Effect of extrusion temperature on the microstructure and thermal conductivity of Mg–2.0Zn–1.0Mn–0.2Ce alloys

Jian Peng a,b,d, Liping Zhong a, Yongjian Wang a, Yun Lu c, Fusheng Pan b,d

1. Introduction

Magnesium alloys are widely used in 3C products and in the automobile and aerospace industries because of their low density, high specific strength and stiffness and high thermal conductivity. Moreover, these alloys have attracted increasing attention because of their novel applications in the radiator structure of electric equipment and radiating module of LED lights [1,2]. With an increase in the component density of integrated circuits and the development of LED lights, the structural materials for heat dissipation must possess light weight and high heat dissipation capability. In general, the thermal conductivity of pure Mg is 158 W/(m·K), and this value is lower than that of pure Cu and pure Al. Given their light weight, Mg alloys may serve as structural materials for heat dissipation. Some researchers have analyzed the thermal conductivity and heat dissipation capability of Mg alloys as structural materials and set a high requirement on the thermal conductivity of Mg alloys [1,3–7]. Huawei Company demands that the thermal conductivity of as-cast and wrought Mg alloys should exceed 100 and 120 W/(m·K), respectively. These Mg alloys are expected to be developed for the structure of communication equipment. Previous studies only focused on the thermal conductivity of Mg–Al based alloys [8,9]. However, the aforementioned demands cannot be easily met because adding aluminum severely decreases the thermal conductivity of Mg alloys [1,2,10]. Thus, other Mg-based alloys should be modified to obtain alloys with high thermal conductivity. The thermal conductivity of ZM21 alloy can be increased to the demanded value of 120 W/(m·K) by adding cerium with an optimal quantity of 0.2–0.6 wt.% [11]. However, chemical composition optimization alone is insufficient to increase the thermal conductivity of the alloys to 130 W/(m·K) [3,6,12]. Moreover, a numerical simulation of heat dissipation between Mg and Al alloys showed that the thermal conductivity of Mg alloys must exceed 130 W/(m·K) to substitute Mg alloys as the heat dissipation structure with Al alloys in applications such as radiating module of LED lights. The effects of extrusion parameters on thermal conductivity should be determined on the basis of chemical composition optimization to reach the expected thermal conductivity of 130 W/(m·K).

Extrusion parameters, especially extrusion temperature influence the microstructure and mechanical properties of Mg alloys. Considerable amount of research [13–16] determined the effects of extrusion parameters on mechanical properties of Mg alloys. However, the effects of extrusion parameters on the thermal conductivity and heat dissipation capability of Mg alloys remain unclear to date. Accordingly, this study investigated the effect of extrusion temperature on the microstructure and thermal conductivity of as-extruded Mg–2.0Zn–1.0Mn–0.2Ce alloys.

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This study may serve as a reference to develop a new Mg alloy with high thermal conductivity and adaptive mechanical properties, and to optimize its feasible extrusion parameters.

2. Experimental procedure

Pure Mg (99.98%), pure Zn (99.98%), Mg–Mn (3.9 wt.%) master alloys and Mg–Ce (20 wt.%) master alloys were used as raw materials to synthesize Mg–2.0Zn–1.0Mn–0.2Ce alloys. The materials were melted in low carbon steel crucible of a 60 kW electric resistance furnace, under the protection of a CO₂ (99.5 vol.%) + SF₆ (0.5 vol.%) mixed gas atmosphere. The No. 5 solvent was used as a refining agent and a covering agent for the melt. When the temperature reached 720 °C, the molten metal was stirred for 5 min, held for 30 min at 720 °C. Subsequently, the molten alloy was cast into cylindrical ingots 92 mm in diameter and 800 mm in length. The actual chemical composition of the alloy was checked using an X-ray fluorescence spectrometer (XRF–1800 CDE) and the results are listed in Table 1.

The cast ingots were homogenized at 420 °C for 12 h in a 12 kW box-type resistance furnace with wind circulation and the ingots were subsequently cooled in open air. The ingots were machined into cylindrical samples 80 mm in diameter and 200 mm in length. Hot extrusion was performed at different extrusion temperatures of 340 °C, 370 °C, 400 °C and 430 °C with a diameter of 16 mm at an extrusion ratio of 28 and an extrusion speed of 200 mm/min under a controlled constant force by an XJ-500 horizontal extrusion machine.

