Effect of sintering atmosphere on the microstructure and properties of nano-WC modified copper-iron-based oil-containing bearing

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Abstract. Nano-WC modified copper-iron-based oil bearing was prepared by powder metallurgy. The effect of sintering atmosphere on the microstructure, crushing strength, hardness and oil content of the oil bearing were studied. The results show that under the sintering condition of 865 °C×30min, when the sintering atmosphere is 100%N₂, the sintering process stays in the early stage of sintering neck growth, there are a large number of irregular pores in the microstructure. The sintering densification is insufficient, and the sample is in the state of undersintering. When the sintering atmosphere is 100%H₂, the dezincification of matrix phase α(Cu) is serious, and there are many long strip microcracks between metal particles. The effective connection between α(Cu) and Fe phase is cut off, so the density of sample is very low. When the sintering atmosphere is 75%H₂+25%N₂, α(Cu) forms a united whole through sufficient sintering diffusion bonding, and encapsulates the Fe-rich phase. The sintering densification is very sufficient, the pores in the microstructure tend to be circular. The sintered samples have good comprehensive properties, the density and oil content are 6.60 g/cm³ and 18.21vol.%, the crushing strength and hardness are 235.81 MPa and 42.41 HB, respectively, showing the best sintering state.

1. Introduction

Copper-based oil-containing bearing has become one of the most widely used powder metallurgy parts in industry because of its good corrosion resistance and grinding properties. It has become an indispensable basic part in automobile, precision machinery and other fields. Fe, Zn, Ni, Mo, P,C, MoS₂ and other components are generally added to the copper-based oil-bearing bearing, thereby forming solution strengthening or reducing the friction and wear. In recent years, some Chinese manufacturers have added a high content of sponge iron powder to the copper powder, so as to prepare the copper-iron-based oil-bearing [1], and the strength and hardness of the material are improved on the basis of ensuring a certain oil content.

The sintering atmosphere has a decisive influence on the density, oil content, crushing strength, hardness, and friction properties of the sintered sample [2]. Qian et al. [3] studied the effect of H₂+Ar sintering protective atmosphere with different H₂ content on the microstructure and properties of CuSn10 oil-bearing materials. As the H₂ content in the sintering atmosphere increases, the oxides on the surface of the powder particles are reduced, the number of pores is decreased, the pore shape tends to...
be spherical and refined. The oil content of sintered samples decreases, but the oil density, crushing strength and hardness of sintered samples are increased. Yan et al. [4] prepared a sample of aluminum-based sintered oil-containing bearing containing 7.5% copper by powder metallurgy. When the sintering temperature was 560 °C and the sintering time was 120 min, the sintered samples had good comprehensive properties, and the crushing strength and oil content were 151.3 MPa and 16.7%, respectively, showing the best sintering state. Wang et al. [5] prepared Cu, Sn mixed powder by high energy ball milling. The oil bearing was sintered at 800 °C×1h in N2 atmosphere. The porosity is 22.45% and the crushing strength is 220.8 MPa.

The effect of 100%N2, 75%H2+25%N2 and 100%H2 sintering protective atmosphere on the structure and properties of the nano-WC modified copper-iron-based oil-bearing is studied in this paper. The thermal behavior, phase composition and microstructure of the material were analyzed by thermogravimetric analysis, X-ray diffraction, zanning electron microscope and energy dispersive spectroscopy.

2. Materials and experimental procedures

The chemical compositions of nano-WC modified oil-containing bearing used in this study are listed in Table 1. The brass powder and iron powder used in study have different particle sizes with irregular shapes as shown in Fig.1. The purity and particle size of the raw material powder for the experiment are listed in Table 2.

Taking the preparation of 100 g powder as an example, the preparation method of the powder comprises the following steps: Firstly, 0.05 g of polyethylene glycol with molecular weight of 400 and 0.15 g of AEO-9 were added to 200mL anhydrous ethanol to obtain dispersed solvent. Then 0.2g of nano-WC is added into the dispersed solvent, and the dispersion liquid is obtained by ultrasonic oscillation and mechanical stirring for 30 min. Then the weighed sponge iron powder, the tin powder, the phosphorus copper powder, the graphite powder and the brass powder are poured into the stainless steel ball-milling pot, the wet grinding is carried out for 6 h, the rotating speed is 130 r/min, the ball material ratio is 5:1. The powder treated by ball milling was dried, and finally the alloy powder was mixed uniformly by V-type mixer for 2 h. The alloy powder is poured into the mold cavity and pressed into a green compact bearing with a green compact density of 6.6g/cm3. The sintering conditions are: under the protection of 100%N2, 75%H2+25%N2, and 100%H2 respectively, the temperature is first increased to 380 °C, the temperature is maintained for 17 min, and then the temperature is increased to 550 °C, the temperature is maintained for 17 min, and then the main sintering is heated to 865 °C, hold for 30min, and finally cool to normal temperature with the furnace after 2h.

