**Rare Metal Materials and Engineering**
Volume 47, Issue 8, August 2018
Online English edition of the Chinese language journal

Available online at www.sciencedirect.com

ScienceDirect

**Cite this article as:** Rare Metal Materials and Engineering, 2018, 47(8): 2360-2364.

ARTICLE

# Effect of the Pulling Velocity of Directional Solidification on Thermal Conductivity of Mg-Ag-Zn Alloys

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**Abstract:** Specimens of as-cast Mg-1Ag-Zn, Mg-3Ag-Zn and Mg-5Ag-Zn alloys were fabricated, and then the specimens' thermal conductivity was calculated. With the increase of Ag content, the thermal conductivity of as-cast alloy decreases significantly. After that, directionally solidified specimens of the above mentioned as-cast Mg-Ag-Zn alloys were made at three different pulling velocities: $V$=25 μm/s, $V$=50 μm/s, $V$=75 μm/s, and then their thermal conductivity was calculated again. The results show that with the increase of the pulling velocity, the thermal conductivity of alloys decreases significantly. Variations in the solute content and the pulling velocities are believed to play important roles in the thermal conductivity of Mg-Ag-Zn alloys. Since these two factors can strengthen the electron's scattering process, reduce their free path, and thereby reduce the alloys' thermal conductivity.

**Key words:** Mg alloy; directional solidification; Ag content; thermal conductivity

Magnesium has many merits, such as high specific strength and specific stiffness, high radiation tolerance, good thermal and electrical conductivity[1,2]. The thermal conductivity coefficient of magnesium is much higher than those of steel and plastics. Magnesium and its alloys have been taken as a kind of important structural and functional material. The directional solidification technique can help to control the growth direction of grains in the solidification process and reduce the quantity of axial grain boundaries, thus remarkably enhancing alloy's axial thermal conductivity[3,4]. This paper mainly studied the thermal conductivity behavior of directionally solidified (DS) Mg-Ag-Zn alloys.

Ying et al[5,6] studied the thermal conductivity of as-cast and as-extruded Mg-Al and Mg-Zn alloys. The results showed that the thermal conductivity of the as-extruded alloys was lower than that of as-cast alloys. There are more defects after extrusion, such as the increase of the grain boundaries. The as-extruded Mg-Al alloy shows anisotropy of thermal conductivity, and thermal conductivity in the direction parallel to extrusion direction is lower than that perpendicular to the extrusion direction due to the texture formed during extrusion. Shi[7] studied thermal conductivity of LPSO reinforced Mg-Zn-Y(-Gd) alloys, and the results showed that the phonons' diffusion motion shall be inhibited by the grain boundaries' scattering effect. The smaller the grains are inside the alloy and the more the grain boundaries are, the stronger the gain boundary's scattering effect is. The grain boundary's scatting is proportional to phonon's mean free path, but inversely proportional to grain's diameter. Rudajevová et al[8] indicated that the solid solution can also enhance scattering and reduce the thermal conductivity and the thermal diffusivity of Mg-Al alloys. Yuan et al[9] studied the thermal conductivity of Mg-1Zn-Mn alloy, and the results showed that the second phase enhance the scattering.

Therefore, the solute content and the grain boundaries are believed to play important roles in the thermal conductivity of Mg alloys. In the present paper, Mg-1Ag-Zn, Mg-3Ag-Zn and Mg-5Ag-Zn alloys were used as the research objects. First, their specimens were fabricated at different pulling velocities, and then the influence of pulling velocities ($V$=25 μm/s, $V$=50 μm/s, $V$=75 μm/s) on the alloy's thermal conductivity was analyzed. The atomic radius sizes of Zn and Mg are close to each other. Because of their small radius difference, the alloy's crystal lattice distortion is small, which leads to the small

