Study on microstructure and mechanical properties of as-cast Mg-Zn-Sn-xCu(x=0,0.5,1.0,1.5wt.%) alloys

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Abstract. In this paper, with the help of optical microscope, X-ray diffraction, scanning electron microscope and mechanical testing machine, the microstructures of ZT63-xCu (x=0,0.5,1.0,1.5wt.%) magnesium alloys were investigated and their mechanical properties were explored. It was found that the structure of as-cast alloys presented a typical dendrite morphology. The eutectic structure was refined by the addition of a certain amount of Cu. When Cu content continued to increase, the volume fraction of the eutectic structure increased and its continuity enhanced. The alloy without Cu addition was composed of α-Mg, MgZn\textsubscript{2} and Mg\textsubscript{2}Sn phases. With the addition of Cu elements, MgZnCu phase was formed in the alloy, in addition to α-Mg, MgZn\textsubscript{2} and Mg\textsubscript{2}Sn phases. With the increase of Cu content, the volume fraction of MgZnCu phase increased, and the proportion of MgZn\textsubscript{2} phase gradually decreased. ZT63 alloy had the best matching of mechanical properties, its tensile strength and yield strength were 231Mpa and 83Mpa respectively, and the elongation reached 14.5\%. With the increase of Cu, the mechanical properties of the alloys declined. When the Cu content is 1.5wt.\%, tensile strength of the alloy decreased to 174Mpa, and the elongation was only 7\%. The reduction of mechanical properties was related to the increase of MgZnCu phase.

1. Introduction
Magnesium alloy has the advantages of low density, high specific strength and stiffness, and is the lightest metal structural material at present. It has important applications in the fields of transportation, aerospace and military [1-2]. At present, the main magnesium alloys used in the industry are Mg-Zn, Mg-Al, Mg-RE based alloys. However, Mg-RE based alloys are limited by their high price; and the mechanical properties of Mg-Al alloys will decrease at elevated temperature due to β-Mg\textsubscript{17}Al\textsubscript{12} phase. The strength of Mg-Zn alloys is not enough to meet industrial demands. Many attempts have been made to improve the mechanical properties of Mg-Zn based alloys. When Cu element is added to Mg-Zn alloys, high melting point MgZnCu phase is formed, and the mechanical property of the alloy is significantly improved after the deformation treatment [3-4]. Moreover, it has been shown that the addition of Sn element to magnesium alloy can improve the plastic deformation ability of the alloy [5]. Mg\textsubscript{5}Sn phase formed in the matrix can effectively improve the mechanical properties of the alloy [6-7]. El Mahallawy [8] and Sasaki [9] find that Mg\textsubscript{5}Sn phase plays an important role in strengthening the
magnesium alloys. Based on this truth, we designed Mg-Zn-Sn-Cu alloys with different Cu contents to study the influence of Cu on the microstructures and mechanical properties of the alloys. Such a study will provide more evidences for the mechanical property’s improvement of Mg-Zn alloys.

2. Materials and methods

2.1. Materials preparation

The experimental raw materials were commercial pure Mg, pure Zn, pure Sn and pure Cu. Before the smelting process started, oxides on the surface of the raw materials were removed and the materials were dried to remove moisture. The size of the steel crucible used was φ120×400 mm. The magnesium ingots were put into crucible and heated to 700℃ in a medium-frequency electromagnetic induction furnace, then the temperature was raised to 750℃, pure Zn, pure Sn, pure Cu were put into the crucible. After that the temperature was raised to 780℃, and kept for 3 minutes to make the metal completely melt and then stirred for 2 min to let the alloying elements fully diffuse and evenly distribute in the magnesium matrix. After holding at this temperature for 3 min, the temperature was lowered. When the temperature dropped to about 700 ℃, the crucible was taken from the furnace and put into the water to get the sample cooled rapidly. The analyzed composition of the alloys determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) was shown in Table 1, it can be seen that the alloys met the design requirements.

