Effect of Mg-Zn-Nd spherical quasicrystals on microstructure and mechanical properties of ZK60 alloy

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Abstract: To improve the strength, toughness, heat-resistance and deformability of magnesium alloy, the microstructure and mechanical properties of ZK60 alloy strengthened by Mg-Zn-Nd spherical quasi-crystal phase (I-phase) particles were investigated. Mg_{40}Zn_{55}Nd_{5} (I-phase) particles in addition to \(\alpha\)-Mg, MgZn phase and MgZn_{2} phases can be obtained in ZK60-based composites under normal casting condition by the addition of quasi-crystal containing Mg-Zn-Nd master alloy. The experimental results show that the introduction of Mg-Zn-Nd spherical quasi-crystal phase into ZK60 alloy makes a great contribution to the refinement of the matrix microstructures and the improvement of mechanical properties. While adding Mg-Zn-Nd spherical quasi-crystal master alloy of 4.0wt.%, the ultimate tensile strength and yield strength of ZK60-based composite at ambient temperature reach their peak values of 256.7 MPa and 150.4 MPa, which were about 17.8% and 24.1% higher respectively than those of the ZK60 alloy. The improved mechanical properties are mainly attributed to the pinning effect of the quasi-crystal particles (I-phase) at the grain boundaries. This research results provide a new way for strengthening and toughening of magnesium alloys as well as a new application of Mg-based spherical quasi-crystals.

Key words: spherical quasi-crystal; ZK60 alloy; quasi-crystal-reinforced composites; microstructure; mechanical properties

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Quasi-crystal is a kind of phase with long-range quasi-periods translational order and non-crystallographic rotational symmetry solid state order. The characteristics of high hardness, high thermal-dynamical stability, anti-corrosion, low friction coefficient and low surface energy make it quite suitable for its application as a strengthening phase in toughness matrix materials. The spherical morphology of the reinforcing particles and their dispersive distribution in the matrix bring about lower rending effects on the matrix and reduce stress concentration. Controlled interfacial reactions between the reinforcing phase and the matrix result in stronger interfacial bonding. Based on the above, it is predicted that a magnesium alloy with high strength, high toughness and high heat resistance can be obtained. The purpose of this investigation was to observe the effect of Mg-Zn-Nd spherical quasi-crystals on the microstructure and mechanical properties of ZK60 alloy. The Mg-Zn-Nd spherical quasi-crystal master alloy was introduced into the ZK60 alloy using the method of external addition. This research results may provide a new way for composite strengthening of Mg-based alloys and create a new method for industrialization of Mg-Zn-Nd spherical quasi-crystal master alloy.

1 Experimental procedure

The chemical compositions of ZK60 alloy is listed in Table 1.
Mg-Zn-Nd spherical quasi-crystal master alloy was made in our laboratory. The ZK60 alloy was prepared by induction melting a mixture of high purity Mg(99.9wt.%), Zn(99.9wt.%) and Mg-30Zr(wt.% ) master alloy. These were melted in an electric resistance furnace under the novel mixed gas atmosphere of CO₂ and CH₂FCF₃ in the ratio 96 : 4. After the pure Mg and Zn melted, the Mg-Zr master alloy was added into the melt at a temperature range from 780 to 800°C. When the temperature reached 700°C, the Mg-Zn-Nd spherical quasi-crystal master alloy was added into the molten metal using the method of external addition. The molten metal was then held for homogenization. After 10 min the molten metal was refined by adding refining flux. The molten metal was held for 30 min to allow inclusions to settle to the bottom of the crucible. Then, the molten metal was poured into steel molds (preheated to approximately 200°C) to form cast ingots with dimensions of 130 mm × 20 mm × 35 mm. The microstructure and mechanical properties were examined according to the requirements of the testing standard.

Table 1: Chemical composition of ZK60 alloy (wt.%)

<table>
<thead>
<tr>
<th></th>
<th>Zn</th>
<th>Zr</th>
<th>Mg</th>
</tr>
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<tbody>
<tr>
<td>Nominal composition</td>
<td>5.50</td>
<td>0.60</td>
<td>Bal.</td>
</tr>
<tr>
<td>Actual composition</td>
<td>5.24</td>
<td>0.47</td>
<td>Bal.</td>
</tr>
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</table>

As-cast specimens and heat-treated specimens were etched in a 4vol.% nital solution and then in a solution of 1.5 g picric acid + 5 mL acetic acid + 25 mL ethyl alcohol +10 mL distilled water for microstructure observation. The grain size was determined using a linear intercept method from a large number of non-overlapping measurements. Tensile tests were performed on a DNS100 electronic universal material test machine with an extension ratio of 0.5 mm·min⁻¹ at ambient temperature. Phase constitution analyses were performed with an X-ray diffractometer (XRD, Y-2000) using monochromatic CuKα radiation. The microstructures and compositions of different phases in the alloy were investigated using a scanning electron microscope (SEM, JSU-6700F) equipped with energy dispersive spectroscopy (EDS). The macro-hardness was examined using a HB-3000A Brinell hardness tester.

