MICROSTRUCTURES OF A NOVEL HIGH STRENGTH AND WEAR-RESISTING ZINC ALLOY①

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ABSTRACT Based on the results of observation and microanalysis by scan electron microscopy (SEM) and electron probe microanalysis (EPMA), the morphologies and microconstituents of different phases in a novel high strength and wear-resisting zinc alloy (ZMJ) were determined. The results of structural determination by X-ray diffraction (XRD) and transmission electron microscopy (TEM) indicate that the crystal lattice parameters of some phases in this alloy are changed due to the solute elements. It is also found that the microhardnesses of different phases are varied in a large range. Phases containing Mn are much harder than the matrix phase and despersion of tiny hard phases in the soft matrix is the general characteristic of this novel alloy.

Key words zinc alloy microstructure strength wear-resistance

1 INTRODUCTION

As an ideal high strength and wear-resisting material for worm gears and bearings etc, it should possess the characteristics of high strength, impact resistance and fatigue resistance in view of mechanical design, in the meantime, it ought to have excellent antifriction, wear-resistance, seizure resistance and load-bearing properties according to the need of tribology. By adding Mn, R. E, Ti, B elements to the traditional ZA-27 zinc alloy and by means of modifying and alloying processing, the authors of this paper have developed successfully a novel zinc alloy, named as ZMJ and also the engineering components of this alloy, such as the worm gears and bearing. The results of a large number of comparative experiments and industrial application have shown that the properties, especially the tribological behaviors of this alloy and its components are much superior to those of the phosphor-tine-bronze ZCuSn10P1 (GB1176—87) with a cost saving by 40%, energy saving by 25% at the same time[1,2]. However, due to the lack of further investigation in the microstructures and phase structures in multinary Zn-Al, the strengthening mechanisms and tribological behaviors of this new alloy have not been understood clearly now. In this paper, the authors intend to reveal the microstructures of this new alloy and give supplements to the theories on this alloy by a systematical investigation.

2 EXPERIMENTAL MATERIALS AND METHOD

2.1 *Fabrication of the Materials*

The novel zinc alloy (ZMJ) is prepared by Al (Al99.7%), Zn (Zn—1), Cu (Cu—1), Mg (Mg99.95%) with tiny Mn, R. E, Ti, B elements introduced in the form of master alloy. The approximate chemical composition (mass percent) of the alloy is 26%~29%Al, 2.0%~2.5%Cu, 0.03%~0.06%Mg, tiny

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Mn, R. E, Ti, B and the balance of Zn. The melting temperature is controlled to about 700 C and the sand casting temperature is about 580 C.

2. 2 *Microstructural Analysis*

The experimental materials were cut from the sand casting ingot (d25 mm × 50 mm). After prepared with the conventional mechanical polishing and chemical erosion method, the metallographic specimens were first observed by optical microscope, and then investigated by electron probe microanalysis (EPMA) and scan electron microscopy (SEM) to determine the morphologies and microconstituents of various phases in the alloy, so that the approximate chemical formula for some new phases were obtained. Besides, bulk X-ray diffraction specimens (10 mm × 10 mm × 25 mm) and transmission electron microscopy (TEM) thin film specimens were prepared to carry out the analysis in crystal structure of some phases. The TEM specimen was prepared by the following way: electrical discharge cutting → mechanical polishing → electropolishing. Based on the results of the above microstructures and microconstituents analysis, the morphologies, chemical compositions, crystal lattice forms and parameters of the main phases in the novel alloy could be determined to some degree of accuracy. At last, the microhardness of various phases were measured by a Model-71 microhardness tester with load of 10～50 grams for 10 seconds to characterize the mechanical properties of the concerned phases further.

3 RESULTS AND DISCUSSION

Fig. 1 and Fig. 2 show the morphologies of various phases in the point analysis scope by SEM and EPMA. Table 1 shows the approximate chemical formula corresponding to these phases after the constituents analysis.

On the basis of the results, it is found that besides the α (Al), β (Zn) and ε phases, some new phases, such as $Al_9(MnZn)_2$, Al_5MnZn and $Al_{65}Mn(R.E)_6Ti_4Zn_{36}$ have formed in this novel alloy during the crystallization procedure due to the addition of elements of Mn, R. E, Ti, B. Thus new phases are very interesting and have not even been reported before as far as the authors know.