| Element | Fe | Sn | Cu-8P | C | WC | Cu-31.9Zn |
|---------|----|----|-------|---|----|-----------|
| wt.%    | 35.5 | 0.5 | 3 | 0.5 | 0.2 | Bal. |

Table 1 Chemical composition of the bearing. (wt.%).

| Element | Fe | Sn | Cu-8P | C | WC | Cu-31.9Zn |
|---------|----|----|-------|---|----|-----------|
| Purity/% | 99.8 | 99.8 | 99.8 | 98 | 99.9 | 99.8 |
| Particle size /μm | <180 | <45 | <75 | 2-3 | <0.06 | <150 |

Table 2 The purity and particle size of the raw material powder.

After sintering, the phase composition was analyzed by D8 Advance X-ray diffractometer, and quality change of alloy powder were analyzed by NETSCH STA449 F3 synchronous thermal analyzer. The microstructure of the sintered samples was observed by DMI500 M intelligent inverted metallographic microscope and Nova Nano SEM 430 scanning electron microscope. According to GB/T 5163-2006, the density and oil content of oil-containing bearing were determined by archimedes drainage method. The hardness was tested by XHB- 3000 digital display Brinell hardness tester. The applied load was 62.5 kgf and the holding time was 15 s. Five points were randomly selected on the surface of the sample during the test, and finally the average value was calculated. The radial crushing strength of bearings is measured on CMT4102 electronic universal tester. The radial crushing strength of the bearing is measured on a CMT4102 electronic universal testing machine. The compression rate is 1mm/min. The crushing strength K is calculated as:
Where F is the crushing force of the bearing, N; D, e are the outer diameter and wall thickness of the sample, mm; L is the length of the sample, and mm.

3. Result and discussion

3.1. Effect of sintering atmosphere on microstructure of copper-iron based oil-containing bearing

Fig. 2 shows the TG-DTG curve of alloy powder with heating rate of 10 °C/min in high purity N₂ atmosphere. As the temperature rises from room temperature to 304.8 °C, the quality of the powder gradually decreases to 99.8%. Because as the temperature increases, the water and gas adsorbed by the powder particles evaporate, and some Sn particles melt and flow out. When the powder increases from 304.8 °C to 737 °C, the mass of the powder increases gradually to 101.6%, which may be due to the reaction of N₂ and Fe powder at high temperature, which produces a similar effect of nitriding, and the powder sample gained weight [6]. Above 737 °C, as the temperature increases, the quality of the powder decreases sharply. Especially at 850.4 °C, the rate of mass decrease is the largest. This is because at this temperature, some Zn in Cu-Zn alloy is dissociated due to the fracture of metal bond and migrated to the crystal surface [7]. The boiling point of Zn is 907 °C. Therefore, when the temperature rises to 850 °C, the phenomenon of dezincification is intensified, and the removal of a large amount of Zn causes a sharp reduction in powder quality.
Fig. 3 is an XRD pattern of a sample with a sintering temperature of 865 ℃. It was found that the sample was composed of α(Cu), Fe and WC. However, the compounds of Sn, P and C were not found, probably because their content was too low to be detected.

