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ARTICLE

Effect of Zn on Microstructures and Properties of Mg-Zn Alloys Prepared by Powder Metallurgy Method

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Abstract: Mg-Zn alloys were prepared by a powder metallurgy method using Mg powder and Zn powder as starting materials. The effects of the Zn content on sintering density, microstructure, phase composition, bending properties and micro-hardness of the Mg-Zn alloys were studied. The corrosion resistance of the Mg-Zn alloys was also measured. The function mechanism of Zn element during the powder metallurgy process was analyzed. Results show that the sintered compacts have finer grain size and higher sintered density upon Zn addition. The density of the sintered products increases with the increasing of Zn content. XRD analysis shows that the Mg-3 wt% Zn alloy is mainly composed of α-Mg phase. When the content of Zn is 4 wt%, the Mg-Zn alloys is composed of α-Mg and $MgZn_2$ phases. With the increase of the Zn content, the bending strength of the Mg-Zn alloys first increases and then decreases, but the micro-hardness HV of Mg-Zn alloys always increases. The bending strength and micro-hardness of Mg-3 wt% Zn alloys are 123.6 MPa and 1017 MPa, respectively, which are 58% and 45% higher than those of pure Mg samples. Corrosion resistance measurements show that the corrosion rate of the Mg-Zn alloys decreases with the addition of Zn element, and the Mg-3wt% Zn alloy shows the lowest corrosion rate and the best corrosion resistance.

Key words: powder metallurgy method; Mg-Zn alloy; Zn content; microstructure; property

Lightweight metals such as magnesium alloys are of increasing interests because of their potential applications in a lot of fields, such as transportation, aerospace and biomedical areas[1]. The need to reduce weight to increase payload, and to minimize fuel consumption and the emission of the greenhouse gas CO_2, have lead to a growing number of applications for magnesium alloys [2-4]. Furthermore, magnesium has been recently recognized as a promising biomaterial for bone substitution due to its excellent properties, e.g., a relatively low Young's modulus and a proper strength [5], excellent biocompatibility [6,7], biodegradability and bioresorbability [8,9]. However, Mg alloys prepared by common solidification generally show coarse microstructure and severe segregation, resulting in low corrosion resistance and mechanical properties at room temperature and high temperature[8,10]. As a result, these Mg alloys are difficult to satisfy the requirement for structural application requiring high properties, and thus their wider applications are restricted. Powder metallurgy technology is one of effective methods for preparing materials with high properties due to its excellent superiority of refining grain sizes, decreasing composition segregation and increasing solid solubility of alloy elements in the Mg matrix and forming metastable phase, which can greatly improve the mechanical properties and corrosion resistance behaviors. Since the mechanical properties and corrosion resistance of Mg-alloys are affected by the combined effects of the alloy's chemical composition and its microstructure[11,12], Mg-Zn alloys were prepared by the powder metallurgy method in the present paper. The purpose is to

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improve the poor corrosion behavior of commercial magnesium alloys added with Fe, Cu, Ni elements. The addition of Zn element has important effects on refining grain size and improving the mechanical properties and corrosion resistance of Mg alloys. In the present paper, the effects of Zn content on porosity, sintering shrinkage, microstructure, phase composition, bending properties and micro-hardness of Mg-Zn alloys were studied. The corrosion resistance of Mg-Zn alloys was measured. The function mechanism of Zn element during the powder metallurgy process was analyzed.

1 Experiment

Mg powder and Zn powder, both of purity 99.99%, with particle size 74 and 37 μm, respectively, were used as starting materials. The morphologies of Mg and Zn powders are shown in Fig.1. The two powders were mixed at desired ratios and then pressed into rectangle green compacts (50 mm×10 mm×10 mm) at the pressure of 100 MPa. The Zn content was changed from 0 wt% to 4 wt% in the green compacts. The cold compacted samples were heated to 893 K for 2 h in a furnace in Ar atmosphere. Microstructure of the specimens was analyzed using scanning electron microscopy (S-3000) on polished surfaces. Average size of Mg grains was measured by statistical analysis of the image on the several SEM photos. The sintering density of Mg-Zn alloys was measured with Archimedes method. The phase structure was determined by X-ray diffraction analysis (D/Max-2500 /PC). Bending strength was measured using a universal testing machine (WDW-10) with a loading rate of 0.5 mm/min. The micro hardness was measured by a micro hardness tester (HVS-1000). The corrosion resistance was tested in 3.5 wt% NaCl solution. The corrosion time was 24 h. The corrosion rate was calculated by the following equation[13]:

$$v_{CORR} = \frac{8.76\times10^4(W_1 - W_2)}{ATD} \quad (1)$$

where, v_{CORR} is corrosion rate (mm/a), W_1 is mass after corrosion (g), W_2 is mass before corrosion (g), A is corrosive surface (cm^2), T is corrosive time (h), and D is density of Mg alloys (g/cm^3).

2 Results and Discussion

2.1 Effect of Zn content on sintering density of Mg-Zn alloys

Table 1 shows the sintering relative density of Mg-Zn alloys with different Zn contents. The relative density of Mg-Zn alloys increases from 97.2% to 99.1% when Zn content varies form 0 wt% to 4 wt%. The reason for the enhanced density with Zn addition can be analyzed as follows. Although both Mg and Zn particles are of spherical shape, the average size of Mg particles is larger than that of Zn particles. When the two powders are mixed, the smaller Zn particles can fill into the intervals of the bigger Mg particles while in compaction, resulting in increasing green compact density. As a result, the diffusion distance between Mg and Zn particles becomes shorter, and the diffusion reaction of Mg and Zn particles proceeds more completely. Under these conditions, the samples are easy to be sintered to a denser microstructure. Furthermore, according to Mg-Zn phase diagram, liquid phase formation is quite possible when Zn content is beyond 3 wt% at 893 K, as shown in Fig.2[14]. The diffusion rates of Mg and Zn particles may be greatly enhanced due to the involvement of liquid phase during sintering, resulting in higher density of sintered bodies[15]. It should be also noted that only minor increase of sintering density is observed when the content of Zn is beyond 3 wt%.