Received date: August 25, 2017
Foundation item: Innovation Projects Post-graduate Education Program of Shanxi Province (2016BY137)
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influence on the alloy's thermal conductivity. The atomic Mg-Ag co-clusters were formed by adding Ag into the Mg substrate, which leads to influence on the growth of the grains. The main aim of this paper is to study the effect of pulling velocity and Ag content on the thermal conductivity of Mg alloys

## 1 Experiment

The as-cast Mg alloys were fabricated with pure Mg (99.9%), pure Ag (99.9%), and pure Zn (99.9%) using a medium frequency induction heating furnace. Covering powder was added on the solution surface to prevent it from oxidation and burning. The Mg-Ag-Zn alloy's nominal chemical composition is shown in Table 1.

The DS specimens were fabricated at different pulling velocities ($V$=25, 50, 75 μm/s) by Bridgman DS apparatus. The DS parameters are shown in Table 2.

All of the as-cast specimens and DS specimens were the same size with a diameter of 8 mm and a length of 120 mm, and at least three specimens were fabricated for each parameter in order to provide valid experimental data. And all of them were ground, polished, and then etched in 10% solution of nitric acid and alcohol. Microstructure observation was carried out by LEICA DM6000 M optical microscope. The D/MAX2000/PC type X-ray diffractometer was adopted to analyze the phase of the alloy. The JSM-1T300LV type of scanning electron microscope (SEM) and the X-max20 type of energy dispersive spectrometer (EDS) were used to analyze the composition and distributions of the alloy's precipitated phase.

The thermal diffusivity of specimens was measured by a laser flash method using LINSEIS L 70/2171 apparatus at room temperature[5-7]. The as-cast and DS specimens were cut into the shape of disk with a diameter of 7 mm and thickness of 4 mm. In order to reduce the errors, three specimens were fabricated for each kind. Every specimen was measured 5 times. In particular, the thermal diffusivity of as-cast and DS specimens were measured in axial direction. Then, their thermal conductivity was calculated by Formula (1).

**Table 1 Mg-Ag-Zn alloy's nominal chemical composition (wt%)**

| Alloy | Mg | Ag | Zn |
|---|---|---|---|
| Mg-1Ag-Zn | 98 | 1 | 1 |
| Mg-3Ag-Zn | 96 | 3 | 1 |
| Mg-5Ag-Zn | 94 | 5 | 1 |

**Table 2 Experimental parameters of Mg-Ag-Zn alloys**

| Alloy | Pulling velocities/ μm·s$^{-1}$ | Diameter of DS specimen/mm |
|---|---|---|
| Mg-1Ag-Zn<br>Mg-3Ag-Zn<br>Mg-5Ag-Zn | 25, 50, 75 | 8 |

$$\lambda = C_p \alpha \rho \quad (1)$$

where, $C_p$-metal's specific heat capacity; $\alpha$-metal's thermal diffusivity; $\rho$-metal's density.

The specimens with a diameter of 7 mm and a length of 20 mm were used to be melted in the Bridgman DS apparatus. Temperature sensor was applied to measure the temperature difference in the melting region. The temperature gradient can be calculated by Formula (2).

$$G = (T_0 - T_1)/L \quad (2)$$

where, $G$-temperature gradient; ($T_0$–$T_1$)-temperature difference; $L$-length.

## 2 Results and Discussion

Table 3 shows the thermal conductivity in axial direction of as-cast and DS specimens. And the temperature gradient is about 70 K/cm.

Fig.1 shows the microstructures of as-cast Mg-1Ag-Zn and Mg-5Ag-Zn alloys. XRD patterns of DS Mg-1Ag-Zn, Mg-3Ag-Zn and Mg-5Ag-Zn alloys are shown in Fig.6, and the alloys consist of $\alpha$-Mg and $Ag_{7.96}Mg_{25.04}$ binary phase. At room temperature, the equilibrium solid solubility of Zn in Mg is about 2 wt%. When the Zn content in Mg is less than 2 wt%, almost all the Zn exist as solute atoms, so Zn's intermetallic compounds (the second phase) may not exist in Mg substrate.

