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Fabrication of sintered Zn-27%Al and comparison of its tribological behavior with cast alloy①

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[Abstract] High quality Zn-base powder with low oxygen content, fine particle size and fine microstructure can be obtained by gas atomization using nitrogen. Cast and sintered Zn-27%Al alloys (ZMJ) were prepared. Tribological behaviors of the cast and sintered alloys under lubricated and non-lubricated conditions were studied and compared. Worn surfaces and microstructures of these alloys were examined. Results indicate that although the strength of the sintered alloy is considerably less than that of the cast alloy, the sintered alloy has a better wear resistance. The fine microstructure obtained by rapid solidification is beneficial to the wear-resisting property. The wear volume of sintered ZMJ is only 36% and 59% of the wear volume that found in cast ZMJ under non-lubricated and lubricated conditions, respectively. For lubricated wear test, abrasive wear is the major wear mechanism and for non-lubricated wear test, oxidation wear and adhesive wear are the major wear mechanisms.

[Key words] powder metallurgy; Zn-27%Al; tribological behavior; intermetallic phases; undulated surface
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1 INTRODUCTION

Zinc-based alloys with high Al contents such as ZA-12 and ZA-27 were developed in the 70's of the last century. Relative low density and good mechanical property, castability, machinability and tribological behavior are advantages of these alloys in replacing cast iron, steel, bronze and aluminum based alloy. They have found wide applications in automobile and other industries[1~3], for example, replacing some steel parts in the wheeling system and replacing cast iron in gearboxes. In addition to its outstanding mechanical property, the remarkable tribological behaviors of ZA-27 make it find success in replacing bronze as engineering parts such as bushes, bearings and worm gears in the machinery industry. It attracted great attention in the bearing industry[4~6]. Literature shows that under low speed (27.44 m/min) and heavy load (6.89 MPa) condition, ZA-27 has a better wear resistance, run in ability and lower friction coefficient when compared with lead bronze[1, 2, 5]. However, due to the lost of strength at elevated temperature the maximum sliding speed for ZA-27 is limited to 7.1 m/s and the maximum working temperature is limited to no more than 150 ℃[1, 6]. Li et al[7~9] developed a high strength, wear-resisting zinc alloy (ZMJ) based on the composition of ZA-27. The maximum sliding speed and working temperature of the ZMJ have been extended to 8.0 m/s and 170 ℃, respectively, about 12% better than those of ZA-27. With its remarkable tribological behaviors ZMJ have already found success in replacing aluminum bronze as elevator tractor's worm gear in several models of elevators. If the maximum sliding speed and working temperature can be extended further, with only two third of the density of bronze and high strength, Zn-27%Al alloy should find wider applications in the coming years, especially in the fields of wear-resisting parts.

Rapid solidification can refine grain size, extend solid solubility and avoid segregation. All these effects are helpful in developing an alloy with better high temperature strength. Adding reinforcing particles to the metal matrix is another way to promote high temperature property. Research on ZA-27 based metal matrix composite has already been carried out for several years. Most of them employed cast methods such as squeeze casting, liquid melt infiltration, semisolid-slurry processing[10], and in-situ reaction forming cast[11] as well recently spray deposition method was reported[12], but very little attempt was made in using powder metallurgy (P/M) method. The biggest problem in preparing the P/M zinc alloy is the oxide film that covers the powder surface. Zn and Al form oxides readily in atmosphere and it is hard to be reduced. This oxide film hinders the sintering process. By overcoming this hindrance we successfully developed a P/M Zn-27%Al alloy, which is the first step in our goal to achieve P/M zinc-based metal matrix composite. In this paper, the preparation of this P/M alloy is briefly described and its tribological behavior is studied and compared with those of the cast coun-

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terpart.

2 EXPERIMENTAL

The material used in this study was a high-strength, wear-resisting zinc-based alloy (named ZMJ), which was developed by our group based on the chemical composition of ZA-27. It contains 26% ~ 29% Al (mass fraction), 2.0% ~ 2.5% Cu and 0.3% ~ 0.6% Mg as major alloying elements, and is modified by Mn, Ti, B and rare earth elements (RE). Commercially pure Zn, Al, Cu, Mg, Mn and master alloys containing modifying elements were weighted and melted in a graphite crucible. Processing temperature was controlled below 700 ℃ to avoid the lost of Zn. The molten alloy was then atomized at 550~ 600 ℃ by nitrogen with a gas pressure of 1 MPa. The particle size and particle size distribution was measured by sieve analysis. Flowability, apparent density, micro hardness and oxygen content of the pre-alloyed powder were also measured. A Leco TC30 nitrogen and oxygen analyzer was used to measure the oxygen contents. Scanning electron microscope (SEM) and optical microscope were used to study the morphology and microstructure of the powder.