Fig. 4 is a metallographic micrograph of the sample in different sintering atmosphere at 865 ℃. The yellow area is α(Cu), the gray area is the Fe-rich phase, and the black area is the pore and the graphite. As can be seen from Fig. 4, in addition to the many pores in the α(Cu), there are many pores in the Fe-rich phase, because the iron powder added in the raw material is sponge iron powder, and its interior contains many pores. In addition, the pores in the remaining part are the gaps between the powder particles and the pores generated by melting and flowing out of tin powder and phosphor copper powder during sintering [8]. When sintered in 100% N₂ atmosphere, there is a clear gap between the brass particles. The sintering neck is hardly formed, the metallurgical bonding is poor, the sintering densification is not sufficient, and the sample is under the state of under-sintering. Many irregular pores are present in the matrix tissue, and the size is between 30 and 50 μm. When sintered in 75%H₂+25%N₂ atmosphere, the diffusion bonding between the brass particles and the diffusion bonding of the brass particles and the iron particles are very sufficient, the sintering densification is sufficient. The pores in the tissue tend to be circular, and the size is about 10 μm. When sintered in 100% H₂ atmosphere, the profile of the powder particles is very obvious, and the dezincification phenomenon of the α(Cu) is serious, resulting in obvious gaps between the brass particles and between the brass particles and the iron particles. The metallurgical bonding is poor, the sintering densification is low, and the size of pores in the matrix structure are different.
scanning of α(Cu) was carried out. A small amount of Fe and C atoms were found for the α(Cu) of the sample in the three sintering atmospheres, indicating that a small amount of Fe and C elements in the sintering process were diffused into α(Cu) by diffusion. The Zn content of α(Cu) was the highest in 75%H2+25%N2 atmosphere, the mass fraction was 26.84%. The Zn content of α(Cu) in 100%N2 atmosphere was moderate, the mass fraction was 26.27%. But the Zn content of α(Cu) in 100%H2 atmosphere was the lowest, the mass fraction was only 18.22%. Compared with 31.9wt.% Zn in raw brass powder, the Zn content of α(Cu) in three sintered atmosphere was decreased by about 5% and 13%. In addition to the loss caused by the diffusion of Zn atoms to Fe phase during sintering, the decrease of Zn content is mainly due to the dezincification of brass when sintered at 865 °C. The Zn content of α(Cu) in 100%N2 and 75%H2+25%N2 sintering atmosphere is basically the same, and the degree of dezincification is light. In the 100% H2 sintering atmosphere, the Zn content of α(Cu) decreased drastically. Plug-like dezincification occurred, the dissolution of local zinc resulted in the formation of corroded pores, and finally a loose porous copper layer was formed [9]. When sintered in 100%N2 sintering atmosphere, due to the lack of reductive gas in the atmosphere, it is difficult to completely remove the oxides on the surface of the alloy particles caused by the reduction reaction caused by copper-phosphorus eutectic powder. Therefore, the wettability between particles is poor, the formation of firing neck is difficult, the metallurgical bonding is poor, and the shrinkage of the sample is low, so there are a large number of irregular pores in the microstructure. In 75%H2+25%N2 sintering atmosphere, high concentration of H2 reduces the metal oxide, letting the surface of metal particles exposed. At high temperatures, the atoms between the brass particles diffuse rapidly and form an adhesive surface between the particles. The sintering neck is formed under the push of chemical level difference and gradually grows up, and the final pore is gradually reduced and spherical, and the sintering densification is sufficient. In the 100%H2 sintering atmosphere, the sintering process should have been more fully completed, but during the sintering process, a large amount of zinc was removed from the α(Cu) grain boundary, and obvious intergranular corrosion occurred [10], resulting in a large number of microcracks.

Fig. 5. SEM morphology and energy spectrum analysis of samples in different sintering atmospheres, (a),(b)100%N2; (c),(d) 75%H2+25%N2; (e),(f)100%H2.
3.2. Effect of the sintering atmosphere on the physical and mechanical properties of the copper-iron-based oil-containing bearing

Fig. 6. shows the comparison of the shrinkage of the samples in different sintering atmosphere at 865 °C. It can be found that when sintered in 100%N₂ atmosphere, the shrinkage of the sample is the lowest, and the radial and axial shrinkage are 0.64% and 1.1%, respectively. When sintered in 100%H₂ atmosphere, the shrinkage of the sample is the highest, and the radial and axial shrinkage are 0.9% and 1.9%, respectively. The shrinkage of the samples sintered in 75%H₂+25%N₂ atmosphere is between the two.