Fig.2 shows the axial microstructures (columnar grains) of Mg-1Ag-Zn alloys at the temperature gradient of 70 K/cm and at the pulling velocities of 25 and 75 μm/s. It can be observed that the well-ordered columnar grains of Mg-1Ag-Zn alloys are obtained. The max diameter of the columnar grains can reach 200~300 μm at the pulling velocity of 25 μm/s and 150~250 μm at the pulling velocity of 75 μm/s. Although different diameters are formed at two velocities, both columnar grains shown in Fig.2 are very long in the axial direction. The angles of columnar grains along the axial direction are about 75°.

Fig.3 shows the axial microstructures (columnar grains) of Mg-3Ag-Zn alloys at the temperature gradient of 70 K/cm and

**Table 3 Thermal conductivity in axial direction of as-cast and DS Mg-Ag-Zn alloys**

| Alloy | Pulling velocity, $V$/μm·s$^{-1}$ | Thermal conductivity, $\lambda$/W·m$^{-1}$·K$^{-1}$ |
|---|---|---|
| Mg-1Ag-Zn | 25 | 149.2 |
| | 50 | 147.2 |
| | 75 | 144.7 |
| | Cast | 141.9 |
| Mg-3Ag-Zn | 25 | 142.8 |
| | 50 | 136.8 |
| | 75 | 133.2 |
| | Cast | 131.6 |
| Mg-5Ag-Zn | 25 | 137.9 |
| | 50 | 133.4 |
| | 75 | 129.9 |
| | Cast | 128.2 |

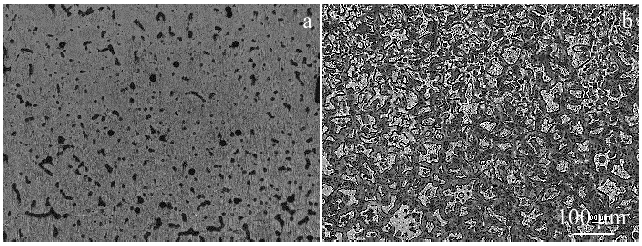


Fig.1 Optical micrographs of as-cast alloys: (a) Mg-1Ag-Zn and (b) Mg-5Ag-Zn

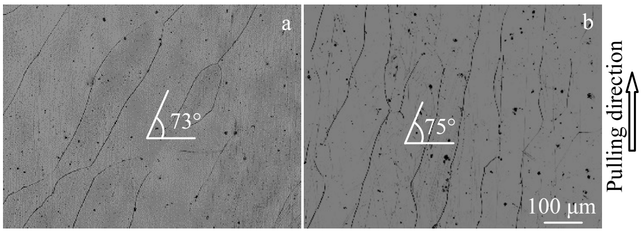


Fig.2 Optical micrographs of DS Mg-1Ag-Zn alloys formed at different pulling velocities: (a) $V$=25 μm/s and (b) $V$=75 μm/s

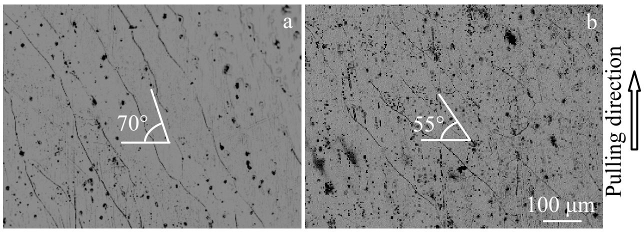


Fig.3 Optical micrographs of DS Mg-3Ag-Zn alloys formed at different pulling velocities: (a) $V$ =25 μm/s and (b) $V$=75 μm/s

