Effect of Cu addition on microstructure and properties of Mg-10Zn-5Al-0.1Sb high zinc magnesium alloy

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Abstract: To improve the strength, hardness and heat resistance of Mg-Zn based alloys, the effects of Cu addition on the as-cast microstructure and mechanical properties of Mg-10Zn-5Al-0.1Sb high zinc magnesium alloy were investigated by means of Brinell hardness measurement, scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), XRD and tensile tests at room and elevated temperatures. The results show that the microstructure of as-cast Mg-10Zn-5Al-0.1Sb alloy is composed of α-Mg, τ-Mg32(Al, Zn)49, φ-Al2Mg5Zn2 and Mg3Sb2 phases. The morphologies of these phases in the Cu-containing alloys change from semi-continuous long strip to black herringbone as well as particle-like shapes with increasing Cu content. When the addition of Cu is over 1.0 wt.%, the formation of a new thermally-stable MgCu phase can be observed. The Brinell hardness, room temperature and elevated temperature strengths firstly increase and then decrease as the Cu content increases. Among the Cu-containing alloys, the alloy with the addition of 2.0 wt.% Cu exhibits the optimum mechanical properties. Its hardness and strengths at room and elevated temperatures are 79.35 HB, 190 MPa and 160 MPa, which are increased by 9.65%, 21.1% and 14.3%, respectively compared with those of the Cu-free one. After T6 heat treatment, the strengths at room and elevated temperatures are improved by 20% and 10%, respectively compared with those of the as-cast alloy. This research results provide a new way for strengthening of magnesium alloys at room and elevated temperatures, and a method of producing thermally-stable Mg-10Zn-5Al based high zinc magnesium alloys.

Key words: microstructure; mechanical properties; high zinc magnesium alloy; MgCu phase

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Mg-Al alloys, such as AZ91 and AM60 alloys, have been widely used in practical applications for their high strength, excellent casting and corrosion-resistant properties at room temperature. However, the application of commercially available Mg-Al-based alloys is limited by their poor creep behavior at elevated temperatures (>120℃) due to the low melting point of the Mg17Al12 phase [1-2]. Previous works [3-5] reported that Mg-10Zn-5Al-0.1Sb system alloys can not only avoid the formation of the β-Mg17Al12 phase but also promote the formation of the thermally stable Mg3Sb2 phase. These two factors could improve the comprehensive mechanical performance at both room and elevated temperatures, especially high temperature performance of Mg alloys. However, the absolute strength of Mg-Zn-Al-Sb system at room and elevated temperatures is still lower compared with that of other heat-resistant Mg alloys. It has been reported that element Cu is effective in improving the heat-resistant behavior due to the formation of the MgCu phase and accelerating the precipitation performance [6-7] of Mg-Zn based alloys. Therefore, it is expected that Cu addition to the Mg-10Zn-5Al-0.1Sb high zinc magnesium alloy is possibly beneficial to the performance improvement in the strength and aging behavior of the alloy. The present work investigated the effects of Cu on the microstructure and mechanical properties of Mg-10Zn-5Al-0.1Sb alloy and provided the methods of producing thermally-stable Mg-10Zn-5Al based high zinc magnesium alloys.

1 Experimental procedure

The nominal chemical compositions of the studied alloys are presented in Table 1. The tested Cu-containing alloys were prepared using pure Mg (99.5%), pure aluminum (99.5%), pure zinc (99.5%) and pure Sb as well as master alloys Al-10%Mn and Al-50%Cu. The experimental alloys were melted in a well-type crucible resistance furnace and protected by mixing gases of CO2 and CH2FCF3. After the master alloys
Al-10%Mn and Al-50%Cu were added into the melt at 720 °C and 740 °C respectively, the pure Sb was added. The melt was held at 740 °C for 20 min to ensure the alloying elements were completely dissolved and diffused. Then, the molten alloy was poured at 700 °C into a cylindrical steel mold with a diameter of 20 mm and a length of 180 mm, which was preheated to 200 °C.

