Effects of Cu addition on microstructure and mechanical properties of as-cast magnesium alloy ZK60

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Abstract: The effects of Cu addition on the microstructure and mechanical properties of the as-cast magnesium alloy ZK60 were investigated with optical microscope, SEM, TEM, XRD, EPMA and tensile tester. The mechanism by which the mechanical properties are affected by Cu addition was discussed. The results show that Cu can effectively eliminate the intragranular solute segregations in the alloy, and the grain size of the alloy is decreased considerably with increasing the Cu amount. A ternary eutectic phase MgZnCu with a face-centered cubic structure is identified in the Cu-bearing alloys, which predominantly distributes at the grain boundary and acts as the nucleation sites of microcracks during the plastic deformation process. It is also found that the tensile properties of the alloy firstly increase by the trace addition of 0.5%−1% Cu and then decrease by a further addition up to 2.0%.

Key words: ZK60 magnesium alloy; Cu addition; MgZnCu phase; grain refinement; mechanical properties

1 Introduction

With the increasing emphasis on the energy conservation and environment protection, magnesium alloys have received considerable attention in the recent decades for their potential engineering applications due to their low density, high specific strength and excellent recycle ability [1]. ZK60 alloy (nominal composition Mg−(5−6)Zn−(0.3−0.9)Zr; in mass fraction, %) is a typically commercial wrought magnesium alloy nowadays. After a proper thermo-mechanical treatment, the specific strength and fracture toughness of ZK60 alloy are comparable with those of 7075 aluminum alloy [2,3]. However, ZK60 alloy exhibits a poor casting performance such as severe solute segregation and hot crack tendency. Besides, the inferior deformability caused by the hexagonal structure limits its widespread applications.

Recently, much effort has been made to improve the mechanical property of ZK60 alloy by alloying rare earth (RE) elements such as Y [4], Ce [5] and Er [6]. However, the addition of RE elements is not an ideal solution from the economical and ecological points of view. In our previous work on the T6-aged Cu-modified ZK60 alloy [7], it was demonstrated that the addition of the cost-effective element Cu could promote the formation of a uniformly distributed and rod-shaped strengthening phase β′1 with a high number density. Consequently, the peak-aged Cu-bearing alloys exhibited a superior mechanical property compared with the corresponding Cu-free one. However, the effect of Cu addition on the microstructure and mechanical properties of the as-cast ZK60 alloy has rarely been studied yet. In view of the significant influence of the as-cast condition on the subsequent deformation or heat treatment process of the alloy, and the fact that the alloy may be used directly in its as-cast condition, we particularly investigated the effects of Cu content on the microstructure and mechanical property of the as-cast ZK60 alloy in the present work, with the purposes of understanding the role of Cu in the alloy, improving the strength and toughness of the ZK60 alloy, and providing a basis for developing new Cu-bearing Mg−Zn−(Zr) alloys.
2 Experimental

ZK60+xCu (x=0, 0.5, 1.0, 2.0; mass fraction, %) alloys were prepared by melting high purity Mg and Zn together with master alloys of Mg−28.78% Cu and Mg−31.63% Zr in a steel crucible under a protective Ar atmosphere. After holding at 750 °C for 30 min, the molten alloy was cast into a preheated permanent mold and a cast alloy block with dimensions of 200 mm×200 mm×40 mm was made. Specimens for optical microscopy were etched by a solution of 3 g picric acid, 50 mL ethanol, 20 mL acetic acid and 20 mL distilled water in order to reveal grain boundaries. The element distribution of the Cu-bearing alloy was studied by a Shimadzu 1600 electron probe microanalyzer (EPMA) using an accelerating voltage of 15 kV and a beam size of 1 μm. The phase constitutions were determined by a Philip X-Pert X-ray diffractometer (XRD) with Cu Kα radiation at 40 mA and 40 kV. Thin foil specimens for transmission electron microscopy (TEM) were prepared by the twin-jet electropolishing method in a solution of 10.6 g LiCl, 22.32 g Mg(ClO₄)₂, 200 mL 2-butoxyethanol and 1000 mL methanol at about −45 °C and 70 V. TEM observations were performed on a Phillips CM120 microscope operated at 120 kV.