2 Results and discussion

2.1 Morphology features of Mg-Zn-Nd spherical quasi-crystals master alloy

The chemical composition of the Mg-Zn-Nd (MZN) spherical quasi-crystal master alloy is Mg-51.5%Zn-2.5%Nd. Figure 1 shows the SEM micrograph and X-ray diffraction pattern of as-cast MZN spherical quasi-crystal master alloy. As can be seen from Fig. 1 (a), the microstructure of as-cast MZN master alloy mainly consists of the gray matrix phase and spherical quasi-crystal phase. According to the X-ray diffraction pattern shown in Fig.1 (b), the gray matrix phase and the spherical particles are identified as Mg₇Zn₃ phase, and Mg₄₀Zn₅₅Nd₅ spherical quasi-crystal phase (I-phase) [6-8].

2.2 Effect of Mg-Zn-Nd master alloy on microstructure of ZK60 alloy

The X-ray diffraction patterns of as-cast ZK60 alloy without and with the addition of MZN master alloy are given in Fig. 2. As can be seen from Fig. 2(a), the as-cast microstructure of ZK60 alloy consists of α-Mg, MgZn phase and MgZn₂ phase. In Fig. 2(b) for the ZK60-based quasi-crystal-reinforced composite (ZK60 + 4.0wt.%MZN), new diffraction peaks for the quasi-crystal phase appear, which indicates that the microstructure of the ZK60-based composite consists of α-Mg, MgZn phase, MgZn₂ phase and Mg₆₀Zn₄₀Nd₅ quasi-crystal phase (I-phase).

Figure 3(a) shows the SEM micrograph of as-cast ZK60 alloy. Figure 3(b), (c) and (d) show the EDS analysis results of points A, B and C, respectively, in Fig. 3(a). The results of EDS examination indicate that the points B and C are comprised of Zn and Mg and the atomic ratio of Zn to Mg is about 0.74 (for B) and 1.89 (for C). These phases can be denoted as MgZn and MgZn₂ according to the Mg-Zn binary alloy diagram. Thus, the microstructure of as-cast ZK60 alloy consists of α-Mg matrix (at point A), quasi-continuous network MgZn phase (at point B) and granule-shaped MgZn₂ phase (at point C).
Figure 4 shows the optical micrographs of ZK60 alloy with different added contents of MZN master alloy. The grain size of alloys decreases continuously and the volume fraction of grain boundary phase (MgZn phase) increases with increasing amounts of MZN master alloy. The MgZn phases changes from a quasi-continuous network to a discontinuous network and the finest grain size was obtained when the addition of MZN master alloy reaches 4.0wt.%. Also, the discontinuous network MgZn phase and granule-shaped MgZn$_2$ phase become smaller. The broken discontinuous network MgZn phase and smaller granule-shaped MgZn$_2$ phase are homogenously distributed in the matrix, as shown in Fig. 4(e). When the addition of MZN master alloy surpasses 4.0wt.%, the grain size of matrix begin to coarsen, as shown in Fig. 4(f). This phenomenon may be explained as follows. There is an optimal addition level of reinforced phase for the grain refinement of the matrix alloy. If the nucleating number is less than the critical value, insufficient nucleating substrates will form and the grain-refining effects will be poor. If the nucleating number is more than the critical value, the nucleating substrates will agglomerate to form clusters and will lose their nucleating functions.

In the solidification process, the I-phase particles congregate at the front of the growing interface and block the diffusion of Zn atoms, which restrains the subsequent growth of $\alpha$-Mg and the MgZn phase; finally the microstructure of alloy is refined. Meanwhile, the quasi-continuous network MgZn phase is broken into a discontinuous network.
2.3 Effect of Mg-Zn-Nd master alloy on mechanical properties of ZK60 alloy

Figure 5(a) shows the macro-hardness curve of the investigated alloys. It is shown that the addition of MZN master alloy can notably increase the macro-hardness of the ZK60 alloy. The macro-hardness reaches its peak value of 66.2 HB in the ZK60 alloy with the addition of 5.0wt.% MZN master alloy, which is 13.4% higher than ZK60 alloy. The improvement of the macro-hardness of ZK60 alloy is mainly attributed to the introduction of the I-phase particles, which are homogenously distributed in the matrix or along grain boundaries. Moreover, the macro-hardness of the I-phase particles is much higher than those of the matrix and eutectic phases. The presence of high-hardness I-phase particles has a positive effect on the improvement of the macro-hardness of ZK60 alloy.

