Microstructure Evolution of Mg–4.3Zn–0.7Y–0.6Zr Alloy during Solution Heat Treatment

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The microstructure evolution in a Mg–4.3Zn–0.7Y–0.6Zr (mass%) alloy was investigated during solution heat treatment from 300 to 500°C for 12 h. In the as-cast and solution-treated at 300°C for 12 h states, the microstructures are consisting of L-phase and α-Mg. After solution treated at 400°C for 12 h, besides L-phase and α-Mg, some long strip precipitates—which are determined as Zn₂Zr phase,—also appear in the microstructure. In the solution-treated sample at 500°C for 12 h, small amounts of Zn₂Zr and Mg₀.⁹Zn₀.₀₃ phases have been found. With the increase of heat treatment temperature, the phase constituents for different states are: α-Mg + L-phase (as-cast) → α-Mg + L-phase (300°C for 12 h) → α-Mg + L-phase + W-phase + Zn₂Zr (400°C for 12 h) → α-Mg + Zn₂Zr + Mg₀.⁹Zn₀.₀₃ (500°C for 12 h).

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1. Introduction

Due to the owning of low density, high specific strength, excellent cast ability, good electromagnetic shielding ability, good damping and ease of recycling, Mg alloys are attractive as light weight structural materials, which leads to the increasing applications, especially in the areas of automobiles, electronic communication, sports and aerospace.¹,² However, low strength, poor ductility and poor corrosion resistance hinder their widespread application. Therefore, great efforts have been spent to improve the strength, ductility and corrosion resistance of Mg alloys.

The Mg–Zn–Y alloy system is rich in intermetallic phases and several stable ternary intermetallic compounds, including an icoshedral quasicrystal phase (I-phase) existing near the Mg–Zn edge, making the system promising for developing Mg-based light metallic alloys with a large variety of candidates of intermetallic reinforcement phases.³ In recent years, many studies have indicated that Mg–Zn–Y alloys containing quasicrystal phase exhibit high strength at ambient temperature, good elevated temperature properties, excellent creep resistance and moderate corrosion resistance. Due to the specially ordered quasi-periodic lattice structure, quasicrystals have many interesting properties, such as high hardness, high corrosion resistance, low coefficient of friction and low interface energy.⁴ Therefore, there has been great interest in Mg–Zn–Y alloys strengthened by I-phase.⁵–⁷ It has been reported⁶ that the interface layer of α-Mg with a 3 to 5 nm thickness still preserved the coherency orientation relationship with the I-phase by introducing steps and ledges periodically along the interface. So the atomic bonding between the I-phase and the hexagonal structure was rigid enough to be retained during plastic deformation. Therefore, quasicrystal strengthening is a very effective method to improve the strength of Mg alloys. It is also well known that Zr can act as an effective nucleus for heterogeneous nucleation of Mg alloys. Moreover, the addition of Zr has no effect on phase constituents of Mg–Zn–Y–Zr alloys.⁸ Therefore, it can also be expected to develop Mg–Zn–Y–Zr alloys containing I-phase.

In recent years, Mg–Zn–Y–Zr system alloys have attracted significant interest due to the high strength at room and elevated temperature. Current research mainly focuses on the microstructures and mechanical properties. Zhang et al.⁹ have studied the effects of Y on microstructures and mechanical properties of extruded Mg–Zn–Y–Zr alloys. Xu et al.¹⁰ have investigated microstructures and mechanical properties of as-cast and as-extruded Mg–Zn–Y–Zr alloys with different Zn/Y ratios. Huang et al.¹¹ has investigated the variation of microstructures with composition during solidification process in Mg–Zn–Y–Zr alloys using thermal analysis with cooling curves. Precipitation hardening is one of the strengthening mechanisms that may be utilized in both the as-cast and the wrought Mg alloys in order to further improve the strength of the alloys. Recently, Hono et al.¹² has discussed the potential to develop high-strength low-cost wrought Mg alloys through precipitation hardening, and they concluded that further investigations of microalloying elements that enhance the age-hardenening responses of Mg alloys may lead to the development of high-strength age-hardenable wrought Mg alloys. As to Mg–Zn–Y–Zr alloys containing I-phase, it also can undertake heat treatment because the microstructure of alloys is sensitive to heat treatment. However, the microstructure evolution of Mg–Zn–Y–Zr alloys has not yet been well understood during the process of heat treatment. Determining the optimum solution heat treatment condition is a major consideration in the fabrication of high strength Mg–Zn–Y–Zr alloys. Therefore, in the present study, we focus on the microstructure development during the solution heat treatment of the Mg–4.3Zn–0.7Y–0.6Zr (mass%) alloy from 300 to 500°C with 12 h. The effect of solution heat treatment on phase constituents and precipitate morphology under various heat treatment conditions will be emphasized.