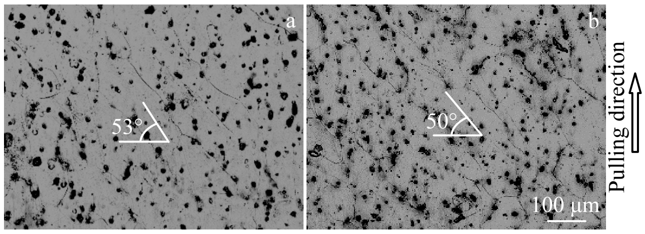


Fig.4 Optical micrographs of DS Mg-5Ag-Zn alloys formed at different pulling velocities: (a) $V$=25 μm/s and (b) $V$=75 μm/s

at the pulling velocities of 25 and 75 μm/s. The columnar grains are also formed well. They are very long in axial direction and their max diameter can reach 100~200 μm at the pulling velocity of 25 μm/s. However, when the pulling velocity comes to 75 μm/s, the columnar grains become unsmooth. It can be observed that with the increase of Ag content, the intermetallic compounds increase, which will cause the columnar grains to grow unsmooth. The angles of columnar grains along the axial direction are about 55°~75°.

Fig.4 shows the axial microstructure of the Mg-5Ag-Zn alloys formed at the pulling velocities of 25 and 75 μm/s. The columnar grains become irregular and unsmooth. The angles of columnar grains along the axial direction are about 50°.

The pulling velocity has a great influence on the formation of columnar grains. The condition to attain the even columnar grains is the stable growth of the solid-liquid interface, and Formula (3) is the basis for judgment.

$$\frac{G}{V} \geqslant m\frac{C_0}{D}\left(\frac{1-K_0}{K_0}\right) \tag{3}$$

where, $G$-temperature gradient; $V$-solidification ratio; $m$-liquidus slope; $C_0$-alloy components; $D$-diffusion coefficient; $K_0$-equilibrium distribution coefficient.

When the G/$V$ ratio value is greater than $mC_0/D(1–K_0/K_0)$, the grains show the behavior of planner growth. And with the further reduction of the G/$V$ ratio, the grains' growth turns to be dendrite growth. When the G/$V$ ratio decreases, or when the temperature gradient $G$ is an invariant, with the increase of the $V$, the solid-liquid interface becomes unstable. When $G$ and $G_0$ are invariants, the shape of the solid-liquid interface is decided only by the $V$.

At the initial period of directional solidification, a relatively wide supercooling region appears in the solid-liquid interface. During the pulling process, this supercooling region narrows down, and the columnar grains gradually grow up. When the pulling velocity is relatively low ($V$=25 μm/s), the interface's growth is close to planar growth, so the grain structure becomes wide columnar grains, as shown in Fig.2a and 2b. When the pulling velocity increases to 50 or 75 μm/s, the growth of columnar grains become discontinuous and uneven and the diameter of the columnar grains becomes relatively small. As shown in Fig.3 and Fig.4, instead of going straight up, the grain boundaries become curved, and the continuity of the grains turns to be even worse. Based on the above mentioned, with the increase of the pulling velocity, the average diameter of columnar grains becomes small, the uniformity of grain distribution gradually decreases, the growth direction of grains gradually deviates from the major axis and the continuity of the grain decreases little by little. So the pulling velocity has a great influence on the formation of columnar grains.

As shown in Table 3, the pulling velocity is inversely proportional to its thermal conductivity, which means the greater the pulling velocity is, the lower the thermal conductivity is. As a kind of planar defect, grain boundaries inhibit the phonons' diffusion motion, and thus have a great influence on the alloy's thermal conductivity. Therefore, the grain boundaries' effect on alloy's thermal conductivity was analyzed from three aspects in this paper. The first one is the amount of the grain boundaries; The second one is the surface state of the grain boundaries; The third one is the angles of the grain boundaries along the axial direction.