Table 1 Sintering density of Mg-Zn alloy with different Zn contents

Zn content/wt%	0	1	2	3	4
Density/%	97.2	97.8	98.5	99.0	99.1

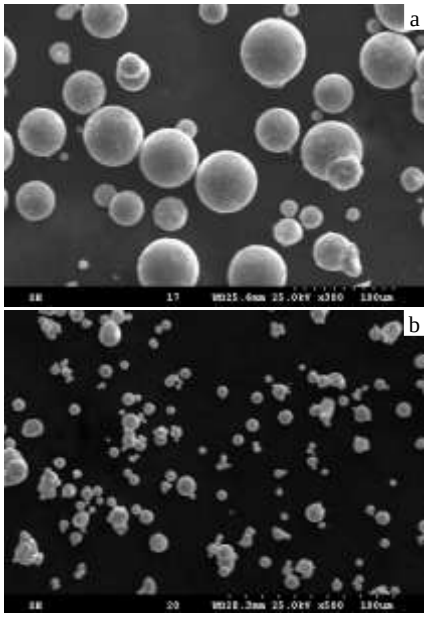

Fig.1 Morphologies of Mg (a) and Zn (b) powders

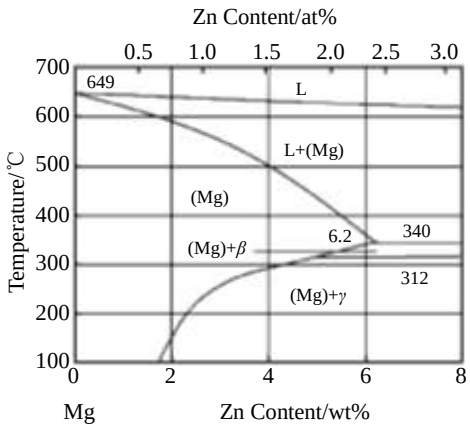

Fig.2 Phase diagram of Mg-Zn alloys

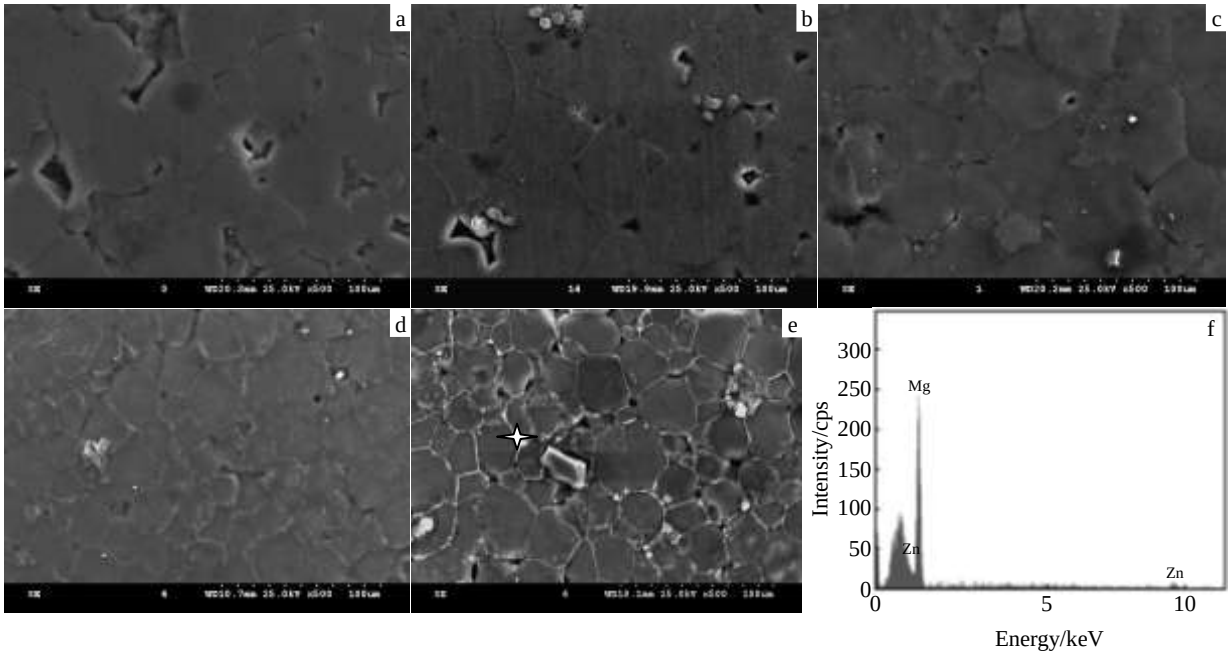

Fig.3 SEM images (a~e) and EDS spectrum corresponding marked with the white asterisk in Fig.3e (f) of Mg-Zn alloys with different Zn contents: (a) 0 wt%Zn, (b) 1 wt%Zn, (c) 2 wt%Zn, (d) 3 wt%Zn, and (e) 4 wt%Zn

2.2 Effect of Zn content on microstructure and phase structure of Mg-Zn alloys

Fig.3 shows the microstructures of the Mg-Zn alloys with different Zn contents. As can be seen in Fig.3, with the increase of Zn content, the pore size of sintered compacts decreases, which is consistent with the results in Table 1. Besides, the grain sizes of the different Mg-Zn alloys decrease form 37.8 μm to 23.2 μm when the Zn content increases form 0 wt% to 4 wt%. The reason for the decreased grain sizes at high Zn content is as follows. First, Mg and Zn metals are both of close-packed hexagonal structure. The diffusion rate of Zn atoms in Mg matrix is faster than that of Mg atoms in Zn matrix. So Zn atoms can easily diffuse into Mg matrix and form the Mg solid solution or intermetallic compound. Fig.4 shows surface scanning images of Mg-Zn alloys with 3 wt% Zn content. Comparing Fig.4a and 4c, it can be found that element Zn is mainly distributed on the surfaces of Mg grains, and no single particle of Zn element could be observed. Because the radius of Zn atom (0.135 nm) is smaller than that of Mg atom (0.16 nm), a tensile stress field at the distorted lattice of Mg matrix is expected when Zn atoms displace Mg atoms. There are gravitation forces between Mg and Zn atoms so Mg atoms are bounded by Zn atoms to some extent and the diffusion rate of Mg atoms decreases. The adjacent Mg particles are not easy to merge and grow up and their grain sizes become smaller. Comparing Fig.1a and Fig.3d, it is found that the grain size of Mg-3%Zn alloys is very close to the size of initial Mg particles, indicating the effects of addition of Zn element in suppressing Mg grain growth. Furthermore, there are some white phase along the Mg grain boundary as can be seen in Fig.3d and 3e. The white phase along the grain boundary increases with the increase of Zn content. The EDS analysis of the white phase (marked with the white asterisk in Fig.3e) indicates a kind of Mg-Zn