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2. Materials and Experimental Procedures

The Mg–4.3Zn–0.7Y–0.6Zr (mass%) alloy was prepared by melting pure Mg, Zn and Mg–30 mass% Zr and Mg–25 mass% Y master alloys in a cemented graphite crucible under protective gas consisting of SF\textsubscript{6} (1 vol%) and CO\textsubscript{2} (bal.) in order to prevent the burning of melts. Pure Mg was used as starting materials. During melting, the element Y and Zr were added as master alloys of Mg–25 mass% Y and Mg–30 mass% Zr prepared beforehand, while Zn was added as high pure Zn (99.99 mass%). The alloy was cast into a steel mould forming a cylindrical ingot with 35 mm in diameter, and 200 mm in height. Specimens were cut from the ingot by electric spark linear cutting machine. Samples were solution treated at 300, 400 and 500°C for 12 h and then rapidly quenched into the cold water. During the heat treatment, samples were encapsulated in an iron tank filled with graphite powder to prevent oxidation.

Microstructure examinations were performed in an optical microscope (OM, OLYMPUS GX71), a scanning electron microscope (SEM, VEGAIIILMH) and a transmission electron microscopy (TEM, Tecnai F30). Phase analysis was determined by a D\textsubscript{Max} 2400 X-ray diffractometer using monochromatic Cu Kα radiation from the sample with a cross-sectional area of 30 × 30 mm. The ingredient percentage of elements Zn, Y and Zr has been measured by the VEGAIIILMH using energy-dispersive spectroscopy (EDS). SEM observations with spectrometer using secondary electron imaging (SEI) have been done to determine microstructures and compositions.

3. Results and Discussions

3.1 As-cast microstructures

Figure 1 is a schematic isothermal section of Mg–Zn–Y near Mg-rich corner at 673 K based on the calculation of Shao et al.\textsuperscript{3}) The chemical position of the alloy in present study neglecting element Zr (Mg–4.3 mass% Zn–0.7 mass% Y or Mg–1.68 at% Zn–0.2 at% Y) is also indicated in this figure. Generally, there exist three kinds of ternary equilibrium phases in Mg–Zn–Y systems:\textsuperscript{3–7} i.e., I-phase (Mg\textsubscript{12}Zn\textsubscript{y}Y, icosahedral quasicrystal structure with five-fold symmetry), W-phase (Mg\textsubscript{3}Zn\textsubscript{y}Y\textsubscript{2}, cubic structure) and X-phase (Mg\textsubscript{12}Zn\textsubscript{y}Y, 18R long period modulated structure). Moreover, it has been noticed that the phase constituents in Mg–Zn–Y alloys are largely dependent on the Zn/Y ratio.\textsuperscript{10,13} When the atomic ratio of Zn/Y exceeds 6 (or the mass ratio exceeds 4.38), it will meet the requirement of forming I-phase completely. Shao et al.\textsuperscript{3}) have pointed out that, the Zn/Y ratio is indeed a controlling parameter for phase constituencies, and alloys of atomic ratio of Zn/Y around 6 are largely located in the α-Mg + I phase region. In the present study, the atomic ratio of Zn/Y is about 8.4 (mass ratio is 6.14), therefore, it is expected that only I-phase will be formed as the second phase in the microstructure.

Figure 2(a) shows the optical microstructures of the as-cast Mg–4.3Zn–0.7Y–0.6Zr (mass%) alloy. As shown in Fig. 2(a), the as-cast sample has a uniform and equiaxed grain structure, with a single phase solid solution and a network of eutectic phase, which is mostly dispersed between the dendrite branches of the Mg solid solution. Some Zr-rich particles are located in the center of the equiaxed grain. The linearly intercepted average grain size of the as-cast sample is about 39 µm. Figure 2(b) shows the X-ray diffraction pattern of the as-cast sample. It can be found that, except diffraction peaks of I-phase, other diffraction peaks with relatively high intensity can be assigned to the α-Mg phase. This indicates that the main phase constituents of as-cast Mg–4.3Zn–0.7Y–0.6Zr alloy are I-phase and α-Mg phase, which is in agreement with previous expectations.