2.2. Research methods

Microstructures of the alloys were characterized by Carl Zeiss optical microscope, scanning electron microscope (SEM, Carl Zeiss EVO18) coupled with an energy dispersive spectrometer (EDS). Phase identification was conducted by X-ray diffraction (XRD) with Cu Kα radiation at 40 kV and 40mA. The samples for OM were etched with a solution of nitric acid and ethanol (96ml ethanol+4ml). Mechanical properties of the alloys were evaluated by tensile testing. The diameter and gauge length of the cylindrical samples were 5 and 25mm. Tensile tests at room temperature were carried out at a speed of 2mm/min.

3. Results

Figure 1 are the microstructure photographs of the as-cast alloys. It can be seen that the as-cast alloys exhibit a typical dendritic morphology, and eutectic structure is distributed at the grain boundary. The addition of Cu has subtle effect on the grain refinement. With the increase of Cu, the eutectic structure content in the alloys shows an increasing trend. When Cu is added to 0.5wt.%, the eutectic structure changes from semi-continuous to discontinuous, and then as the Cu content increases, the continuity of the eutectic structure gradually increases and becomes a network. The grain boundaries of the alloys are particularly sensitive to corrosive solution, which may be related to the enrichment of Zn atoms at the grain boundaries.

XRD patterns of the alloys are shown in Figure 2. We can find that the phases in ZT63 alloy are α-Mg, Mg2Sn, MgZn2. With the addition of Cu, the peak of MgZnCu appears, indicating that MgZnCu phase is formed in the alloy, which is consistent with the results of Wang [8]. With an increase in Cu,
the peak of MgZnCu phase is enhanced, and the peak of MgZn$_2$ phase is weakened, which implies that the proportion of MgZnCu phase increases.

(a) ZT63, (b) ZT63-0.5Cu, (c) ZT63-1.0Cu, (d) ZT63-1.5Cu.

**Figure 1.** Metallographic photographs of the as-cast alloys.

![Figure 1](image1.png)

**Figure 2.** XRD patterns of the alloys.

![Figure 2](image2.png)

**Figure 3.** SEM images of as-cast ZT63-xCu alloys; (a) x = 0 wt.%; (b) x = 0.5 wt.%; (c) x=1.0wt.%; (d) x=1.5wt.%.  

![Figure 3](image3.png)
Table 2. EDS test results of the as-cast alloys (the points of A, B, C correspond to the locations denoted in figure 3).

| Point | Sample ID     | Mg Weight% | Mg Atomic% | Zn Weight% | Zn Atomic% | Sn Weight% | Sn Atomic% | Cu Weight% | Cu Atomic% |
|-------|----------------|-------------|-------------|------------|------------|------------|------------|------------|------------|
| A     | ZT63          | 38.93       | 75.24       | 1.81       | 1.30       | 59.26      | 23.46      | -          | -          |
|       | ZT63-0.5Cu    | 50.76       | 82.94       | 1.84       | 1.12       | 47.13      | 15.77      | 0.28       | 0.17       |
|       | ZT63-1.0Cu    | 40.63       | 76.39       | 1.78       | 1.25       | 57.05      | 21.97      | 0.54       | 0.39       |
|       | ZT63-1.5Cu    | 40.01       | 76.02       | 1.42       | 1.00       | 58.02      | 22.58      | 0.55       | 0.40       |
| B     | ZT63          | 54.36       | 76.37       | 44.75      | 23.38      | 0.89       | 0.25       | -          | -          |
|       | ZT63-0.5Cu    | 67.07       | 84.76       | 24.34      | 11.44      | 1.58       | 0.41       | 7.00       | 3.39       |
|       | ZT63-1.0Cu    | 59.48       | 80.06       | 28.88      | 14.46      | 2.14       | 0.59       | 9.50       | 4.89       |
| C     | ZT63-1.5Cu    | 61.89       | 81.61       | 25.10      | 12.31      | 2.06       | 0.56       | 10.94      | 5.52       |