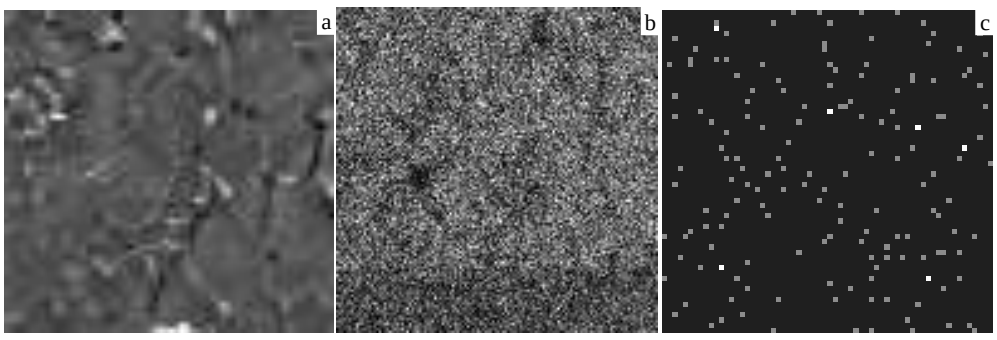

Fig.4 SEM surface morphology (a) and EDS analysis of element Mg (b), and element Zn (c) for Mg-3wt%Zn alloy

intermetallic compound, as shown in Fig.3f. It is known that the second phase along the grain boundary can hinder the movement of the grain boundary and suppress the grain growth. As a result, the refinement of the Mg grains is observed for the sample with high Zn contents.

Fig.5 shows XRD patterns of Mg-Zn alloys with 3 wt% and 4 wt%Zn. As can be seen in Fig.5, Mg-3wt%Zn alloy is composed of single α-Mg phase, and Mg-4wt%Zn alloy is composed of α-Mg and $MgZn_2$ phases. However, the existence of a little amount of $MgZn_2$ (white phase along the Mg grain boundary) is also confirmed for the Mg-3wt%Zn alloy, as shown in Fig.3d. The reason for the different results of SEM and XRD analysis is that the total amount of $MgZn_2$ at Mg-3 wt% Zn alloy is less than 5%, so it is not seen from XRD analysis. The reason of $MgZn_2$ phase formation is as follows. With the increase of sintering temperature, the diffusion rates of Mg and Zn atoms in the adjacent particles increase. Zn atoms can easily diffuse into Mg matrix through sintering necks of Mg and Zn particles. The diffused Zn atoms usually stay near the sintering necks because of the limited diffusion ability of Zn atoms and the lattice distortion of Mg matrix. When the sintering necks transform into the grain boundaries, plentiful Zn atoms situate near the grain boundaries (which can be confirmed in Fig.4). At this time, the ratios of Zn and Mg atoms near the grain boundaries are much larger and satisfy the formation condition of $MgZn_2$ phase.