![Fig. 2 (a) Optical microstructures of the as-cast alloy; (b) its X-ray diffraction pattern.](image-url)
Figure 3(a) is the typical SEM image of the as-cast sample and the high-magnification microstructure of the eutectic compounds is shown in Fig. 3(b). It is found that lamellar structures exist in the triple junction, which is the eutectic phase ($\alpha$-Mg + I phase). The compositions of point A and point B in Fig. 3(b) were determined by EDS as shown in Table 1. Although the amount of Mg in point A is quite high (this may result from the effect of Mg matrix), the atomic percentage of Zn and Y is about 6 : 1, which is in accordance with the atom percentage of the standard I-phase. So the lamellar eutectic structure phase could be confirmed as I-phase and $\alpha$-Mg phase while the matrix is $\alpha$-Mg phase.

To further validate the existence of I-phase in the Mg–4.3Zn–0.7Y–0.6Zr alloy, TEM bright-field image of the as-cast sample is shown in Fig. 4(a). The composition of point B as shown in Fig. 4(a) is determined by EDS as about Mg(33.10 at%) Zn(56.95 at%) and Y(9.90 at%), which is very close to the standard composition of icosahedral quasicrystal Mg$_2$Zn$_9$Y. A typical selected area diffraction (SAD) pattern taken from I phase in the peripheral eutectic region is shown in Fig. 4(b), which is the corresponding electron diffraction pattern of point B as marked in Fig. 4(a). The 5-fold symmetry of diffraction pattern demonstrates that the particle phase presents icosahedral symmetry with a scaling relationship defined by the golden mean, $\tau = (\sqrt{5} + 1)/2$, which indicates the particle phase is an icosahedral quasicrystal phase.14)

It should be noted that solidification segregation is generally found due to the small solubility of alloying elements in the Mg alloys, yielding an enrichment of Zn and Y solute in the liquid. The compositions of $\alpha$-Mg phase (point B in Fig. 3(b)) shown in Table 1 indicate that the solubilities of Zn and Y in $\alpha$-Mg phase are very small, meanwhile the concentration of Zn in $\alpha$-Mg phase are larger than that of Y, which means the Zn/Y ratio in the liquid phase will decrease. So it could be expected that even if the original atomic ratio of Zn/Y is larger than 6 (or the original mass ratio is larger than 4.38), the final phase constituent could include $\alpha$-Mg phase, I phase and W phase, which is the phase constituent for equilibrium solidification with the atomic ratio of Zn/Y between 1.5 and 6. However, the total content of Zn and Y in present study is just 5%, and the atomic ratio of Zn/Y is about 8.4 (the mass ration is 6.14), which is much higher than the lower limit for completely forming $\alpha$-Mg phase and I phase. Therefore, the quantity of the W-phase formed due to solute segregation should be tiny and should hardly be detected for the alloy composition studied here. In the experiments of Lee,13) it has also been found that when the total content of Zn and Y is less than 10% (mass fraction) and the mass ratio of Zn/Y is 5–7, the identified phase constituent in the as-cast microstructure of Mg–Zn–Y system only include $\alpha$-Mg phase and I-phase. But when the total content of Zn and Y is large and the atomic ratio of Zn/Y is just slightly higher than 6, W-phase may be also detected due to the solute segregation in the liquid phase. Actually this has already be confirmed in the experiments of Mg–9.25Zn–1.79Y–7.67Li (mass%) alloy by Xu and coworkers.15)

### 3.2 Microstructures of solution treated alloys with different temperatures

Figure 5 shows the optical microstructures of solution-treated samples with different temperatures for 12 h. After solution treatment at 300°C for 12 h, the microstructure of the alloy remains equiaxed, but a small amount of point-like or flaky structures appear in some grains. In this case, the grain size increases from 39 µm of the as-cast state to 45 µm. After solution treatment at 400°C for 12 h, many more block-like and petal-like structures appear in grains, and the grain size

<table>
<thead>
<tr>
<th>Mg (at%)</th>
<th>Zn (at%)</th>
<th>Y (at%)</th>
<th>Zr (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>79.59</td>
<td>17.60</td>
<td>2.81</td>
</tr>
<tr>
<td>B</td>
<td>97.99</td>
<td>1.63</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Table 1 Composition of as-cast sample measured by EDS.