The specimens were cut from extruded rods at cross section in the form of disks with a size of ø12.7 × 3 mm. The density of samples was determined as 1.7767 g/cm³ through the Archimedes method at room temperature. The thermal diffusivity and specific heat capacity of the alloys were measured at the room temperature in Ar atmosphere by using LFA447 flash analyzer Netzsch apparatus and Netzsch STA 449, respectively. The thermal conductivity λ [W/(m·K)] was calculated as follows:

\[
\lambda = \alpha \cdot \rho \cdot C_p
\]

where \(\alpha\) is the thermal diffusivity (m²/s), \(\rho\) is the density (g/cm³), and \(C_p\) is the specific heat capacity at constant pressure (J/(g·K)). The uncertainty of the thermal conductivity was estimated to be less than 2%.

After being etched with the etchant (5 g of picric acid, 10 ml of acetic acid and 70 ml of alcohol), the microstructures of the as-extruded alloy were analyzed by an optical microscope (NEISS NEOPHOT 30). In addition, the grain sizes were measured and calculated using IPP (Image Pro-Plus). Phase constitution analyses were characterized using an X-ray diffractometer with Cu Kα radiation (XRD, Rigaku D/Max 2500PC). The micro-hardness of alloy matrix was tested using an HXS-1000AK Type digital LCD intelligent micro-hardness tester, with a minimum load of 0.098 N for 10 s.

3. Results

3.1. Effect of extrusion temperature on thermal properties

The specific heat capacities \(C_p\) of Mg–2.0Zn–1.0Mn–0.2Ce alloys, extruded at different temperatures, are shown in Table 2. The specific heat capacity initially increases and then decreases with increasing extrusion temperature. However, the amplitude of specific heat capacity fluctuation in the alloy is relatively small.

3.2. Microstructures of as-extruded alloys

The optical microstructures of the samples extruded at different extrusion temperatures are shown in Fig. 2. The deformation fabric structure is surrounded by fine equiaxed recrystallized grains in the alloys extruded at different temperatures. This finding indicates that incomplete recrystallization occurs during hot extrusion deformation. Non-basal slip is activated hardly through a broadly extended dislocation, because of the low stacking fault energy of Mg alloys. This phenomenon simplifies dynamic recrystallization (DRX) [17,18]. Meanwhile, the deformation fabric structure is un-recrystallized because of the insufficient deformation or deformation temperature. The volume fraction of un-recrystallized grains decreases from 30.4% to 15.1% when the extrusion temperature increases from 340 °C to 430 °C (Table 3).

The grain size distribution of Mg–2.0Zn–1.0Mn–0.2Ce alloys at different extrusion temperatures is illustrated in Fig. 3. The average grain size of recrystallized grains increases from 1.6 μm to 3.9 μm when the extrusion temperature increases from 340 °C to 430 °C. Recrystallization and grain growth are thermally activated processes. The driving force for recrystallization and grain growth increases with increasing extrusion temperature. This result can be attributed to the fact that an increase in grain boundary diffusion and migration enlarges the average

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Chemical compositions of the Mg–2.0Zn–1.0Mn–0.2Ce alloys (wt.%).</th>
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</thead>
<tbody>
<tr>
<td>Alloys</td>
<td>Zn</td>
</tr>
<tr>
<td>Mg–2.0Zn–1.0Mn–0.2Ce</td>
<td>1.92</td>
</tr>
</tbody>
</table>

Fig. 1. Thermal conductivity and thermal diffusivity of Mg–2.0Zn–1.0Mn–0.2Ce alloys extruded at different temperatures.
3.3. Evaluation of the solid solubility of heterogeneous atoms in the matrix

Micro-hardness usually measured to evaluate the microstructure changes, such as the amount of heterogeneous atoms in the matrix. These changes consequently influence the corresponding thermal conductivity of the alloys [7]. Fig. 4 shows the micro-hardness values of Mg–2.0Zn–1.0Mn–0.2Ce alloys extruded at different temperatures. A micro-hardness of approximately 59 HV is maintained at extrusion temperature lower than 400 °C. However, micro-hardness sharply increases up to 74.0 HV when the alloy is extruded at 430 °C.