2.3 Effect of Zn content on bending strength and micro-hardness of Mg-Zn alloys

Table 2 shows the bending strength and microhardnesses of Mg-Zn alloys with different Zn contents. From the table it is clear that the bending strength of Mg-Zn alloys firstly increases and then decreases with the increase of Zn content. The reason is as follows. Firstly, the sintered compacts have higher densities, less pores and defects at high Zn contents, which can decrease the crack source and contribute to improvement of the bending strength of the compacts. Secondly, the lattice distortion resulting from the solution of Zn in Mg matrix can inhibit the dislocation motion and further improve the bending strength. Lastly, the smaller grain

Table 2 Bending strength and microhardness of Mg-Zn alloys with different Zn contents

Zn content/ wt%	Bending strength/MPa	Microhardness, HV/MPa
0	78.2	695
1	97.5	843
2	111.7	952
3	123.6	1017
4	87.3	1057

can increase grain boundary and decrease stress concentration. The surface increase and the twists of grain boundaries can hinder the crack propagation. So the bending strengths of Mg alloys increase at lower Zn contents, whereas the bending strength of Mg-Zn alloys decreases when Zn content is at 4 wt%. This is because a lot of $MgZn_2$ phases exist at the Mg grain boundaries and form coarse net structure (Fig.3e). When the cracks in Mg matrix are extended to the grain boundaries, the extension rate of the cracks increases because coarse $MgZn_2$ net are hard and brittle. So the bending strength of the Mg-Zn alloy with 4 wt% Zn decreases.

The micro-hardness of Mg-Zn alloys increases with increasing of Zn contents. This is because the sintered compacts have higher density, lower defects and proper lattice distortion at high Zn content. At the same time, the hard $MgZn_2$ phases in the Mg-4 wt% Zn alloys can contribute to the further improvement of the micro-hardness of the sintered compacts.

The bending strength and micro-hardness HV of sintered Mg-3wt%Zn alloy are 123.6 MPa and 1017 MPa, respectively, which is 58% and 45% higher than those of pure Mg samples.

2.4 Effect of Zn content on corrosion resistance of Mg-Zn alloys

Fig.6 shows the corrosion rates of Mg-Zn alloys with different Zn contents. As can be seen in Fig.6, the corrosion rate of pure Mg is the fastest. With the increase of Zn content, the corrosion rate of the Mg-Zn alloy first decreases and then increases at the same corrosion time. The reason is that the corrosion potential of Mg (–2.37 V) is much lower than that of Zn (–0.76 V). The corrosion potential of Mg matrix increases