Fig. 3 (a) SEM image of the as-cast sample; (b) its high-magnification microstructure of the eutectic compounds.

Fig. 4 (a) TEM bright-field image of the as-cast sample; (b) corresponding SAED pattern obtained from point B.
Precipitates can be determined as cubic Zn$_2$Zr intermetallic compounds. Figure 6(b) shows the micro-area diffraction pattern from a [112] zone axis of precipitate revealing the presence of the Zn$_2$Zr phase. In Mg alloys containing Zn, it has been found that Zn usually combines with Zr to form some intermetallic compounds, such as Zn$_2$Zr$_3$ and ZnZr$_2$.\(^{16}\) When the alloy is solution-treated at 400°C for 12 h, Zr atoms will diffuse from the Zr-rich zone to the neighbouring area to decrease the concentration gradient of Zr. During the process of heat treatment, the morphology of precipitates develops slowly from point-like or flaky to block-like or petal-like. Strip precipitates with the average size up to 100 nm in length and 20 nm in width are found in petal-like structures. Figure 6(a) shows the TEM bright-field diffraction contrast image after solution treated at 400°C for 12 h; (b) micro-area diffraction from a [112] zone axis of precipitate revealing the presence of the Zn$_2$Zr phase.

The X-ray diffraction patterns of three solution-treated alloys were shown in Fig. 8. It reveals that the main phase components of the solution-treated alloys at 300°C for 12 h, 400°C for 12 h and 500°C for 12 h are α-Mg + I-phase, α-Mg + I-phase + W-phase and α-Mg + Zn$_2$Zr phase, respectively. When the solution treatment temperature is 300°C, the quasicrystal phase exhibits good stability due to the low heat treatment temperature, so the microstructure is still consisted of α-Mg and I-phase. With the increase of heat treatment temperature, the ability of atomic diffusion will be strengthened, which results in that some atoms in grain boundaries will diffuse into the grain. Zn and Y elements are enriched in grain boundary originally, and the diffusion ratio of Y is relatively low. Therefore, I-phase with high Zn content may transform into W-phase with low Zn content in grain boundary after water-quenching. From Fig. 6, it also indicates that the Zn$_2$Zr phase does exist in the matrix.

![Fig. 5 Optical microstructures of solution treated samples with different temperatures for 12 h; (a) 300°C; (b) 400°C; (c) 500°C.](image)

![Fig. 6 (a) TEM bright-field diffraction contrast image after solution treated at 400°C for 12 h; (b) micro-area diffraction from a [112] zone axis of precipitate revealing the presence of the Zn$_2$Zr phase.](image)

![Fig. 7(a), there are three types of precipitates in the structure: irregular block-like precipitates (marked A), long strip precipitates (marked B) and regular polygonal precipitates (marked C). The compositions of these different precipitates, determined by EDS, are shown in Table 2. From Table 2 we see that precipitate A is almost composed of element Mg. Figure 7(d) shows the selected area diffraction pattern of this precipitate, which corresponds to a [1213] zone axis of Mg. Furthermore, the c/a ratio (about 1.6492) is near to that of Mg (1.6235), so the precipitate is α-Mg slightly modified with Zn. Figures 7(b) and 7(c) are high magnification images for precipitates B and C, respectively. Twins are clearly visible in these HRTEM images. Figures 7(e) and 7(f) are the microdiffraction patterns of precipitates B and C, respectively. From Table 2 it can be seen that their Zn/Zr ratio is about 2, and the crystal structure of B is cubic with lattice parameter $a = 0.752$ nm, very close to Zn$_2$Zr (0.733 nm). Moreover, the diffraction spots of precipitate C are similar to B, indicating that C is also Zn$_2$Zr.