The Mg–Zn and Mg–Mn phase diagrams [19] in Figs. 5 and 6 show that the solid solution content of Zn slightly changes and the solid solution content of Mn progressively increases as extrusion temperature increases from 340 °C to 430 °C. The average size of the recrystallized grains and the solid solution of Mn should both be considered to explain the variation tendency of alloy micro-hardness at different extrusion temperatures. When the extrusion temperature increases from 340 °C to 370 °C, the average grain size slightly changes from 1.6 μm to 1.9 μm, and the micro-hardness slightly depresses. By contrast, the solid solution of Mn element slightly increases, thereby slightly enhancing the micro-hardness. Thus, the micro-hardness is kept almost constant. The average grain size changes from 1.9 μm to 2.8 μm when the extrusion temperature increases from 370 °C to 400 °C. Meanwhile, the solid solution of Mn element changes obviously. These two contradictory factors simultaneously influence the micro-hardness, which then remains almost constant. Fig. 6 shows that the increasing trend of the solid solution of Mn in the Mg matrix becomes apparent as the temperature exceeds 400 °C. The micro-hardness of matrix significantly increases when the extrusion temperature changes from 400 °C to 430 °C. This result can be attributed to the large amount of Mn atoms that are dissolved in the matrix.

Table 3
The volume fraction of un-recrystallized grains at different extrusion temperatures.

<table>
<thead>
<tr>
<th>Extrusion temperature/°C</th>
<th>340</th>
<th>370</th>
<th>400</th>
<th>430</th>
</tr>
</thead>
<tbody>
<tr>
<td>The volume fraction of un-recrystallized grains/%</td>
<td>30.4</td>
<td>25.9</td>
<td>21.9</td>
<td>15.1</td>
</tr>
</tbody>
</table>

The c/a axial ratio was calculated from the XRD test result of Mg–2.0Zn–1.0Mn–0.2Ce alloys extruded at 400 °C and 430 °C (Table 4). The crystal lattice distortion becomes more serious as the content of heterogeneous atoms increases. This phenomenon causes the c/a of Mg solid solution to deviate from the c/a of pure Mg. Therefore, the c/a can be used to evaluate the degree of lattice distortion and the solid solution of the heterogeneous atoms. Compared with the c/a of pure Mg, the crystal lattice of the Mg–2.0Zn–1.0Mn–0.2Ce Mg alloys extruded at 430 °C displays a more serious distortion than those of alloys extruded at 400 °C. Therefore, significantly more solute atoms are dissolved in the α-Mg matrix at 430 °C than at 400 °C.

4. Discussion

The thermal conductivity of the as-extruded Mg–2.0Zn–1.0Mn–0.2Ce alloys with increasing extrusion temperature from 340 °C to 430 °C was measured. The microstructure of the alloys and the solid solubility of the heterogeneous atoms in the matrix were investigated to explain the corresponding variations in thermal conductivity.

The microstructure affects the thermal conductivity of as-extruded alloys. The amount of un-recrystallized grain volume fraction significantly decreases as the extrusion temperatures increased. Uncompleted recrystallization occurs because of the limited driving force for recrystallization and grain growth at low extrusion temperatures. This outcome results in a large amount of deformation fabric structure that exists in the alloy. High density dislocation accumulates near these areas during deformation. Dislocations that function as lattice defects affect the thermal conductivity and serve as scattering centers for electrons and phonons. The scattering centers decrease the mean free path of electrons and phonons as well as the thermal conductivity of alloys [20]. Fig. 5 shows that the average grain size increases with increasing extrusion temperature. Thus, the volume fraction of grain boundary decreases. The grain boundary is also one of the scattering centers that block the free movement of electrons. Therefore, the mean free path of electrons decreases and the grain boundary reduces the thermal conductivity of alloys. The finer grain size results in lower thermal conductivity [6,21]. Therefore, the thermal conductivity of the as-extruded Mg–2.0Zn–1.0Mn–0.2Ce alloys increases when the extrusion temperature increased from 340 °C to 400 °C.