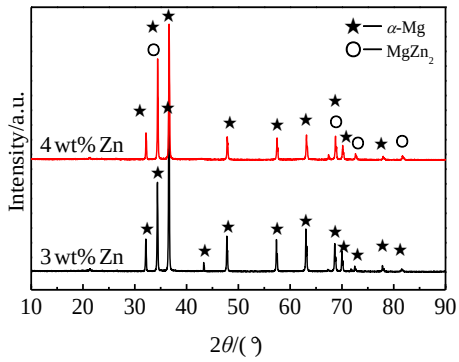

Fig.5 XRD patterns of Mg-Zn alloys with 3 wt% Zn and 4 wt% Zn

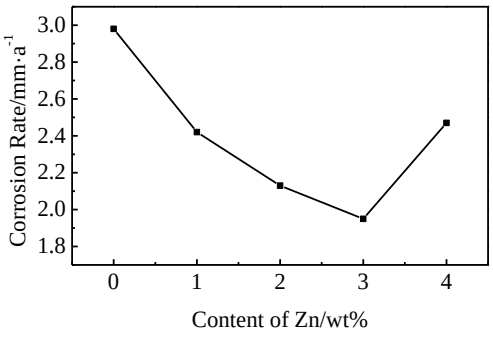

Fig.6 Corrosion rates of Mg-Zn alloys with different Zn contents

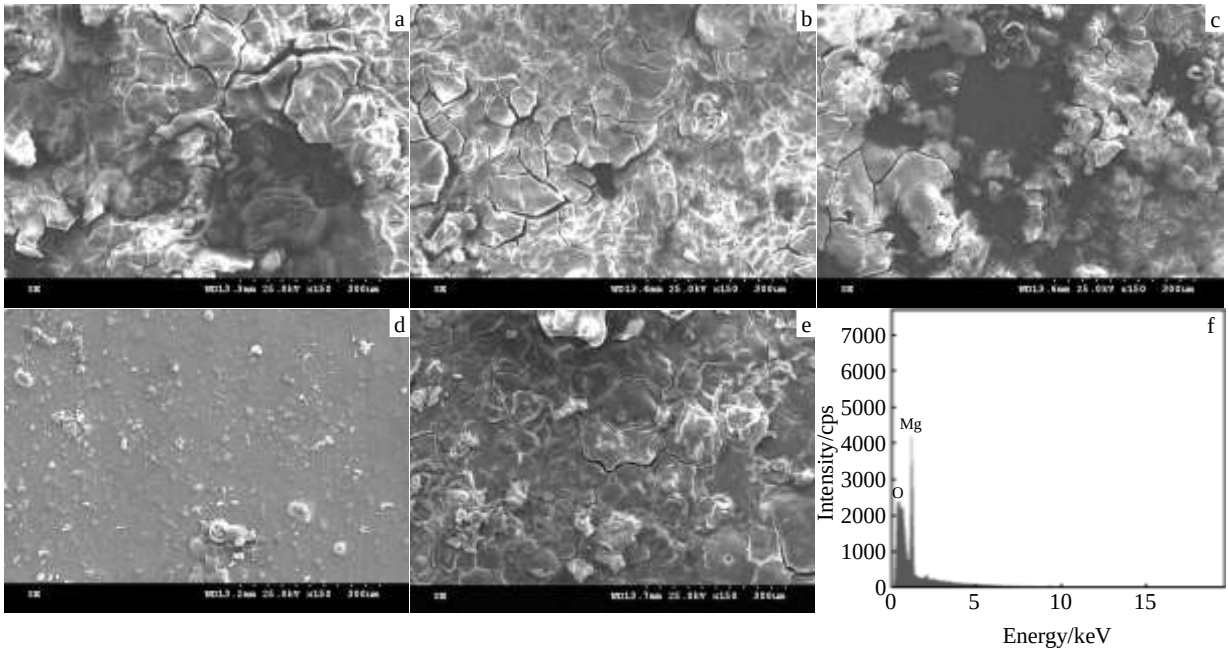

Fig.7 SEM images of Mg-Zn alloys with different Zn contents: (a) 0 wt%Zn, (b) 1 wt%Zn, (c) 2 wt%Zn, (d) 3 wt%Zn, and (e) 4 wt%Zn; (f) EDS spectrum of Mg-3wt%Zn alloy

when Zn is dissolved in Mg matrix. Simultaneously, at high Zn content, the sintered compacts have higher density and corrosion resistance of the Mg-Zn alloys. The increase of corrosion rate for alloy with 4 wt% Zn can be attributed to the lower defects, which can contribute to the improvement of the occurrence of reticular $MgZn_2$ phase along the Mg grain boundaries, which is a strengthening phase of cathode and can accelerate the corrosion of the Mg anode.

The corrosion rate of Mg-3wt%Zn alloy is 1.95 mm/a, which is 34.6% lower than that of pure Mg compact. Mg-3wt%Zn alloy has the best corrosion resistance.

Fig.7 shows microstructures and EDS analysis of the corroded surfaces of the Mg-Zn alloys with different Zn contents. Pure Mg sample displays the worst corrosion surface, and the corrosive degrees of the Mg-Zn alloys decrease at high Zn contents. Mg-3wt%Zn alloys has less corrosion products on the surface and the corrosive degree is the slightest. The corrosive degree becomes more severe for Mg-4wt%Zn alloy as compared with Mg-3wt%Zn alloy because of a lot of reticular $MgZn_2$ phase at the grain boundaries. Clearly, Mg-3wt%Zn alloy has better corrosion resistance. Fig.7f shows EDS analysis of the corrosive products of Mg-3wt%Zn alloy. There are elements Mg and O in the corrosive products, which shows the corrosive products on the surface of Mg-Zn alloys are the oxide of Mg.

3 Conclusions

1) The sintered Mg-Zn alloys have higher density and smaller grain size at higher Zn content. Mg-3wt%Zn alloy is mainly composed of α-Mg phase and Mg-4wt%Zn alloy is composed of α-Mg and $MgZn_2$ phases.