The room-temperature tensile test was conducted on a standard electronic universal testing machine (CMT 1505) at a crosshead speed of 1 mm/min. The tensile bars were fabricated to a gauge length of 30 mm and a diameter of 10 mm by electric discharge wire cutting. At least three tests were performed for each alloy. The fracture surface observation and qualitative microanalysis were carried out on a Philip LEO 1530 VP scanning electron microscope (SEM) with an attached Oxford energy dispersive X-ray spectrometer (EDX) operated at 20 kV.

3 Results and discussion

3.1 Effects of Cu on grain size of as-cast ZK60 alloy

Figure 1 shows the optical micrographs of the as-cast ZK60+xCu alloys. It is revealed that all alloys are of typical non-equilibrium solidification microstructures, namely, the primary α-Mg grains and eutectic intermetallics dispersed mostly along the grain boundaries and a few inside the grains. It is noted that the α-Mg grains shown in Fig. 1 are actually the intersections (by the cut surface) of the dendritic, primary α-Mg, and the eutectic intermetallics (MgZnCu) are solidified between the branches of the dendritic structure. Therefore, it is appropriate to assume the size of the dendritic branch to be the grain size of the α-Mg alloy, or simply the grain size of the alloy. It is clear from Fig. 1 that the degree of forming the dendritic structure is increased with increasing the Cu content, indicating that the eutectic, inter-dendritic MgZnCu can promote the development of the dendritic structure. There is petal-shaped structure visible inside the grains of the Cu-free alloy (Fig. 1(a)), an indication of solute intragranular segregations occurring in the α-Mg grains. This phenomenon is associated with the incomplete

![Fig. 1 Optical micrographs of as-cast ZK60+xCu alloys: (a) x=0; (b) x=0.5; (c) x=1.0; (d) x=2.0](image-url)
diffusion of Zn and Zr in the alloy [8]. However, Fig. 1 shows no such a petal-like structure, and the grain boundaries become extremely distinct in the Cu-bearing samples. This suggests that Cu can enhance the diffusivity of the solute elements Zn and Zr in the magnesium lattice, which is possibly caused by the strong affinity between Cu atoms and vacancies in magnesium [9].

Obviously, the grain size of the ZK60 alloy is greatly affected by the Cu content. The average grain-size number estimated by the method described in the standard GB/T 6394—2002 was 3.1, 3.4, 4.3 and 4.5 for ZK60, ZK60+0.5Cu, ZK60+1Cu and ZK60+2Cu, respectively. The grain refinement of the Cu-bearing alloys can be explained as follows. On one hand, the addition of Cu can change the solidus of the alloy, which shortens the solidification time and thus refines the microstructure [9]. On the other hand, the initially formed Cu-containing intermetallics with high melting point disperse predominantly at the grain boundaries and bring about an intensive constitutional undercooling in a diffusion layer ahead of the advancing solid/liquid interface, which restricts the grain growth and thus refines the grain size. Generally, the refinement efficiency of an element can be estimated by the grain refinement factor (GRF) [10]. The GRF value is equal to

\[ \sum_{i} m_i C_{0,i} (k_i - 1), \]

where \( m_i \) is the slope of the liquidus line in the binary phase diagram, \( C_{0,i} \) is the initial concentration of element \( i \) and \( k_i \) is the solute distribution coefficient. According to the Mg–Cu binary phase diagram, \( m_{Cu} \) and \( k_{Cu} \) are −5.37 and 0.02, respectively. Therefore, the GRF value becomes large when the concentration of the element Cu is increased, which is consistent with the finer grain size with increasing Cu content as shown in Fig. 1.