The hardness was measured by a Brinell hardness tester (HB-3000B) with a loading force of 625 N for a holding time of 30 s. Each measurement was the average value of at least 3 individual measurements. The tensile tests were carried out using a DNS100 universal electronic testing machine with a tensile speed of 0.5 mm·min⁻¹, at both room temperature and elevated temperature (200 °C). For the elevated temperature tensile specimen, the holding time was 30 min, each measurement was the average value of at least 3 individual specimens. The dimensions of the tensile specimen are shown in Fig. 1. The impact toughness was determined by means of a JB-30B impact testing machine, and the micro-hardness of the phase was confirmed by a HVST-1000A micro-hardness tester with a load of 0.49 N and a holding time of 15 s. All samples for optical microscopy (OM) were polished and then etched in a solution of nitric acid. JSU-6700 Field scanning electron microscopy (FSEM) and energy dispersive spectroscopy (EDS) were used to study the morphological and micro-chemical characterization of the second phase. The heat treatment of the experimental alloys was carried out using a SX2-8-10 box-type resistance furnace with the following technological parameters: the solid solution temperature: 350 °C, protective agent: MgO powder, holding time: 24 h, quenching medium: hot water of 70 to 80 °C; aging temperature: 180 °C, holding times: 12, 24, 36 and 48 h, respectively. Finally, the specimens were cooled in air.

2 Experimental results and analysis

2.1 Analysis of microstructure

Previous reports [8-11] indicated that the as-cast microstructure of high Zn content Mg-10Zn-5Al-0.1Sb alloy consists of α-Mg matrix, τ-Mg₃₂(Al, Zn)₄₉, φ-Al₂Mg₅Zn₂ and Mg₃Sb₂ phases. Figure 2 shows the as-cast microstructures of high Zn content Mg-10Zn-5Al-0.1Sb alloys with different Cu contents. Figure 2(a) shows the microstructure of the Cu-free Mg-10Zn-5Al-0.1Sb alloy. As indicated, the grey matrix is α-Mg phase. The semi-continuous long strip and some massive structures on the grain boundary are τ-Mg₃₂(Al, Zn)₄₉ phase and φ-Al₂Mg₅Zn₂ phase, respectively; corresponding to B and C as shown in Fig. 2(a). In addition, the fine dispersed black granular structure in the grain is Mg₃Sb₂ phase [arrow
As shown in Fig. 2(a), when 0.5 wt.% Cu is added to the Mg-10Zn-5Al-0.1Sb alloy, the strip-like $\tau$-Mg$_{32}$(Al,Zn)$_{49}$ phase at the grain boundary remained little changed. Furthermore, when the Cu content was increased to 1 wt.%, the formation of black herringbone phase can be observed and the amount of massive $\phi$-Al$_2$Mg$_5$Zn$_2$ phase increases [See Figs. 2(b) and (c)]. In addition, the $\tau$-Mg$_{32}$(Al,Zn)$_{49}$ phase in the alloy was changed from semi-continuous long strip to particles and a large amount of black herringbone $\tau$-Mg$_{32}$(Al,Zn)$_{49}$ phase forms at the same time when the addition of Cu was increased to 1.5 wt.%, as shown in Fig. 2(d) (arrow D). The amount of black herringbone $\tau$-Mg$_{32}$(Al,Zn)$_{49}$ phase increases continuously with increasing Cu content and the $\tau$-Mg$_{32}$(Al,Zn)$_{49}$ phase aggregated along the grain boundary in the alloys with Cu content higher than 1.5 wt.%, as shown in Figs. 2(e), (f) and (g).

Figure 3 shows the optical microstructure of the alloys after solid solution treatment at 350°C for 24 h. After adding Cu into the alloy, partial $\tau$-Mg$_{32}$(Al,Zn)$_{49}$ phase and $\phi$-Al$_2$Mg$_5$Zn$_2$ phase dissolve into the $\alpha$-Mg matrix and the semi-continuous long strip $\tau$-Mg$_{32}$(Al,Zn)$_{49}$ phase was modified and/or refined. However, not all the second phases were dissolved into the matrix after the solid solution treatment, the volume fraction of remained phases increased with the increasing Cu content. It is attributed to the high melting points (568°C, 535°C and 393°C for Mg$_2$Cu, $\tau$-Mg$_{32}$(Al,Zn)$_{49}$, $\phi$-Al$_2$Mg$_5$Zn$_2$ phases, respectively [8]) of these phases, which are higher than the temperature of solid solution treatment. Therefore these thermally stable phases related to the Cu addition can improve the thermal stability of the alloys.

