entropy alloys with different compositions was observed by SEM to analyze the micro-morphology of high-entropy alloys. *Figure 3* is an SEM micro-morphology of a FeAlCoCrNiTi0.5 high-entropy alloy sintered at 650°C, 750°C, 850°C, and 950°C in an inert atmosphere.

It can be clearly seen from *Figure 3* that the macrostructure of the high-entropy alloy after sintering is equiaxed. We can also observe that the microstructure of the alloy is denser after sintering, and a nanocrystalline phase is produced. This may be because, during the sintering process, the alloy undergoes crystal deformation and phase transformation, resulting in a shear stress in some directions in the crystal lattice.

When the stress exceeds the critical shear stress of a particular twin system, the twin system is activated, and some specific crystal planes in some grains will be relatively slipped, resulting in deformation twins [11]. But at the same time, it can be found that there are still some pores in the sintered block.

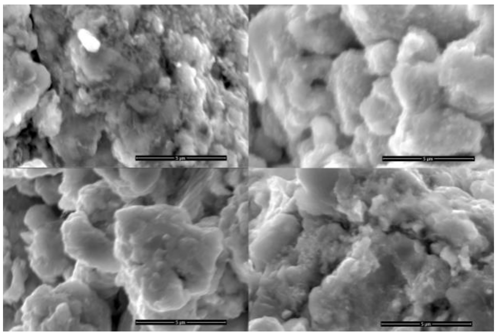

Figure 3: SEM photographs of 30000-fold magnification of samples incubated at 650°C, 750°C, 850°C, and 950°C

When the maximum temperature is 650°C, the alloy has less bulk structure, the fracture shows different degrees of grain polyhedron shape, the graininess is obvious, and there are still many holes because the inside of the grain in the alloy is mostly composed of amplitude modulation structure [12].

When the temperature rises to 750°C and 850°C, the graininess of the alloy is significantly reduced, the porosity is lowered, the agglomeration phenomenon in the alloy is obvious, the density is increased, and the crystal grains are gradually refined because the elevated temperature increases the diffusion efficiency of the element and makes the alloying elements more uniform. However, when the sintering temperature rose to 950°C, we observed that the grains were continuously roughened.

This is because as the heat treatment temperature is further increased, the grain size of the alloy is continuously increased, but the degree of growth is small, the atomic diffusion coefficient is large, and the grain boundaries are more likely to migrate, so the crystal coarsening becomes larger. But at 950°C we can clearly observe the appearance of a network in the alloy. Here we believe that the nanocrystalline phase that occurs at lower sintering temperatures is interwoven at high temperatures.

Thereby the phase in the alloy is more stable.

- ***Hardness analysis***

Due to the large number of main elements of high-entropy alloys and the high degree of atomic disorder in the alloy system, the atomic diffusion rate in the system is slow during solidification crystallization, and many atoms will exist in the form of interstitial atoms in the solid solution to form a "Super solid solution" with a simple crystal structure and severe lattice distortion. Adding large atomic radius elements such as Al and Ti to high-entropy alloys can enhance lattice distortion and solid solution strengthening. A large number of solid solution atoms hinder the movement of dislocations, thereby increasing the strength and hardness of the alloy [13]. In addition, the synergistic diffusion between the elements in the multi-principal high-entropy alloy is difficult, which hinders the growth of the new phase and forms the nanophase, so that the strength of the alloy will be further improved [14].

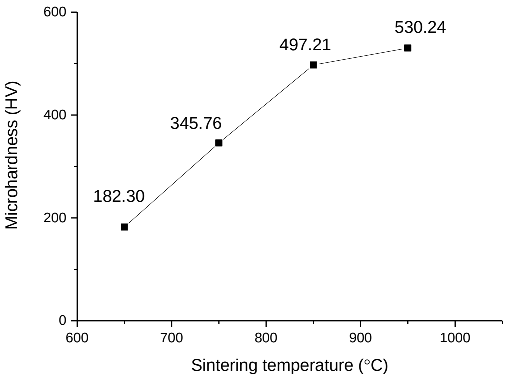

Figure 4: Microhardness values of specimens incubated for 2 hours at different sintering temperatures

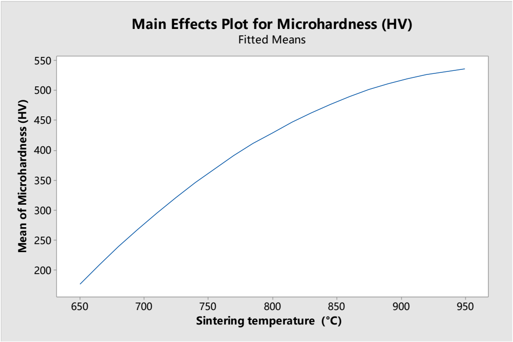

Figure 5: A plot of the fitting curve of hardness and sintering temperature

The hardness measurement results are shown in *Figure 4*, and *Figure 5* is a plot of the fitting curve of hardness and sintering temperature using Minitab. It can be seen from *Figure 4* and *Figure 5* that as the holding temperature increases, the hardness gradually increases and the hardness reaches a maximum at 950°C, reaching 530.24 HV. It can be seen from the analysis of XRD that as the sintering temperature increases, the phase structure of the high-entropy alloy changes continuously from the Al-Ni phase to the Fe-Cr phase, while the Fe-Cr solid solution has higher hardness and stability.