X-ray diffraction (XRD) and TEM were employed to determine the crystal structure and lattice parameters of some concerned phases. The results are tabulated in Table 2. Fig. 3 shows the morphologies and diffraction

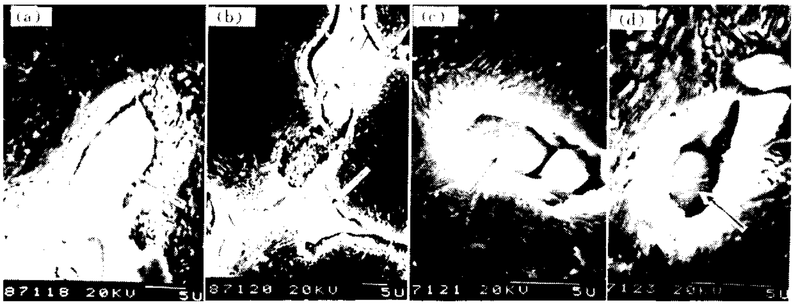

Fig. 1 Morphologies of phases observed by SEM
(a) ($\alpha + \beta$)binary eutectic; (b) ($\alpha + \beta + \gamma$) ternary eutectic; (c) β; (d) ε ($CuZn_3$)

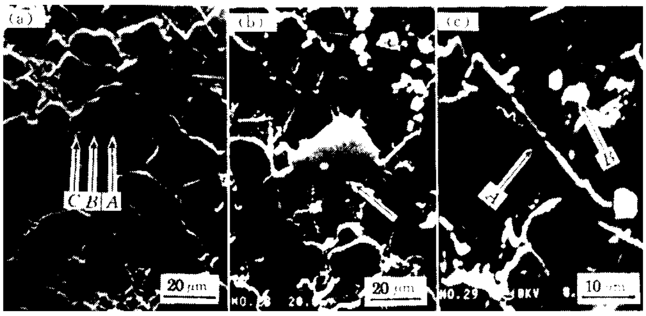

Fig. 2 Morphologies of phases observed by EPMA
(a) α phase; (b) $Al_9(MnZn)_2$; (c) white bar
A: Al_5MnZn, bright spot *B*: $Al_{65}Mn(R.E)_6Ti_4Zn_{36}$

Table 1 Results of the microanalysis and microhardness test of various phases

Figure No.	Location or form	Phase, structure or formula	Microhardness (HV)*
Fig. 1(a)	α interdentritic white bars	(α + β) binary eutectic	49.1
Fig. 1(b)	α interdentritic grey networks	(α + β + γ) ternary eutectic	49.1
Fig. 1(c)	grey rectangles in α base	β	—
Fig. 1(d)	dark grey squares in α base	ε ($CuZn_3$)	230.1
Fig. 2(a)	α phase center (point *A*)	α	82.2
Fig. 2(a)	Zn rich area at the edge of α phase (point *B*)	α	55.7
Fig. 2(b)	α interdentritic white polygons	$Al_9(MnZn)_2$	560.9
Fig. 2(c)	white bar *A*	Al_5MnZn	616.8
Fig. 2(c)	bright spot *B*	$Al_{65}Mn(R.E)_6Ti_4Zn_{36}$	380.8

* The microhardness in the table is the average value of five testing points.

Table 2 Results of X-ray and TEM diffraction analysis in the novel ZMJ alloy

Phases	Crystal structure	X-ray test values/Å		TEM test values/Å		ASTM data/Å	
		a	*c*	*a*	*c*	*a*	*c*
α (Al)	*fcc*	4.0655	—	3.7052		4.0494	—
β (Zn)	*hcp*	2.6744	4.9128	—	—	2.6650	4.9470
ε ($CuZn_3$)	*hcp*	2.7695	4.3070	2.7644	4.3068	—	—
Cu_9Al_4	complicated cube	—	—	8.4210	—	8.7027	—

patterns of corresponding phases observed in TEM. By the accurate XRD and TEM measurement, it is discovered that the lattice parameters of α and β, the two general phases in Zn-Al-Cu alloy are different from those of the pure Al and pure Zn, as shown in the ASTM card.