SEM and EDS are used to further determine the composition of the second phases in the alloys. It can be seen in figure 3 that the addition of a certain amount of Cu can change the morphology of the alloy eutectic structure and refine its dendritic structure. The grain size of the alloys is 30, 28, 25, and 32 μm, respectively. With the change of Cu content, the grain size of the alloy decreases first and then increases. When the Cu content is 1.0 wt.%, the grains of the alloy are the finest. The reason for this phenomenon is that the addition of a certain amount of Cu can form tiny MgZnCu phases distributed at grain boundaries, which prevent grain boundary migration, resulting in grain refinement. However, when Cu is added too much, the size of MgZnCu phase becomes too large and it loses the ability to hinder grain boundary migration, thus the size of the grain increases again. The phases in the ZT63 alloy are α-Mg, MgZn2, and Mg3Sn. The eutectic structure composed of MgZn2 and Mg3Sn phases is semi-continuously distributed at grain boundaries, and the eutectic exhibits a lamellar structure. After adding 0.5wt.% of Cu, the eutectic structure in the alloy is intermittently distributed at the grain boundary, and the MgZnCu ternary phase is newly formed in the alloy. When the content of Cu is 1.0 wt.%, the volume fraction of the eutectic structure is obviously increased, and it is distributed in a continuous network at grain boundary. The interior of the eutectic structure is still lamellar, and the main phases in the alloy are α-Mg, Mg3Sn, MgZnCu. When the Cu content is 1.5 wt.%, the inner layer of the eutectic structure is arranged more regularly, and α-Mg, Mg3Sn phase, MgZnCu phase exist in the alloy. From the Table 2 we can find that as the Cu content increases, the proportion of Cu atoms in the MgZnCu phase increases.

To further observe the distribution of different elements, mapping analysis is used. Figure 4 shows mapping analysis results of the alloys. It reveals that bright white phases in the alloys are rich in Sn atoms, and this kind of phase corresponds to Mg2Sn phase. In the ZT63 alloy, dense lamellar structure is rich in Zn atoms, which means its MgZn2 phase. When Cu elements are added, Cu atoms are also enriched at the lamellar structure and their positions are overlapped with Zn atoms. This reflects that the phase is MgZnCu phase. We can see that the results are consistent with the EDS results in table 2.

When the Cu content is low, the eutectic structure in the alloy is finely fractured, and then as the Cu content continues to increase, the continuity of the eutectic structure is enhanced. The reason for this phenomenon is that when Cu is not added, a large amount of MgZn2 phase and Mg3Sn phase are formed at the grain boundary. After the addition of Cu, the alloy tends to form the MgZnCu phase. However, since the addition of Cu is very small, MgZnCu phase is insufficient to form a network, so it is intermittently distributed at the grain boundary. As the Cu content continues to increase, more MgZnCu phases form at the grain boundary, and the eutectic structure gradually changes into a network.

The mechanical properties of the alloys are shown in figure 5. It is obvious that the addition of Cu reduces the mechanical properties of the alloys. The tensile strength of the ZT63-xCu (x=0, 0.5, 1.0, 1.5wt. %) alloys are 231, 221, and 206,174MPa, respectively. When the addition of Cu is more than 1.0 %, the properties sharply deteriorate, which indicates that network-like MgZnCu phases are harmful to the mechanical properties of the as-cast alloys. The reason for this phenomenon may be...
that MgZnCu phase is a brittle phase, which causes stress concentration [10], thus leading to the failure of alloys.

![Figure 4. Mapping analysis of as-cast alloys.](image)

![Figure 5. Mechanical properties of as-cast alloys.](image)

4. Conclusions

By studying the as-cast microstructures of ZT63-xCu (x=0, 0.5, 1.0, 1.5wt.%), it was found that Cu can refine grains and eutectic structures to some extent, but when the addition of Cu is excessive, it will lead to coarsening of grains and eutectic structures. Phase composition of ZT63 alloy is α-Mg, MgZn2, and Mg2Sn phase, and a high melting point MgZnCu phase is introduced after Cu is added.
With increased MgZnCu phase, the mechanical properties of the alloys deteriorate, because MgZnCu phase is brittle.

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