From Fig. 5(b), it can be seen that the elongation of the ZK60 alloy is initially increased after the addition of MZN master alloy. When the addition of master alloy is 1.0wt.%, the elongation reached its maximum value of 25%, which is about 42.8% higher than that of ZK60 alloy without MZN. However, Figure 5(b) also shows that the elongation decreases sharply with MZN master alloy addition of above 1.0wt.%. The minimum value of the elongation, obtained from ZK60 + 5.0wt.% MZN master alloy, is 19.2%, which is still about 9.7% higher than that of ZK60 alloy without MZN. This phenomenon is mainly attributed to the quasi-periodic lattice of the I-phase particles providing a stable and perfect interface with the matrix. Its high symmetry provides more chances that one of its faces will have a local atomic match with one of the planes of the matrix. The stability of both the quasi-crystalline particle and the α-Mg matrix.

Figure 5(b) also shows the ultimate tensile strength (UTS) and yield strength (YS) curves of the investigated alloys at room temperature (RT). It can be seen that the UTS of ZK60 alloy at RT is improved with MZN master alloy addition. The UTS of ZK60 alloy with 4.0wt.% MZN master alloy at RT reaches its maximum value of 256.7 MPa, which is an increase of about 17.8% compared with the ZK60 alloy without MZN. However, on further increasing the addition level to 5.0wt.%, the UTS decreases slightly from the peak. This phenomenon is mainly attributed to the pinning effect of the I-phase particles at the grain boundaries, which blocks the movement of dislocations during deformation. However, if the addition level of the reinforced phase is too high, the precipitated phase in large quantity at the grain boundaries will agglomerate to form clusters, reducing the bonding strength and increasing stress concentration at the grain boundaries. These grain boundaries are prone to initiation and propagation of micro-cracks during plastic deformation and lead finally to a decrease in the mechanical properties of the ZK60 alloy.

In view of solution treatment having little effect on the grain size, the grain size after solution treatment reflects the as-cast grain size. In order to show the grain boundary, heat treatment process was formulated as solution heat treatment at 350°C for 1 h, quenched in hot water at 80°C. For the as-cast ZK60-4.0wt.% MZN master alloy, the average equiaxed grain size was refined to 35.5 μm, i.e. 56.8% less than that of as-cast ZK60 alloy, as shown in Fig. 6(e). Clearly, the 0.2% proof of stress strongly depends on the grain size in magnesium alloy and obeys the role of the Hall–Petch relationship $\sigma = \sigma_0 + K_d d^{1/2}$, where $\sigma$ is the 0.2% proof stress (YS, MPa), $\sigma_0$ the lattice friction stress related to movement of individual
dislocation, $K$, a constant and $d$ is the grain size in μm. Under certain conditions, the finer the grains, the larger the area of grain boundaries; and the hindering effect of grain boundary on dislocations becomes more obvious and the yield strength is higher. From Fig. 5 (b), it can also be found that the YS of ZK60 alloy at RT is improved greatly due to MZN master alloy addition. When the addition of MZN master alloy is 4.0wt.%, the UTS reaches its peak value of 150.4 MPa, which is nearly 24.1% higher than that of ZK60 alloy without MZN. However, on further increasing the addition level to 5.0wt.%, the YS begin to decline. Therefore, the addition of MZN master alloy is beneficial to the improvement of mechanical properties of ZK60 alloy at ambient temperature.

2.4 Fracture analysis of ZK60 alloy tensile samples

Figure 7 shows SEM images of the tensile fracture surfaces of as-cast ZK60 alloy without and with 4.0wt.% MZN master alloy, respectively. As can be seen from Fig. 7, the failure surfaces of both the alloys are composed of cleavage planes and tear ridges. However, the average size of the cleavage planes in ZK60 + 4.0wt.% MZN master alloy is about half of that in ZK60 alloy because of the smaller grains. More importantly, a specified volume of dimples can be observed on the fracture surface of ZK60 + 4.0wt.% MZN master alloy (shown in Fig. 7b). This phenomenon may be attributed to the slower migration of grain boundaries and postponed crack initiation and propagation resulting from the pinning effects of the spherical quasi-crystal phase particles which are homogeneously distributed in the $\alpha$-Mg matrix and near the MgZn phase. Due to the grain-refining effect of spherical quasi-crystal particles on the $\alpha$-Mg matrix, small tear ridges as well as a certain amount of dimples can be observed on
the fracture surface (shown in Fig. 7b), showing obviously improved plasticity of ZK60 alloy with the addition of MZN master alloy.

2.5 Strengthening mechanism of Mg-Zn-Nd master alloy on ZK60 alloy

To obtain magnesium alloys with high strength and toughness, it is indispensable to add the reinforcing phase into the magnesium alloys. The optimization and stability of the interface structure between the reinforced phase and the matrix is the key to promoting the mechanical properties of Mg-based composites and to obtain optimal comprehensive performance.