Based on the Zn-Al-Cu ternary diagram

and some relative binary diagrams, the equilibrium solidification of Zn-Al-Cu alloy is analyzed as follows. At 377 ℃, liquid phase with constituents of 89. 1%Zn, 7. 05%Al, 3. 8% Cu would take place an eutectic reaction: $L \rightarrow \alpha_1 + \beta + \gamma$. In the transformation products, α_1 is *fcc* aluminium-based solid solution, dissolving 79% Al and 2%Cu; β is *hcp* zinc based solid solution with 1%Al and 3%Cu. α_1 phase is unstable, it tends to transform into α phase automatically as the temperature goes down and takes the eutectoid reaction: $\alpha_1 \rightarrow \alpha + \beta$ at 274 ℃. At room temerature, α phase can dissolve 3%Zn and 1%Cu; β phase can dissolve 0. 2%Al and 0. 8% Cu. In the real situation, after undergoing nonequilibrium solidification, the microstructure of Zn-Al-Cu alloy at room temperature is composed of dentritic α phase, interdendritic ($\alpha + \beta$) binary eutectic and a few of interdendritic ($\alpha + \beta + \varepsilon$) ternary phase. During the solidification procedure, α phase has a serious "Center" segregation. In the constituent analysis by EPAM, it is found that the ratio of Zn:Al:Cu in the central-point *A* , point *B* and edge-point *C* in Fig. 1(a) of α phase is 23. 2:74:2. 4, 28. 9:68. 2:2. 8 and 47. 9:46. 4:3. 0, respectively. This demonstrates that α phase is Al rich in center and Zn rich at the edge. This conclusion is well consistent with the phase diagram analysis. In the novel ZMJ alloy, the addition of elements Mg, Mn, R. E, Ti and B does not influence the solidification procedure in a large degree due to their tiny contents. They would either dissolve in α, β phases or form intermetallic compounds. Tiny amount of Mg (0. 05% in our experiment) could dissolve in α phase. Tiny amount of Mn (0. 09% in our experiment) could dissolve in α phase, but it would form intermetallic compound in case of Mg surplus. Other elements have few solubility or no solubility in α or β phase and exist in form of compounds. Experimental results show that the lattice parameters of α and β phases are actually varied with the solute elements and their contents. Dissolution of Zn, Cu in α phase lessens its crystal lattice and on the contrary, Mg enlarges it. Dissolution of Al in β phase also has a dilated effect. In Table 2, it is found that the lattice parameters of α phase tested by X-ray are different from those tested by TEM. Besides the experimental errors, this might greatly lie in the facts that 1) α phase has composition segregation during the solidification procedure; 2) α phase lattice parameters are affected by the solute elements; and 3) the X-ray testing specimen and TEM specimen are cut from different locations in the casting ingots. The structure of ε phase is in great dispute now. Some researchers regarded it as $CuZn_4$-based electronic compound[3]. Some reported that it was $CuZn_3$-based electronic compounds[4,5]. Some suggested it to be the solid solution of Cu rich intermetallic compound $ZnCu_3$[6]. In this paper, the structure of ε phase is decided by the authors according to the following steps. First, delete the diffraction peaks of α and β phases from the X-ray diffraction spectrum and summarize the rest to get a set of d_i (spacing of the diffraction lattice planes) and I_i/I (relative diffraction density). And then, the diffraction angle θ, $\sin\theta$ and 25 $\sin\theta$ are counted out. At last, the Hole-Davis diagram[7] is used to confirm that these diffraction peaks belong to the ε phase of the hexagonal closed packed (*hcp*) structure. The ratio of Cu to Zn in ε phase is determined to be 1:3 by the analysis in SEM and EPMA. Based on the above results, the authors conclude that ε phase is the solid solution of intermetallic compound $CuZn_3$. $CuZn_3$ is also found in the TEM experiment. The crystal lattice parameters of $CuZn_3$ calculated by TEM diffraction pattern agree with those by XRD and hence our analysis as above is proven. The structure of Cu_9Al_4 is confirmed by TEM diffraction. However, because of dissolution of some Zn and Mg, its lattice parameters are a little smaller than the ASTM data. The structures of $Al_9(MnZn)_2$ and $Al_{65}Mn(R.E)_6Ti_4Zn_{36}$ phases are under investigation. Although not all of the phases in the novel alloy can be structurally determined at presnt, another aspect of these phases, the microhardness is tested to characterize the alloy. The results