### 3.3 Phase constituents of Mg–4.3Zn–0.7Y–0.6Zr alloy after solution treatment

The X-ray diffraction patterns of three solution-treated alloys were shown in Fig. 8. It reveals that the main phase components of the solution-treated alloys at 300°C for 12 h, 400°C for 12 h and 500°C for 12 h are α-Mg + I-phase, α-Mg + I-phase + W-phase and α-Mg + Zn$_2$Zr phase, respectively. When the solution treatment temperature is 300°C, the quasicrystal phase exhibits good stability due to the low heat treatment temperature, so the microstructure is still consisted of α-Mg and I-phase. With the increase of heat treatment temperature, the ability of atomic diffusion will be strengthened, which results in that some atoms in grain boundaries will diffuse into the grain. Zn and Y elements are enriched in grain boundary originally, and the diffusion ratio of Y is relatively low. Therefore, I-phase with high Zn content may transform into W-phase with low Zn content in grain boundary after water-quenching. From Fig. 6, it also indicates that the Zn$_2$Zr phase does exist in the matrix.

### Table 2 Composition of precipitates measured by EDS in the 500°C for 12 h solution-treated samples.

<table>
<thead>
<tr>
<th></th>
<th>Mg (at%)</th>
<th>Zn (at%)</th>
<th>Y (at%)</th>
<th>Zr (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>96.78</td>
<td>2.68</td>
<td>0.25</td>
<td>0.29</td>
</tr>
<tr>
<td>B</td>
<td>34.13</td>
<td>43.71</td>
<td>0.33</td>
<td>21.83</td>
</tr>
<tr>
<td>C</td>
<td>40.07</td>
<td>39.80</td>
<td>0.69</td>
<td>19.42</td>
</tr>
</tbody>
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but it cannot be detected due to the very low content. Therefore, the microstructures of solution treated alloy at 400°C are composed of \(\alpha\)-Mg, I-phase, W-phase and Zn\(_2\)Zr phase.

When the solution treatment temperature rises to 500°C which exceeds the melting point of eutectic phase (about 440 to 450°C\(^\circ\))\(^\circ\), the phases in the eutectic pockets begin to transform and quasicrystal phase disappears. According to the phase diagram, the limit solid solubility of Zn and Y in Mg are about 6.2 and 11 mass\%, respectively. Meanwhile, the Zn content is about 6 times as much as the Y content in the grain boundary. So after solution treated at 500°C for 12 h, Y atoms almost dissolved into the matrix to form the solid solution with Mg. However, because Zn cannot completely dissolve into the matrix, Zn and Zr will enrich in somewhere to form new phases. At the same time, small amount of Zn and matrix Mg will form the new phase of Mg\(_{0.97}\)Zn\(_{0.03}\), but it cannot be detected within the sensitivity limits of XRD due to its low content. Therefore, the phase constituents for the solution-treated sample with 500°C for 12 h were \(\alpha\)-Mg, Zn\(_2\)Zr and Mg\(_{0.97}\)Zn\(_{0.03}\).

### 4. Conclusions

In this paper, the microstructure development during the solution heat treatment of a Mg\(_{4.3}\)Zn\(_{0.7}\)Y\(_{0.6}\)Zr (mass\%) alloy from 300 to 500°C with 12 h is investigated. The effect of solution heat treatment on phase constituents and precipitate morphology under various heat treatment conditions are discussed. The microstructures of the as-cast Mg\(_{4.3}\)Zn\(_{0.7}\)Y\(_{0.6}\)Zr alloy are composed of \(\alpha\)-Mg, I-phase, W-phase and Zn\(_2\)Zr phase.

When the solution treatment temperature rises to 500°C which exceeds the melting point of eutectic phase (about 440 to 450°C\(^\circ\)), the phases in the eutectic pockets begin to transform and quasicrystal phase disappears. According to the phase diagram, the limit solid solubility of Zn and Y in Mg are about 6.2 and 11 mass\%, respectively. Meanwhile, the Zn content is about 6 times as much as the Y content in the grain boundary. So after solution treated at 500°C for 12 h, Y atoms almost dissolved into the matrix to form the solid solution with Mg. However, because Zn cannot completely dissolve into the matrix, Zn and Zr will enrich in somewhere to form new phases. At the same time, small amount of Zn and matrix Mg will form the new phase of Mg\(_{0.97}\)Zn\(_{0.03}\), but it cannot be detected within the sensitivity limits of XRD due to its low content. Therefore, the phase constituents for the solution-treated sample with 500°C for 12 h were \(\alpha\)-Mg, Zn\(_2\)Zr and Mg\(_{0.97}\)Zn\(_{0.03}\).
Acknowledgements

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