Samples for radial crushing strength tests and friction and wear tests were prepared from the gas atomized ZMJ powder by applying a specific pressure of 600 MPa to form compacts in steel molds. Subsequently they were sintered at a temperature of 400 ℃ for about 40 min in dissociated ammonia atmosphere after pre-sintered at 350 ℃ for 20 min. Additives were added into the zinc-based alloy powder to activate the sintering process. For comparison, samples for friction and wear tests were cast from ZMJ melt also.

Samples for radial crushing tests were hollow cylinders with outer diameter of 30 mm, inner diameter of 22 mm and height of 18 mm. Its relative density is controlled to approximately 83% when compared with pore free ZMJ.

Cylinder-on-ring wear testing machine was used to measure the temperature rise during wear test. Wear sample was a cylinder with a diameter of 12 mm and a height of 15 mm. Its relative density is controlled within the range of 85% to 90%. The wear test counterpart was a GCr15 steel ring with a hardness of HRC 52~ 54. A linear speed of 53.16 m/min and a load of 686 N were used. Commonly used engine oil was used as lubricant. The oil temperature rise was recorded every 5 min using a mercury thermometer. The running time for each test was 30 min.

Lubricated and non-lubricated wear tests were carried out on a MM-200 tribometer. The wear test sample was a 10 mm × 10 mm × 10 mm cube and its relative density is controlled between 85% and 90%. The wear test counterpart was a ring made of GCr15 steel with outer diameter of 46 mm, inner diameter of 16 mm, thickness of 10 mm and hardness of HRC 52 ~ 54. Revolving speed of 400 r/min (57.8 m/min) was used in this study. Friction torque data were recorded every 5 min. For non-lubricated test a load of 147 N and a testing time of 30 min were used. For lubricated test a load of 294 N and a testing time of 90 min were used. Engine oil was dripped into the samples as lubricant at a rate of 50 to 60 drops per minute.

Wear volume was determined by measuring the width of the worn surface using a traveling microscope in all wear tests. These wear volume data were verified by measuring the mass loss of the worn samples by a sensitive digital balance accurate to 0.1 mg. Chemical compositions of the samples were analyzed by SEM equipped with an energy dispersive X-ray (EDX) analyzer.

3 RESULTS AND DISCUSSION

Results show that high-quality ZMJ powder with an average particle size of 58 μm, apparent density of 2.37 g/cm^3, flow rate of 0.696 s/g, microhardness of HV 64.9 and oxygen content of 0.1% (mass fraction) can be obtained by gas atomization. Microstructure of the rapidly solidified ZMJ powder contains fine grains in the size range of microns. They were much finer than that of cast ZMJ, which has grain sizes in the range of tens of microns. It composed mainly of α matrix (fcc solid solution of Al) and eutectics with intermetallic phases evenly distributed among the matrix and they are much smaller than those in the cast sample. Fig. 1(a) and (b) show the microstructures of cast and sintered ZMJ, respectively. In Fig. 1(a), gray areas are α matrix, dark areas are eutectics and the white blocks and rods are intermetallic hard phases, some of them have a size as large as 0.1 mm in length. While in Fig. 1(b) dark gray areas are α matrix, white spots are intermetallic hard phases and large dark areas are pores. In contrast with cast ZMJ no block and rod shaped intermetallic phases can be seen in the sintered sample.

Table 1 lists the EDX chemical composition results of samples prepared by casting and powder metallurgy. Although the preparation methods are different, the final composition of the cast and sintered samples are very close. Both Al and Zn are readily oxidized in air. These oxides seriously hinder the sintering of the alloy. The powder obtained through gas atomization using nitrogen containing a low level of 0.1% of oxygen is a good starting material for our study.