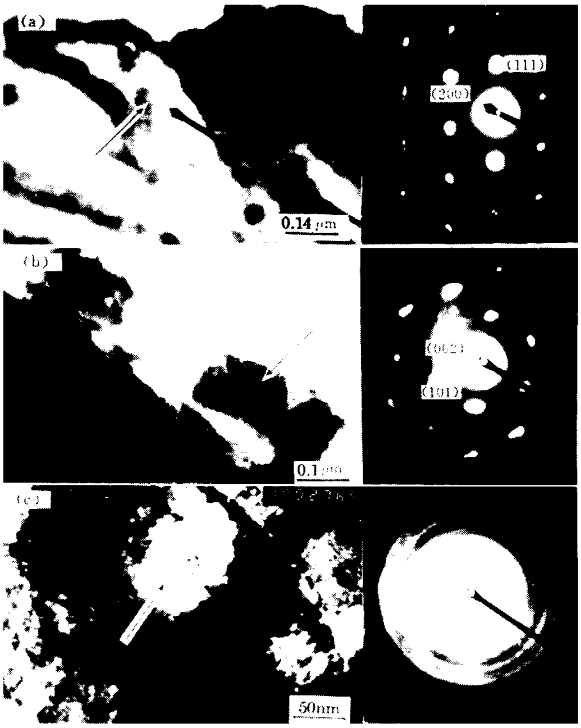

Fig. 3 Phases observed in TEM and their diffraction patterns in ZMJ alloy

(a)—Left: morphology of α phase, Right: diffraction pattern;
(b)—Left: morphology of ε phase, Right: diffraction pattern;
(c)—Left: morphology of Cu_9Al_4 phase, Right: diffraction pattern

are listed in Table 1.

From Table 1, it is found that the microhardness of different phases are quite different. All the phases containing Mn possess very high microhardness values, while α phase, (α + β) binary eutectic and (α + β + γ) ternary eutectic are soft. The result of quantitative metallographic measurement shows that the ratio of hard particles:eutectic:α phase is about 15 : 7 : 78 in ZMJ alloy. Therefore, the major characteristic of this

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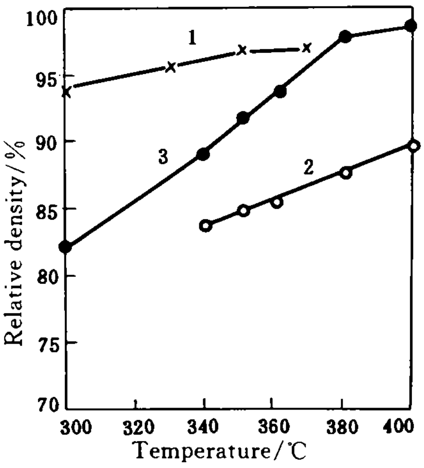

Fig. 7 Relative density of hot pressed compacts as a function of temperature

1—22 h milled powders, hot pressed for 10 min;
2—43 h milled powders, hot pressed for 10 min;
3—43 h milled powders, hot pressed for 30 min

than simple annealing, exhibiting deformation enhanced grain growth behavior. In addition, the grain growth was more sensitive to temperature in hot hydrostatic extrusion than in hot pressing.

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(*From page 88*) novel alloy is tiny hard phases dispersing in soft matrix. This kind of microstructure may not only upgrade the mechanical properties of the alloy, but also fit well into the requirement of tribology.

4 CONCLUSIONS

(1) The novel zinc-alloy (ZMJ) contains new phases of Cu_9Al_4, Al_5MnZn, $Al_9(MnZn)_2$, and $Al_{65}Mn(R.E)_6Ti_4Zn_{36}$ besides α (Al), β (Zn) and ε phases.

(2) The lattice parameters of α, β and Cu_9Al_4 are changed due to the solute elements. ε is solid solution of intermetallic compound $CuZn_3$.

(3) Phases containing Mn, such as Al_5MnZn, $Al_9(MnZn)_2$, and $Al_{65}Mn(R.E)_6Ti_4Zn_{36}$ are much harder than α phase and distribute uniformly in the matrix in forms of block or rod. The content of such hard particles in the sandy casting ZMJ alloy is about 15%.

(4) Some tiny hard phases with certain forms dispersing in the soft matrix is the main characteristic of this novel alloy.

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