The thermal conductivity of the DS alloys is better than that of as-cast alloys, because the columnar grains produced by directional solidification can largely reduce the grain boundaries. There is a large difference between the grain boundaries of as-cast alloys and DS alloys. After directional solidification, the columnar grains are formed in the alloys, and so the amount of grain boundaries has been greatly reduced. As the scattering source of electrons and phonons, the grain boundaries will impede their motion. So, too many grain boundaries shall reduce the free path of electrons and phonons, and thus shall decrease the thermal conductivity of alloys[10,11].

The surface states of the columnar grains are related to the pulling velocity. By studying the formation of the columnar grains, it could be known that the greater the pulling velocity is, the rougher the grain boundaries' surfaces are. Compared with grain boundaries with smooth surface, those irregular ones have greater influence on the scattering of phonons and photons, and finally cause the decrease of the alloy's thermal conductivity.

Under ideal conditions, the columnar grains will grow vertically along the direction of heat flow and their preferred growth orientation is (1010). However, in actual tests, certain angles form between the growth direction and the pulling direction of columnar grains, which could be shown in two aspects. On the one hand, with the increase of the pulling velocity, the angles become bigger; and on the other hand, with the increase of Ag content, the angles also become bigger. There are mainly two reasons that cause these phenomena. The first reason, during the directional solidification process, the molten solution around the mould wall dissipates heat faster than that in the center part of the mould. So there will be a small temperature gradient inside the mould vertical to the pulling direction, which will prohibit the columnar grains from complete growth the along the vertical direction. When the pulling velocity is relatively low, the heating of alloys by induction coil is relatively sufficient, and so the melting region is relatively large, which lead to the relatively stable growth of columnar grains. Under this circumstance, the angles between the growth direction and the pulling direction of columnar grains are relatively small. The second reason, the existence of intermetallic compounds in the solid-liquid interface can affect the growth of columnar grains. With the increase of Ag content, the amount of intermetallic compounds increases and might cause the growth direction of columnar grains to deviate from the vertical direction. According to Formula (3), when the $G$ and $V$ are invariants, with the increase of the $C_0$, the solid-liquid interface grows unstable. It is obvious that the intermetallic compounds as precipitates can hinder the grain from growing up. Thus, the more the intermetallic compounds are, the more grain boundaries arise.

Therefore, the bigger the angles between the grain boundaries and the axial direction are, the more the grain boundaries are within unit length in the axial direction, and so the greater the influence is on the thermal conductivity of alloy in the axial direction. That is the bigger the included angles, the lower the thermal conductivity is, which is in accordance with the experimental results.

Besides, intermetallic compounds are another factor that affects the alloy's thermal conductivity. The intermetallic compounds have a great influence on the growth of columnar grains and the formation of grain boundaries[12]. Ag was added into the Mg substrate to form atomic Mg-Ag co-clusters, which are the $\Omega$ phase[13-15]. Fig.5 shows the SEM image and EDS spectra of position 1 (intermetallic compounds) and position 2 (substrate) of as-cast Mg-3Ag-Zn alloys. Position 1 has relatively more Ag that is atomic Mg-Ag co-clusters, which can be known as $Ag_{7.96}Mg_{25.04}$ according to XRD patterns (Fig.6). With the increase of the Ag content, the quantity of atomic co-clusters increases in alloys and the free electrons' scattering effect is enhanced, which lead to the decrease of alloy's thermal conductivity.