Table 2 lists some mechanical property and tribological behavior of the cast and sintered ZMJ samples. Very fine debris were found in sintered ZMJ experiments, while the debris found in cast ZMJ experiments were significantly larger in all wear tests. The smaller debris found in sintered ZMJ tests is because of the finer microstructure and the higher micro hardness of the matrix. Worn surfaces of the samples after non-lubricated and lubricated wear test were analyzed by using SEM and EDX. For lubricated wear test ploughs can be seen in all samples and minor adhesion of Fe was found on the sample surface by EDX. For all lubricated tests, abrasive wear is the major wear mechanism under this experimental condition. For non-lubricated wear tests worn surface turned dark soon after the test started. Ploughs were not as obvious and adhesion of Fe became serious in all samples. For all non-lubricated wear tests adhesive wear and oxidation wear were the major wear mechanisms.

Although the sintered ZMJ has a lower apparent hardness of HB 62 compared to HB 110 for the cast ZMJ due to its porosity, the rapidly solidified ZMJ has a higher micro hardness than that of the cast ZMJ since it has much finer microstructure and it contains supersaturated solid solutions of α(Al). Micro hardness of the sintered ZMJ matrix was HV 60.4 compared to HV 46.5 for the cast ZMJ matrix. Wearing is a microscopic process, the micro hardness of materials plays a more significant role than the apparent hardness. The finer microstructure and the harder matrix help reduce the plough out of large material pieces. The much smaller debris found in the sintered ZMJ wear tests proved this. For both non-lubricated and lubricated wear tests, the non-lubricated wear volumes (W_{dry}) and lubricated wear volumes (W_{lube}) in sintered ZMJ are considerably less than those in cast ZMJ. As pointed out by Li et al[7, 8], at the early stage of the friction process, part of the relatively soft α matrix was removed from the contact interface, meanwhile, hard intermetallics were exposed and formed "ridges" and "valleys" on the alloy's surface. Their EDX results[7] showed that the concentration of Mg, Ti, Mn and RE were found in these "ridges", which indicated that hard phases were present in this area, while only Al, Zn, Cu and RE were found in these "valleys", which indicated that these area consists of mostly α matrix and eutectics. At the ZMJ-steel contact interface, the evenly distributed and bulged hard intermetallic phases that inlaid in the matrix support the load and directly take the pressure that exerted from the steel mating counterpart. The relatively soft matrix is just barely in contact with the steel surface, its primary function is to hold the particles in place and disperse the load evenly in all

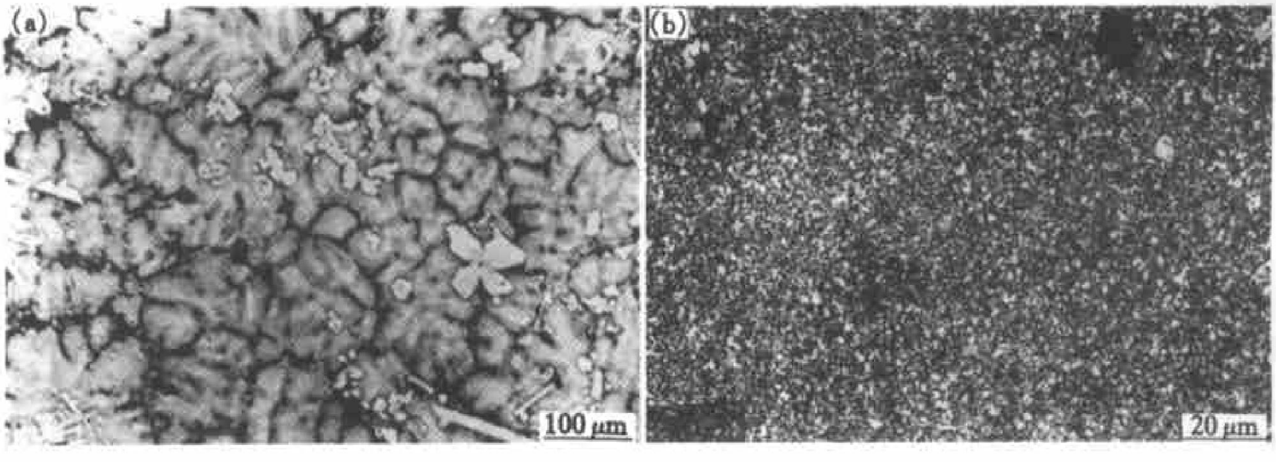

Fig. 1 Microstructures of cast (a) and sintered (b) ZMJ

Table 1 EDX chemical composition results of samples (mass fraction, %)

Sample	Al	Cu	Mg	Mn	Ti	B	RE	Zn
Sintered	25.6	2.5	< 1	< 1	< 1	< 1	< 1	Bal.
Cast	26.4	4.3	< 1	< 1	< 1	< 1	< 1	Bal.