The solidification microstructure of ZK60 magnesium alloy reinforced by Mg_{40}Zn_{55}Nd_{5} (I-phase) particles under normal casting condition is fine, as the reinforcing phase, I-phase particles are distributed in the α-Mg matrix or along grain boundaries, with smaller particle size than that fabricated by other methods. Due to the low surface energy of the quasi-crystal phase \[9\] as well as the similarity between the quasi-crystal phase and the alloy matrix, excellent wetting of the quasi-crystal phase with the matrix can be obtained. Therefore, the spherical quasi-crystal phase has less rending effect on the matrix; and the degree of stress concentration in the matrix is much lower \[5, 10\]. More importantly, the Mg_{40}Zn_{55}Nd_{5} (I-phase) particles prevent the diffusion of Zn atom and result in fine grain size of α-Mg matrix and discontinuous network morphology of the MgZn phase with granulation tendency.

Figure 8(a) shows the SEM micrograph of solidification microstructure of ZK60 alloy reinforced by MZN under normal casting condition. Figure 8(b) shows magnified SEM micrograph at arrow A in Fig. 8(a). Figure 8(c) shows EDS analysis results at arrow A in Fig.8 (a), verifying the existence of quasi-crystal phases. It can be seen from Fig. 8(b) that there is no interfacial reaction between the quasi-crystal particles and the α-Mg matrix, and no brittle phase existed at the interface, suggesting high interface bond strength. The high strength of the alloy is mainly attributed to the strengthening effect of the quasi-crystal phase with high volume fraction. The low interface energy of the quasi-crystalline phase can restrict its coarsening and promote the formation of a stable interface between the I-phase particles and matrix. The high hardness as well as high strength of ZK60 magnesium alloys is mainly attributed to the stable interface between the quasi-crystal phase and the matrix.

Despite the strengthening effect of the MgZn phase, the introduction of quasi-crystal particles, which have higher hardness and thermal stability than those of the MgZn phase, play a more important role in the strengthening effect on the ZK60 alloy. It can be seen from the as-cast structure that the homogenously distributed quasi-crystal particles play a significant role in the strengthening of the grain boundary. During the deformation processes, dislocations with high density are created around the quasi-crystal particles \[11\], which obviously promote the strength of alloy.

The ZK60 alloy exhibits much higher elongation after the addition of MZN master alloy, which is mainly attributed to two aspects. Usually, the interface between inter-metallic particles and the matrix is weak, which leads to the initiation and propagation of cracks and failure of the Mg alloy \[12\]. In contrast, the quasi-periodic lattice of the I-phase provides a stable and perfect interface with the matrix \[13\]. Its high symmetry provides more chances that one of its faces will have a local atomic match with one of the planes of the matrix. The quasi-periodicity can also be viewed as several varying periodicities, which ensures some kind of an atomic match with a matrix plane \[3, 14\]. Thus, the initiation of voids that lead to deformation failure of the alloy is difficult, and the partial coherence of the I-phase and the matrix can be more effectively preserved during deformation. On the other hand, the large number of quasi-crystalline particles in the ZK60 alloys can effectively prohibit microstructural evolution of the α-Mg matrix during deformation. The I-phase particles in the ZK60 alloy are stable against coarsening during deformation due to their low interfacial energy, thereby forming a stable quasi-crystalline particle/matrix interface \[15, 16\]. The stability of both the quasi-crystalline particles and the microstructure.
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of the ZK60 alloy provides a large elongation with no void opening at the interface between the quasi-crystalline particle and the $\alpha$-Mg matrix.

3 Conclusions

(1) The solidification microstructure of ZK60-based quasi-crystal-reinforced composites (ZK60 alloy with various additions of MZN master alloy) consists of the $\alpha$-Mg matrix, the MgZn phase, the MgZn$_2$ phase and the I phase. A much finer grain size of the $\alpha$-Mg matrix is achieved and the morphology of the MgZn phase transforms from a quasi-continuous network into a discontinuous network after the addition of MZN master alloy to the ZK60 alloy.

(2) Both the UTS and TYS at RT of ZK60 alloy are obviously improved after adding MZN master alloy. When the addition is 4.0wt.%, the values of UTS and YS at RT reach their peak values, 256.7 MPa and 150.4 MPa, respectively, which are increased by 17.8% and 24.1%, respectively, compared with the ZK60 master alloy. When the addition amount is 1.0wt.%, the elongation of the composite is 25.0%, which is 42.8% higher than that of ZK60 alloy without MZN. The elongation then decreases with further increasing MZN master alloy. The minimum elongation of 19.2% is obtained for ZK60-5.0wt.% MZN, which is still about 9.7% higher than that of the ZK60 alloy without MZN. The macro-hardness value of ZK60 alloy increases with an increase in the mass fraction of MZN master alloy.

References

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