![Fig. 6. Comparison of shrinkage of samples in different sintering atmosphere.](image)

Fig. 7. shows the comparison of the oil content and density of the samples in different sintering atmosphere at 865 °C. When sintered in 75%H₂+25%N₂ atmosphere, the oil content and the density of the sample are the highest. The oil content and density of the samples in 100%N₂ sintering atmosphere are slightly lower than those of the former. The oil content and density of the samples in 100%H₂ sintered atmosphere are both the lowest. Fig.8 shows the comparison of the quality reduction rate of samples in different sintering atmosphere at 865 °C. The sample quality reduction rate of 75%H₂+25%N₂ atmosphere and 100%N₂ sintering atmosphere is basically the same, the former is slightly higher, while the sample quality reduction rate of 100%H₂ sintering atmosphere is 9.8%, which is much higher than other atmosphere.

![Fig. 7. Comparison of Oil content and density of samples in different Sintering atmosphere.](image)
Fig. 8. Comparison of quality reduction rate of samples in different Sintering atmosphere.

Fig. 9 shows the comparison of crushing strength and hardness of samples in different sintering atmosphere at 865 ℃. It can be found that the crushing strength and hardness of the samples sintered in 75%H₂+25%N₂ atmosphere are the highest, which are the crushing strength of 235.81 MPa and 42.4 HB. The crushing strength and hardness of the samples in 100%H₂ atmosphere are the lowest, which are 151.84 MPa and 33.2 HB, respectively.

Fig. 9. Comparison of crushing strength and hardness of samples in different Sintering atmosphere.

When sintered in 100%N₂ atmosphere, the sintering process of the sample is not enough, and finally stays in the early stage of sintering neck growth. The pores do not shrink and spherical [10], most of them are irregular long strip cracks. This large pore seriously weakens the hardness of the sample. In addition, the crack is easy to extend along the gap in the process of radial stress, resulting in stress concentration, so it is easy to be crushed. The α(Cu) of the samples sintered in 75%H₂+25%N₂ atmosphere forms a connected whole through sintering diffusion bonding, the powder particles have a good degree of atomic diffusion bonding in the sintering process, and the pores are more uniformly dispersed in the microstructure. Because of their small size and spherical shape, they can be used as good oil storage pores and adsorb lubricating oil by capillary force, so their density and oil content are higher. The higher density increases the effective bearing area of the sample, and the crack is more difficult to produce, thus obtaining excellent crushing strength and hardness. When sintered in 100%H₂
atmosphere, the shrinkage of the sample is the highest. But there is a serious dezincification phenomenon in this atmosphere, which makes the reduction rate of sample quality greatly increase, and the influence on density occupies a dominant position, so its density is the lowest among the three. It can be seen from the metallographic picture that a large number of microcracks occur at the grain boundary of α(Cu), which increases the porosity. But the pore size is large, and is not spherical. It is difficult to absorb the oil through the capillary force, so the oil content is seriously reduced. The microcrack divides the effective connection between the phases. Due to the notch effect, the stress concentration reduces the plasticity of the material, and the crushing strength and hardness are very low.

4. Conclusions
(1) The sintering temperature is above 737 °C, Dezincification occurs in α(Cu), which will cause the sample to lose weight. As the temperature increases, the dezincification phenomenon increases. At 850.4 °C, the quality of the sample decreases most.
(2) The microstructure of nano-WC modified copper-iron-based oil bearing prepared at 865 °C is composed of α(Cu), Fe-rich phase, C and WC. The components are evenly distributed.
(3) Under the sintering condition of 865 °C×30min, when the sintering atmosphere is 100%N₂, the sintering stays at the early stage of sintering neck growth. The pores do not shrink and spheroidize, and there are a large number of irregularly shaped connected interface pores in the sintered structure. When the sintering atmosphere is 75%H₂+25%N₂, α(Cu) forms a connected whole through sintering diffusion bonding. The powder particles have a good degree of atomic diffusion bonding during the sintering process, and the pores are more uniformly dispersed in the structure, and the size is small and the shape tends to be spherical. When the sintering atmosphere is 100%H₂, a large amount of Zn is removed from the α(Cu) grain boundaries during sintering. Obvious intergranular corrosion occurs, which results in a large number of strip-shaped cracks.
(4) Under the sintering condition of 865 °C×30min, when sintered in a 100%N₂ atmosphere, the shrinkage of the sample is the smallest. The density is medium but the oil content, crush strength and hardness are low. When sintered in 75%H₂+25%N₂ atmosphere, the shrinkage of the sample is large, and the density, oil content, crush strength and hardness are the highest. When sintered in a 100%H₂ sintering atmosphere, the shrinkage of the sample is the largest, but the density, oil content, crush strength and hardness are the lowest.

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