Table 2 Mechanical property and tribological behavior of samples

Sample	Maximum lube temp. / ℃	μ_{lube}	μ_{dry}	W_{lube}/ mm^3	W_{dry}/ mm^3	Apparent hardness (HB)	Matrix micro hardness (HV)	Porosity/ %	Crushing strength/ MPa	Compress strength/ MPa
Sintered	78	0.025	0.52	2.7	8.1	62	60.4	13	69	–
Cast	82	0.026	0.52	4.6	22.5	110	46.5	< 1	–	600

directions. Due to the presence of these bulged intermetallic phases, at the ZMJ-steel contact interface there is considerable room for lube oil storage to upgrade the lubricating condition and these spaces provide more room for lube oil to carry away wear debris from the contacting surface and reduce the chances of abrasive wear. The smaller the debris is, the easier it is to be washed away from the contact interface. For lubricated tests in this study, both sintered and cast ZMJ can reach an optimal surface microstructure as mentioned above, but the open pores and the fine microstructure in sintered ZMJ help reduce the forming of large debris. As calculated from results listed in Table 2, the ratio of the sintered ZMJ wear volume to the cast ZMJ wear volume after 90 min of lubricated wear tests was 1∶1.7. For non-lubricated wear test, no lube oil was presented between the sliding surfaces, therefore temperature will rise up to a level that the strength of the matrix decrease significantly. Since rapidly solidified ZMJ has better high temperature strength, the sintered ZMJ shows a much better wear-resisting behavior than the cast ZMJ. As calculated from results listed in Table 2 the ratio of the sintered ZMJ wear volumes to the cast ZMJ wear volume after 30 min of non-lubricated wear test was 1∶2.6. The wear volumes for sintered ZMJ are only 36% and 59% of the wear volume that found in cast ZMJ under non-lubricated and lubricated conditions, respectively. It is surprised that the strength of sintered ZMJ is much lower than that of cast ZMJ, but sintered ZMJ has a better wear-resistance.

Suh et al[13] proposed a concept of undulated surface to reduce friction and wear. Undulated surface consists of a series of parallel or an orthogonal set of microgrooves oriented perpendicular to the direction of sliding, i.e. the microgrooves forming parallel sets of ridges (pads) and valleys (gaps) on the surface. A schematic illustration of this concept is shown in Fig. 2. Wear particle agglomeration may be minimized since wear particles would be trapped in the grooves and removed from the sliding interface by lubricant. An undulated surface will not operate effectively if: (1) $l_g/l_p \ll 1$, (2) $l_p/l_g \ll 1$, (3) $l_p/h_p \ll 1$, where l_g is gap length, l_p is pad length and h_p is pad height. In case (1) the pad length will be long enough to allow ploughing and debris agglomeration, in case (2) insufficient pad area to carry the normal load and in case (3) plastic deformation may occur. In both dry and boundary lubricated sliding, undulated surfaces have been shown to lower friction and wear through reduction of ploughing[14]. Fig. 3 is a schematic diagram showing the sintered ZMJ and steel contact interface. After the run-in period, both the sintered and cast ZMJ surfaces show a structure resemble to the undulated surface. Instead of the 2-dimentional pads, the asperity (exposed intermetallic compounds on the alloy surface) acts as pads of 0-dimension and the exposed pores function as gaps, which help entrapping the debris and for more oil storage. The interconnected pores may help the removal of fine debris from the sliding interface and minimizing the agglomeration. This is the reason why the sintered sample has a better wear-resistivity than those of the cast alloy.