Therefore, the hardness of the high-entropy alloy increases. In addition, it can be seen from the analysis by SEM that as the sintering temperature increases, the crystal grains become thinner and the hardness thereof increases.

- ***Friction and wear analysis***

Good wear resistance is one of the important properties of high-entropy alloys. Therefore, the friction and wear properties of high-entropy alloys after sintering are studied. The effects of different sintering temperatures on the wear resistance of high-entropy alloy FeAlCoCrNiTi0.5 are discussed.

Figure 6 shows the measured friction and wear coefficients, *Figure 7* shows the measured wear, and

Figure 8 shows the fitted curve for the wear and sintering temperatures using Minitab. The coefficient of friction is an important parameter used to indicate the friction properties of a material. The amount of wear is the change in mass of the sample before and after the measurement.

The smaller the coefficient of friction, the less the amount of wear, indicating that the friction properties of the material are better.

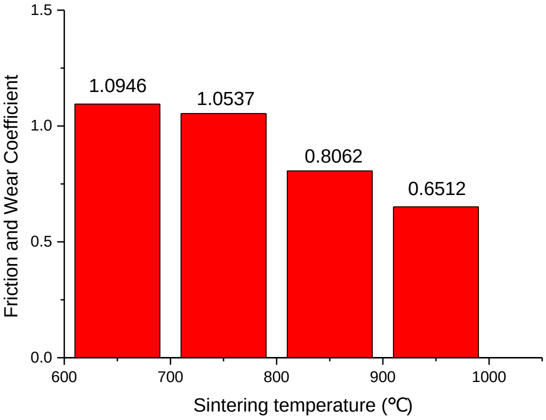

Figure 6: Friction and Wear Coefficient of AlCoCrFeNiTi0.5 at Different Sintering Temperatures

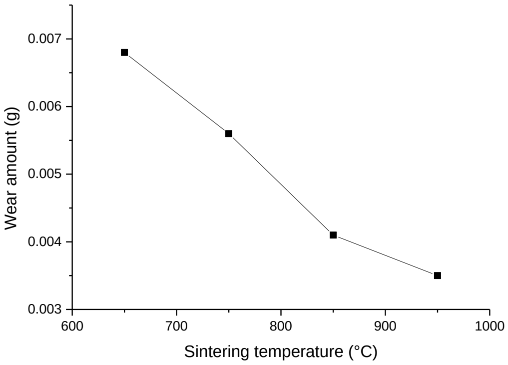

Figure 7: The wear of different sintering temperature specimens

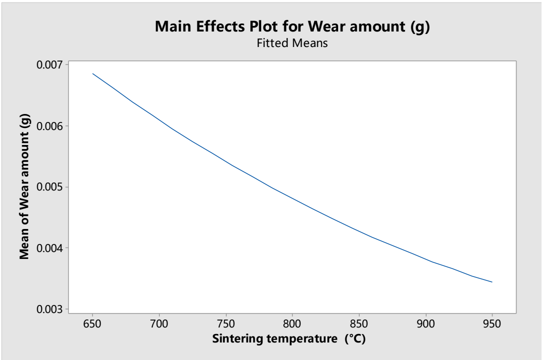

Figure 8: A plot of the fitting curve of the wear and sintering temperatures

As can be seen from *Figure 6* and *Figure 7*, as the sintering temperature increases, the average friction coefficient decreases overall and the amount of wear gradually decreases. According to the SEM analysis, as the sintering temperature increases, some intermetallic compounds or other crystal phases melt and penetrate, filling some pores in the high-entropy alloy, the grain size is reduced, the porosity is lowered, and the alloying elements are more uniform, making the surface

It is flatter, so the friction coefficient is reduced and the amount of wear is reduced.

4. Conclusions

In this paper, the high-entropy alloy was used as the research object, and the structural characteristics and mechanical properties of the alloy were studied by X-ray diffractometer, scanning electron microscope, microhardness tester and surface property tester.

The results show that with the increase of temperature, the main phase of high-entropy alloy FeAlCoCrNiTi0.5 gradually changes from the body-centered cubic BCC1 phase to BCC2 phase.

When it reaches 950°C, the BCC1 phase in the alloy completely transforms into BCC2 phase and ω phase.

The porosity of the high-entropy alloy after sintering will gradually decrease and the structure will be denser.

The sintering time is proportional to the hardness of the alloy and inversely proportional to the friction and wear coefficient.

It shows that increasing the sintering temperature is beneficial to enhance the various comprehensive properties of high-entropy alloys.

Acknowledgements

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