2) With the increase of Zn content, the bending strength of Mg-Zn alloys firstly increases and then decreases, but the microhardness for different Mg-Zn alloys continuously increases with the increasing of Zn content. The bending strength and micro-hardness HV of sintered Mg-3wt%Zn alloy are 123.6 MPa and 1017 MPa, respectively, which is 58% and 45% higher than those of pure Mg samples.

3) The corrosion rates of Mg-Zn alloys decrease when adding element Zn in Mg matrix. The corrosion rate of Mg-3wt%Zn alloy is 1.95 mm/a, which is 34.6% lower than that of pure Mg compact. Mg-3wt%Zn alloy has the best corrosion resistance.

References

1 Kainer K U. *Magnesium Alloys and Technology*[M]. Weinheim: Wiley-vch, 2003

2 Witte F, Fischer J, Beckmann F *et al*. *Scripata Materialia*[J], 2008, 58: 453

3 Tao Jianquan, Wan Yuanyuan, Sun Changjian *et al*. *China Foundry*[J], 2014, 10(4): 244

4 Chen Jun, Li Quannan, Li Jianghong *et al*. *China Foundry*[J], 2009, 6(2): 124

5 Gu X N, Zhou W R, Zheng Y F *et al*. *Materials Letters*[J], 2010, 64: 1871

6 Hao G L, Han F S, Li W D. *Journal of Porous Material*[J], 2009, 16(3): 251

7 Wang X, Li Y X, Liu Y. *Materials Science and Engineering A*[J], 2007, 444(1): 306

8 Kim S H, Kim D H, Kim N J. *Material Science and*

Engineering[J], 1997, A226-228: 1030
9 Mordike B L, Ebert T. *Materials Science and Engineering A*[J], 2001, 302: 37
10 Shepelev D, Bamberger M, Katsman A. *Journal of Materials Science*[J], 2009, 44(20): 5627
11 Gao X, Zhu S M, Muddle B C *et al*. *Scripta Materialia*[J], 2005, 53(12): 1321
12 Oh J C, Ohkubo T, Mukai T *et al*. *Scripta Materialia*[J], 2005, 53(6): 675
13 Li J Q, Du C W. *Corrosion Test Method and Monitoring Technology*[M]. Beijing: China Petrochemical Press, 2007: 17 (in Chinese)
14 Liu C M, Zu X F, Zou H T. *The Phase Diagram Atlas of Magnesium Alloy*[M]. Changsha: Central South University Press, 2006 (in Chinese)
15 Zhou Y J, Yang H S, Liu J X. *Hot Working Technology*[J], 2013, 42(6): 15 (in Chinese)

Zn 对粉末冶金法制备 Mg-Zn 合金组织与性能的影响

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摘　要：以 Mg 粉和 Zn 粉为初始原料，采用粉末冶金技术制备 Mg-Zn 合金。研究了 Zn 含量对 Mg-Zn 合金烧结密度、显微组织、物相组成、弯曲强度和显微硬度的影响。测量了 Mg-Zn 合金的耐腐蚀性，探讨了 Zn 元素在粉末冶金过程中的作用机理。结果表明，添加 Zn 元素后，烧结产物的晶粒细小，烧结密度提高。此外，随着 Zn 含量的增加，烧结产物的致密度持续增加。XRD 分析表明 Mg-3%Zn (质量分数)合金主要由 α-Mg 相组成，而 Mg-4%Zn 合金由 α-Mg 和 $MgZn_2$ 两相组成。随着 Zn 含量的增加，Mg-Zn 合金的抗弯曲强度先增加而后降低，但是显微硬度 (HV) 持续增加。Mg-3%Zn 合金的抗弯强度为 123.6 MPa，显微硬度为 1017 MPa，分别比纯 Mg 样品高出 58%和 45%。耐腐蚀性能测试表明当添加 Zn 元素后，Mg-Zn 合金的腐蚀速率降低，Mg-3%Zn 合金具有最低的腐蚀速率和最佳的耐腐蚀性能。

关键词：粉末冶金；Mg-Zn 合金；Zn 含量；显微组织；性能

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