EDS analysis of 5th alloy (2.0 wt.% Cu) is shown in Fig. 4 and the corresponding composition of the phases are listed in the table. As shown, the grey area (arrow A in Fig. 4) is $\alpha$-Mg matrix containing some dissolved Zn and Al atoms; the separated massive phase, as indicated by arrow B, is $\phi$-Al$_2$Mg$_5$Zn$_2$ phase and the semi-continuous long strip phase; and the phase as indicated by arrow C, is $\tau$-Mg$_{32}$(Al,Zn)$_{49}$ phase. It should be noted that a certain amount of Cu atoms are dissolved in both $\tau$ and $\phi$ phases, indicating that these two phases are modified by Cu atoms.

The magnification of position D in Fig. 4 and EDS analyses are shown in Fig. 5. The EDS results indicate that the Cu content of short block phase is obviously higher than that of phases indicated by arrows B and C in Fig. 4. The atomic ratios of Mg: Cu = 2.44, which is well in agreement with the stoichiometric ratios 2:1, namely the phase can be determined as Mg$_2$Cu phase. The above result indicated that the Cu addition into Mg-10Zn-5Al-0.1Sb alloy can result in the appearance of new herringbone phase apart from the $\tau$-Mg$_{32}$(Al,Zn)$_{49}$ and $\phi$-Al$_2$Mg$_5$Zn$_2$ phases in the Mg matrix.

X-ray diffraction analysis results of the experimental alloys are shown in Fig. 6. As shown, the as-cast high Zn content Cu-free Mg-10Zn-5Al-0.1Sb magnesium alloy (1st alloy) is mainly composed of $\alpha$-Mg matrix, $\tau$-Mg$_{32}$(Al, Zn)$_{49}$, $\phi$-Al$_2$Mg$_5$Zn$_2$ and Mg$_3$Sb$_2$ phases. After adding 2.0 wt.% Cu into the Mg-10Zn-5Al-0.1Sb alloy (5th alloy), the new phase of Mg$_2$Cu can be observed. Furthermore, thermally stable Mg$_2$Cu, $\tau$-Mg$_{32}$(Al, Zn)$_{49}$ and $\phi$-Al$_2$Mg$_5$Zn$_2$ phases are still present in the experimental alloys after T4 and T6 treatments.

2.2 Mechanical properties of experimental alloy

Figure 7 shows the tensile strengths of the as-cast and heat-treated alloys at both room and elevated temperatures. As
shown, the tensile strengths of as-cast Cu free Mg-10Zn-5Al-0.1Sb alloy are 161 MPa and 120 MPa at room and elevated temperatures, respectively. The strength firstly increases and then decreases as the Cu content is increased. Both the room and elevated temperature tensile strengths of the as-cast Mg-10Zn-5Al-0.1Sb alloy reach their peak of 190 MPa and 160 MPa, respectively when the Cu content is 2.0wt.%. The increment of tensile strengths compared to those of Cu-free Mg-10Zn-5Al-0.1Sb alloys are 21.1% and 14.3%, respectively. After T6 treatment, the tensile strengths of the alloys at room and elevated temperatures were further increased by 20% and 10%, respectively compared to those of the as-cast alloys, due to the second phase strengthening.

Figure 8 shows the hardness and impact strength curves of the experimental alloys. Similar to the trend of tensile strength, the Brinell hardness of the alloys firstly increases and then decreases with the rising of Cu content. The peak value of the alloy containing 2.0wt.% Cu is 79.35 HB, increased by 9.65% compared to that of the as-cast Cu free alloy. When the Cu content is over 1.0wt.%, the micro-hardness of Mg-Cu phase reaching 79.2 HV, increased by 17.2% compared to that of Mg-Cu phase in the Cu-free alloy (1\textsuperscript{st} alloy). Meanwhile, the herringbone phase Mg\_Cu formed on Mg-Cu phase is a highly hardening phase with micro-hardness of 92.7 HV. This demonstrates that Cu plays a great role in enhancing both strength and hardness in Mg-10Zn-5Al-0.1Sb alloy.