The amount of heterogeneous atoms in the matrix apparently affect the thermal conductivity of the alloy [1,2,10,22–25]. The average grain
The size reaches the maximum at an extrusion temperature of 430 °C. Thus, the volume fraction of grain boundary decreases to the minimum value. On the basis of the effects of grain refinement on thermal conductivity, the maximum thermal conductivity of the alloy is supposed to be achieved at the extrusion temperature of 430 °C. However, the thermal conductivity of the alloys extruded at 430 °C is lower than those of the alloys extruded at 400 °C and 370 °C.

The abovementioned outcome is attributed to the large amount of solute atoms that dissolve in the Mg matrix. More Mn atoms dissolve in the α-Mg matrix at a higher extrusion temperature (430 °C). Hence, the content of Mn atoms in the Mg matrix increases. Meanwhile, the solute atoms are scattering sources that hinder the free movement of electrons. Therefore, the mean free path of electrons decreases and the thermal conductivity becomes lower [1,2,26,27]. The weight content of Mn element is 0.91 wt.%, but the actual saturated solid solution of Mn element in the as-extruded alloy can only be determined by the temperature for preheating and deforming of extrusion. The Mg–Mn phase diagram in Fig. 6 shows that the equilibrium solid solubility of Mn element increases with increasing temperature, and has an accelerated increasing rate when the temperature exceeds 400 °C. The results of micro-hardness test and c/a calculation confirm that the content of Mn solute atoms in the α-Mg matrix is much higher at 430 °C than at 400 °C. This outcome decreases the thermal conductivity. By contrast, larger grain size and fewer un-recrystallized grains increase the thermal conductivity. Eivani et al. [28] reported that the increase in thermal resistivity caused by the alloying element as the solute atoms are dissolved in the α-Mg matrix is much higher than that when intermetallic compounds are used. These factors in the contradictory trends simultaneously influence the thermal conductivity, however, the increase in Mn content predominantly affects the thermal conductivity. Moreover, the thermal conductivity of the alloy extruded at 430 °C is lower than those of the alloys extruded at 400 °C and 370 °C.

Fig. 3. Grain size distribution at different extrusion temperatures (a) 340 °C, (b) 370 °C, (c) 400 °C, and (d) 430 °C.

Fig. 4. Micro-hardness of alloys at different extrusion temperatures.
Under the co-interaction of the volume fraction of un-recrystallized grains, the average size of recrystallized grains, and the solid solution of Mn in the \( \alpha \)-Mg matrix, the thermal conductivity of Mg–2.0Zn–1.0Mn–0.2Ce alloys initially increases to reach the maximum value of 131 W/(m·K) when the extrusion temperature is 400 °C, and then decreases when the extrusion temperature further increased to 430 °C.

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**Fig. 5.** The Mg–Zn phase diagram.

**Fig. 6.** The Mg–Mn phase diagram.
In the current paper, the thermal conductivity of 130 W/(m·K) for the radiator structure application of Mg alloy is achieved by optimizing the extrusion temperature. This study may serve as a guide for further research that aims to increase the thermal conductivity of Mg-Zn-Mn serial alloys by controlling the extrusion temperature under 400 °C. This study also provides the beneficial implications to develop a new Mg alloy with high thermal conductivity and adaptive mechanical properties, and to obtain its feasible extrusion parameters.

5. Conclusions

1) The extrusion temperatures significantly influence the thermal conductivity of Mg–2.0Zn–1.0Mn–0.2Ce alloys. At the optimized extrusion temperature of 400 °C, the thermal conductivity of the alloy can reach the expected value of 130 W/(m·K).

2) The thermal conductivity of Mg–2.0Zn–1.0Mn–0.2Ce alloys initially increases and subsequently decreases when the extrusion temperature increases from 340 °C to 430 °C. For the alloy that contains Mn element, the solid solution of Mn rapidly increases, which then decreases the thermal conductivity of the alloy, when the extrusion temperature exceeds 400 °C.

3) The thermal conductivity variation of Mg–2.0Zn–1.0Mn–0.2Ce alloys with increasing extrusion temperature is attributed to the combined effects of the volume fraction of un-recrystallized grains, the average size of recrystallized grains, and the solid solution of Mn in the matrix of the as-extruded alloy.

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References