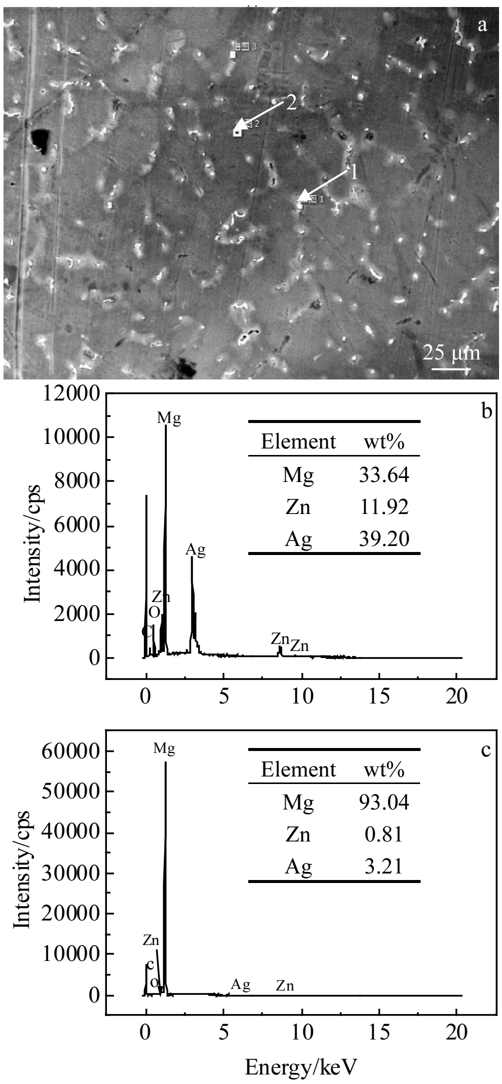


Fig.5 SEM image (a) of as-cast Mg-3Ag-Zn and EDS spectra of point 1 (b) and point 2 (c) in Fig.5a

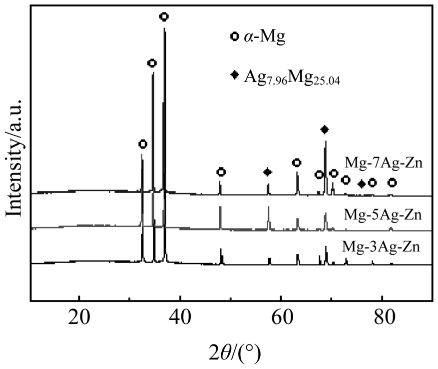


Fig.6 XRD patterns of Mg-Ag-Zn alloys

## 3 Conclusions

1) In the as-cast and DS Mg-Ag-Zn alloys at pulling velocities from 25 μm/s to 75 μm/s and with Ag content from 1 wt% to 5 wt%, the smaller the grains are and the more the grain boundaries are, the stronger the gain boundaries' scatting effect and the lower the thermal conductivity of alloys are. Thus, the thermal conductivity in axial direction decreases gradually with the increase of pulling velocity.

2) The DS alloys show higher thermal conductivity than as-cast alloys.

3) Because of the intermetallic compounds' pinning effect in the alloy's substrate, they will inhibit the growth of columnar grains in directional solidification. So the higher the content of intermetallic compounds in alloy, the more irregular the columnar grains grow to be, and the lower the alloy's thermal conductivity is.

4) The more the intermetallic compounds precipitate from the alloys, the stronger diffusion effect they shall have on phonons, and so the alloy's thermal conductivity becomes lower.

5) The bigger the angles of columnar grains along the axial direction are, the lower the DS alloy's thermal conductivity is in the axial direction.

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# 定向凝固速度对 Mg-Ag-Zn 合金导热率的影响

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**摘　要**：制备铸态 Mg-1Ag-Zn，Mg-3Ag-Zn 和 Mg-5Ag-Zn 合金试样，并计算其导热率。随着 Ag 含量的增加，铸态合金试样的导热率减小。再将其铸态合金的试样以 3 种不同的定向凝固速率（$V$=25 μm/s, $V$=50 μm/s, $V$=75 μm/s）制备成定向凝固试样，计算其定向凝固试样的导热率。结果显示：随着定向凝固速率的增加，合金的导热率降低。合金中溶质元素的含量与定向凝固速率是影响导热率的重要因素，这 2 个因素可以增强电子和声子的散射过程，减少自由行程，最终降低合金的导热率。

**关键词**：镁合金；定向凝固；Ag 含量；导热率

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