### 3.2 Element distribution and phase identification in Cu-modified alloy

Figure 2 shows the EPMA element mapping images of the typical ZK60+1Cu alloy in the as-cast condition. The values on the right column of each image correspond to the counts recording the relative concentration of each element in the microstructure, which is represented by different colors. As clearly seen from Fig. 2(d), the element Cu is predominantly distributed at the grain boundary of the alloy. In order to identify the existing form of Cu, XRD and TEM analyses were carried out. Figure 3 provides the XRD patterns of the as-cast ZK60+xCu alloys. By comparing the profile of the Cu-free alloy with those of the Cu-bearing ones, the ZK60 alloy consists of \( \alpha \)-Mg matrix and the MgZn\(_2\) phase while the Cu-bearing alloys include additional diffraction peaks from the MgZnCu phase. The trace MgZn\(_2\) is believed to be precipitated during cooling of the solidified alloy. The three symmetric electron diffraction patterns obtained from the particle shown in Fig. 4(a) by systematically tilting the TEM foil around the normal to (111) during TEM operation, as shown in Figs. 4(b)–(d), confirm that the particle at the grain boundary was indeed the MgZnCu phase with a face-centered cubic structure (\( a = 0.7169 \) nm). It is worth mentioning that the MgZnCu phase can be either cubic or tetragonal according to International Centre for Diffraction Data (ICDD #65–7003 and #41–0778). However, the presence of MgZnCu phase was demonstrated only from XRD or EDX results in the previous studies on the magnesium alloys containing Zn.

![Fig. 2 Back-scattered electronic image (BEI) (a) and EPMA element mapping images of Mg (b), Zn (c), Cu (d), Zr (e) of as-cast ZK60+1Cu alloy](image)
Fig. 3 XRD patterns of as-cast ZK60+xCu alloys

and Cu [11−13]. Therefore, the cubic crystal structure of the MgZnCu phase in the Mg−Zn−Cu alloys is precisely determined in the present study. Recently, the MgZnCu particle in ZC62 alloy (Mg−(5.5−6.5)Zn−(1.4−1.8)Cu−0.2Mn, %) was reported to have a tetragonal structure by LI et al [14]. It is speculated that the crystal structure of MgZnCu intermetallics might vary due to the difference in alloy composition and the growth history.

3.3 Effects of Cu on tensile properties and fractography of as-cast ZK60 alloy

Figure 5 shows the variations of the room temperature tensile properties, including the ultimate tensile strength (UTS), 0.2% proof yield strength (YS) and elongation to failure, of the as-cast ZK60+xCu alloys with different Cu contents. The small amount of Cu addition (0.5%, 1%) considerably improved the mechanical properties of the alloy, particularly giving an excellent tensile elongation of over 9%. This is probably due to the fact that trace Cu addition can remarkably eliminate the intragranular segregations (Fig. 1(a)) and decrease the grain size of ZK60 alloy. In addition, it was reported [15,16] that the c/a axial ratio of the Mg matrix has a marked influence on the elongation of cast magnesium alloys; a reduction in the c/a ratio can generally stimulate the activation of non-basal slips, so as to facilitate the room-temperature plastic deformation. Recently, GANESHAN et al [15] reported that a c/a reduction of 0.657% for a Mg−Cu alloy could result in an excellent ductility based on the first-principles calculation. The XRD results indicate that the c/a reduction values for ZK60+xCu (x=0, 0.5, 1.0, 2.0) alloys are 0.012%, 0.328%, 0.168% and 0.078%, respectively. It is therefore probable that the enhanced ductility of Cu-bearing alloys could be partially due to the reduced c/a ratio by the Cu addition (the alloys with 0.5% and 1.0% Cu with a large reduction in the c/a ratio), although the mechanism for the influence of the Cu content on the c/a ratio of magnesium is unclear at present. However, a higher addition of 2%Cu has caused

Fig. 4 TEM image of grain boundary of MgZnCu particle in as-cast ZK60+1Cu alloy (a) and selected area diffraction patterns (b, c, d) with different electron beam directions of $B=[\overline{1}0]_{\text{MgZnCu}}$, $B=[\overline{3}2\overline{1}]_{\text{MgZnCu}}$ and $B=[\overline{1}3\overline{1}]_{\text{MgZnCu}}$.
Fig. 5 Room-temperature tensile properties of as-cast ZK60+xCu alloys

an excess formation of the network-like MgZnCu intermetallics and thus an inferior room-temperature tensile performance of the alloy.