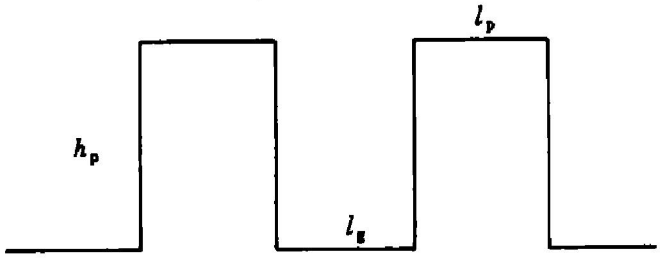

Fig. 2 Schematic illustration of undulated surface

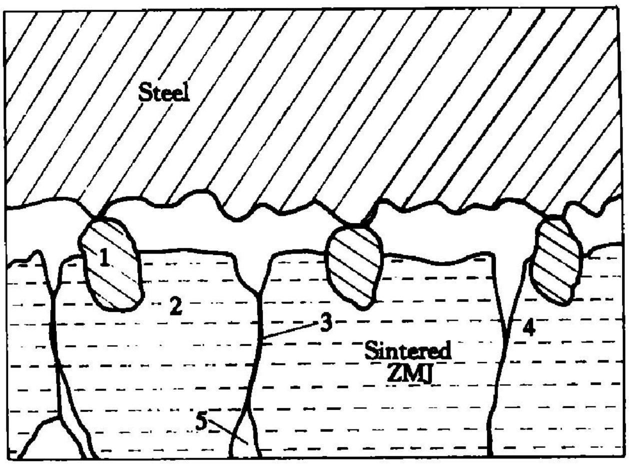

Fig. 3 Schematic diagram showing contact interface

1 —Exposed intermetallic hard phases; 2 —Metal matrix; 3 —Particle boundary; 4 —Open pore; 5 —Closed pore

Both sintered and cast ZMJ samples show a similar smooth friction process as soon as they reach an optimal surface condition after the run-in period. As shown in Table 2, both cast ZMJ and sintered ZMJ have a same value of approximately 0.025 for lubricated friction coefficient (μ_{lube}), and have a same value of 0.52 for non-lubricated friction coefficient (μ_{dry}). They have the same friction coefficient is expectable since they have the same micro constituents, although the microstructure for the sintered sample is much finer. The refined microstructure plays a more significant role on the wear-resisting behavior rather than the frictional coefficient of the material. Suh et al[15] proposed that friction coefficient, μ, is a function of three mechanism: asperity deformation, adhesion, and ploughing of the interface by wear particles. The total friction coefficient is the weighted sum of these three components, depending on the local friction condition that prevails at the sliding interface, i.e. $\mu = f_d \mu_d + f_a \mu_a + f_p \mu_p$, where f_d, f_a and f_p are the weighted factors, which may vary as function of time, and μ_d, μ_a and μ_p are the deformation, adhesion and ploughing components of the friction coefficient, respectively. The asperity deformation and adhesion components of the friction coefficients for the sintered and cast alloys are the same since they have similar phase constituents. The only difference is the ploughing component, which depends on the material's strength and grain size. However, for non-lubricated experiments adhesive wear and oxidation wear are the major wear mechanism. The mating surface become dark in color soon after the beginning of the experiments, indicating that oxides have been formed and covered the mating surfaces. Therefore, the different ploughing effects in the sintered and cast ZMJ do not contribute too much to the friction coefficients. For lubricated experiments, after the run-in period, optimal surface structure are built up on the alloy's contacting surface as mentioned earlier, the real contacts are laid on the asperities and debris are being carried away by lubricating oil, therefore, ploughing factors diminish. The heat generated during the test is a reflection of frictional force; thus, as shown in Table 2, the temperature rises in the lubricating oil for sintered and cast samples are very close also.

From Table 2 we can see that the mechanical property of sintered ZMJ is considerably less than those of cast alloy. This is normal for powder metallurgy materials prepared by conventional method, since the sintered alloy consists of significant amount of pores. Reducing the pore concentration can improve the mechanical property of P/M alloys. The relatively low radial crushing strength is due to problems encountered in sintering process. First of all, due to the low melting point of the zinc-based alloy, sintering temperature is limited to 400 ℃, which is very low for solid-state diffusion. Besides, oxide films that cannot be reduced exist on the powder surfaces will create barriers for diffusion and thus seriously inhibit the sintering process. A radial crushing strength of 69 MPa is relatively low, but considering the relatively low density, the low energy consumption for manufacturing and the near net shape of the powder metallurgy ZMJ parts, from an economy point of view, the material developed in this study has a potential to find wider applications in the future. Therefore further study is worth to improve its mechanical property.

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