In addition, it should be noted that the addition of Cu suppresses the diffusion of Zn and Al atoms, leading to their amounts increasing in the matrix. In other words, the addition of Cu can enhance the solid solution strengthening. After the addition of Cu, a great deal of herringbone Mg\_Cu phase forms on Mg-Cu phase. It can be seen from the Mg-Cu binary phase diagram that the melting point of Mg-Cu is 568 °C, which is 30 °C higher than that of the Mg-Cu phase.
This causes the Mg$_2$Cu phase dissevering from the matrix second phase at the grain boundaries become more obvious. Its hardness, room and elevated alloy with the addition of 2.0wt.% Cu exhibits the relatively high zinc magnesium alloy are greatly improved after adding and modify the morphology of second phases. The 0.1Sb high zinc magnesium alloy can refine the microstructure and Mg$_3$Sb$_2$ phases.

After T6 treatment, the strengths of Mg-10Zn-5Al-0.1Sb with different Cu contents at both room and elevated temperatures are further improved by the combination effect of the aging strengthening of Cu and second phase strengthening of other remaining phases in the matrix. However, if the Cu content is over 2.0wt.%, the volume fraction of the black herringbone Mg$_2$Cu phase increases and coarsening and aggregation of the second phase at the grain boundaries become more obvious. This causes the Mg$_2$Cu phase dissection from the matrix and therefore the properties of the experimental alloys are deteriorated.

The effect of Cu addition on the impact toughness of Mg-10Zn-5Al-0.1Sb alloy is not obvious. As the addition of Cu less than 2.0wt.%, the toughness decreased a little with increasing Cu content, further work is required to explain this phenomenon. When the Cu content is 2.0wt.%, the impact toughness increased to 6 J·cm$^{-2}$. This is mainly related to the increasing volume fraction of Mg$_2$Cu phase and suppression of the growth of $\tau$-Mg$_5$(Al, Zn)$_2$ and $\phi$-Al$_2$Mg$_5$Zn$_2$ phases, which leading its morphology of the alloy from net to short block due to the Cu addition. The refinement of the microstructure leads to the increase of toughness of the Mg-10Zn-5Al-0.1Sb-2.0Cu alloy. However, if the Cu content is higher than 2.0wt.%, the aggregation of the second phases can be observed and this will disperse the matrix and provide sites for crack propagation during plastic deformation and finally weaken the impact toughness of the alloys.

3 Conclusions

(1) Adding 0.5wt.% to 3.0wt.% Cu into Mg-10Zn-5Al-0.1Sb high zinc magnesium alloy can refine the microstructure and modify the morphology of second phases. The $\tau$-Mg$_5$(Al, Zn)$_2$ phase in the Cu-containing alloys is changed from semi-continuous long strip net to black herringbone as well as particle-like shapes. In addition, when the Cu content is higher than 2.0wt.%, the formation of new thermally stable Mg$_2$Cu phase can be observed except for $\alpha$-Mg, $\tau$-Mg$_5$(Al, Zn)$_2$, $\phi$-Al$_2$Mg$_5$Zn$_2$ and Mg$_3$Sb$_2$ phases.

(2) The mechanical properties of Mg-10Zn-5Al-0.1Sb high zinc magnesium alloy are greatly improved after adding different contents of Cu. Among the Cu-containing alloys, the alloy with the addition of 2.0wt.% Cu exhibits the relatively optimum mechanical properties. Its hardness, room and elevated temperature strengths are 79.35 HB, 190 MPa and 160 MPa, which are increased by 9.65%, 21.1% and 14.3%, respectively compared to those of the Cu-free alloy. After T6 treatment, the room and elevated-temperature strengths are 228 MPa and 176 MPa, which are improved by 20% and 10%, respectively compared to those of as-cast values. The above results indicate that the addition of Cu can increase the heat resistance of Mg-10Zn-5Al based high zinc magnesium alloys.

References