Figure 6 shows the SEM images of the tensile fracture surfaces for the studied alloys. The ternary ZK60 alloy in Fig. 6(a) exhibits a distinctly brittle intragranular cracking morphology, which is probably due to the severe micro-segregations in the alloy. In contrast, the Cu-modified alloys with trace Cu contents in Figs. 6(b) and (c) display a mixture of quasi-cleavage and ductile fracture characteristic, with many dimples and tearing ridges clearly besides some cleavage steps. However, many intergranular cracks, including broad intergranular cleavage surfaces due to the presence of the grain boundary MgZnCu intermetallics occur in the ZK60+2Cu alloy (Fig. 6(d)). These fractographs are in good agreement with the variation of the tensile elongation with the Cu content as shown in Fig. 5. Examination at a higher magnification reveals that the microcracks predominantly initiated from the bright particles, as marked by the arrows in the inset of Fig. 6(b). EDX analysis indicates that the mole ratio of Mg to Zn to Cu is approximately 67:15:18. Considering the contribution of Mg from the surrounding matrix, it can be concluded that the cracked particles are the MgZnCu intermetallics. This suggests that the MgZnCu particles become the nucleation sites of microcracks when the alloys are subjected to the extensive plastic deformation, which is confirmed by much more bright MgZnCu particles present on the fractured surfaces and the deteriorated tensile properties of the ZK60+xCu alloys with a higher Cu content.

4 Conclusions

1) The Cu addition can effectively eliminate the intragranular segregation and refine the grains (i.e. the branches of the dendritic, primary α-Mg) of the as-cast ZK60 alloy.

![Fig. 6 SEM images of tensile fracture surface for as-cast ZK60+xCu alloys tested at room temperature: (a) x=0; (b) x=0.5; (c) x=1.0; (d) x=2.0](image-url)
2) The alloying element Cu is predominantly distributed at the grain (dendritic) boundaries of the alloy and exists mainly in the form of a ternary MgZnCu phase with a face-centered cubic structure. The amount of MgZnCu intermetallics increases with increasing the Cu content in the alloy.

3) In contrast to the Cu-free ZK60 alloy with an intragranular brittle fracture, the alloy modified with trace Cu of 0.5%–1% exhibits the optimal mechanical properties with an excellent elongation of over 9% and a mixed fracture of quasi-cleavage with ductile rupture. A further Cu addition of 2% results in the formation of coarse network-like MgZnCu particles which embrittle the alloy.

References


Cu 元素对 ZK60 铸造镁合金显微组织和力学性能的影响

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摘 要: 利用光学显微镜、扫描电子显微镜、透射电子显微镜、X-射线衍射仪、电子探针、拉伸测试仪研究 Cu 元素的添加对铸态 ZK60 镁合金显微组织和力学性能的影响, 并讨论了添加 Cu 改善合金拉伸性能的机制。结果表明, Cu 可有效消除 ZK60 镁合金中存在的晶内偏析, 随着 Cu 含量的增加, 合金的晶粒尺寸得到明显细化。含 Cu 镁合金中, 出现了一种具有面心立方结构的 MgZnCu 三元共晶相, 该相主要富集在晶界处且在合金发生塑性变形时成为微裂纹源。拉伸实验表明, 当 Cu 添加量为 0.5%~1% 时, ZK60 镁合金的力学性能得到改善, 当添加量达到 2% 时, 合金的力学性能下降。

关键词: ZK60 镁合金; 铜添加; MgZnCu 相; 晶粒细化; 力学性能

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