A comparative study of Mg-Gd-Y-Zr alloy cast by metal mould and sand mould

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Abstract: The differences of the microstructure and mechanical property between metal mould and sand mould cast Mg-10Gd-3Y-Zr alloy were investigated both under as-cast condition and after solution heat treatment. In the as-cast specimens, the microstructure is similar and composed of $\alpha$-Mg solid solution and eutectic compound of $\alpha$-Mg+ Mg$_2$(Gd,Y)$_5$; whereas the grain size using metal mould and sand mould is 27 μm and 71 μm, respectively. The eutectic compound of metal mould cast alloy was completely dissolved after solution treated at 500 °C for 8 h, however it needs higher temperature (525 °C) and longer time (12 h) to achieve the absolute dissolving under sand mould condition. In contrast to metal mould, the peak time of sand mould alloy aged at 225 °C and 250 °C of was advanced by 4 h and 6 h, respectively. The precipitation reaction sequence in sand mould cast Mg-10Gd-3Y-Zr alloy during isothermal ageing at 250 °C follows S.S.S.S.→$\beta''$($D_0$)→$\beta''$($cboc$)→$\beta''$($fcc$)→$\beta''$($fcc$), which is similar to that in the alloy cast using metal mould.

Key words: Mg-10Gd-3Y-Zr alloy; solution heat treatment; peak time; precipitation sequence

Magnesium alloys containing heavy rare earth elements are of high strength and low density, which makes them very attractive as structural materials in applications, for example, aircraft and space machinery and ground transport including racing automobiles, where weight saving is of great importance[1]. Recently, it has been reported that the addition of Gd is effective for improving elevated temperature strength and creep resistance of the Mg alloys. The equilibrium solid solubility of Gd in magnesium is relatively high (4.53 at.% or 23.49 wt.%) at 548 °C and decreases exponentially, with decreasing of temperature, to 0.61 at.% (3.82 wt.%) at 200 °C, forming an ideal system for precipitation hardening[2-3]. Thus, the Mg-Gd based alloys are prone to form supersaturated solid solution during the solidification. The new strengthening precipitates would readily form by suitable aging treatment[4]. Y and Zr are added to Mg-Gd binary alloy in order to increase aging effect and to refine the grains[5-6]. Mg-10Gd-3Y-0.45Zr alloy exhibits good combination of strength, ductility and creep resistance in the peak-aged condition[7]. Previously, Rokhlin[8], Anthony[9] and He[10] have developed Mg-Gd-Y-Zr alloys which exhibit higher specific strength at both room and elevated temperatures and better creep resistance than WE54 and QE22. They have also investigated the relationship between the mechanical properties and microstructure of these high Gd-containing alloys.

The microstructure and properties of Mg-Gd-Y-Zr alloys formed in metal mould have been well documented[5-10], however the literature about sand mould cast Mg-Gd-Y-Zr alloys are not yet available. The aim of the present paper is to study the difference of the microstructure and mechanical properties between metal mould and sand mould cast Mg-10Gd-3Y-Zr alloys.

1 Experimental procedures

Mg-25Gd (wt.%) and Mg-25Y (wt.%) master alloys were made by melting high purity Mg (>99.9%), Gd(>99.9%) and Y(>99.9%) using a medium-frequency induction furnace under argon atmosphere. During melting, high-purity Mg, Mg-25Gd, Mg-25Y and Mg-30Zr master alloys (with proper portion to make Mg-10.42Gd-3.45Y-0.47Zr alloy)
were pre-heated between 180 °C and 200 °C, and added orderly at the temperature of 500 °C, 720 °C, 740 °C and 760 °C, respectively. Melting was conducted using an electric resistance furnace under a mixed atmosphere of CO₂ and SF₆ with the ratio of 100 : 1. The melt was then pouted into a metal mould and a sand mould (pre-heated to 200 °C). Both ingots were block shape, as shown in Fig.1. The actual chemical composition of the alloy was determined by an inductively coupled plasma (ICP) spectrometer (Perklin-Elmer, Plasma 400).

Specimens cut from the block-shaped ingot were solution treated from 500°C to 535°C for a period of 4–12 h and then quenched into hot water of 70–80°C. Cast specimens and cast-T4 specimens were etched using 4vol.% nital. Vickers hardness testing was taken using 49 N load and holding time of 15 s. The grain size was determined using a linear intercept method from a large number of non-overlapping measurements. Microstructure observation was performed using an optical microscope (Leica MEF4M) and a scanning electron microscopes (FEI-Sirion 200). Dog bone tensile samples of 3.5 mm width, 2 mm thickness and 15 mm gauge length, as shown in Fig.2, were cut by an electric-sparking wire-cutting machine. Tensile testing was carried out on a Zwick-20KN material test machine at a crosshead speed of 1 mm/min.

2 Results

2.1 As-cast microstructures

The microstructures of metal mould and sand mould cast Mg-10Gd-3Y-Zr alloy are shown in Fig.3. It can be seen clearly that a network of eutectic compound mostly distributed at the grain boundaries, and the average grain size of the alloy cast using metal mould and sand mould are about 27 μm and 71 μm, respectively. However, the different forming mode did not influence the microstructure of as-cast alloy. Figure 4 shows the compositional XRD spectra, which indicates that Mg-10Gd-3Y-Zr alloy mainly consists of α-Mg solid solution and eutectic compound of α-Mg₆(Gd,Y)₁₃.
2.2 Solution heat treatment

The temperature of solution treatment of Mg-10Gd-3Y-Zr alloy was determined on the basis of former research and differential thermal analysis (DTA) curves. Figure 6 shows the DTA curves of as-cast alloys made by using of different moulds. Noticeable endothermic signals (associated with solute dissolution and melting, at low and high temperatures, respectively) were observed both under metal mould and sand mould cast conditions. Two peak temperatures of metal mould cast alloy are 537.7 °C and 627.7 °C, and those of sand mould cast alloy are 557.4 °C and 630.1 °C. According to the peak temperature of solute dissolution reaction (Fig.6) and the microstructure of as-cast alloy (Fig.3), three solution treatment temperatures were selected: 500, 525 and 535 °C and the samples were solutionized for a time period of 4, 8 and 12 h.

The typical microstructures of as-cast alloy after solution treatment at various temperatures for different period of time are presented in Fig.7. It can be seen that there are significant changes in both grain size and the amount of eutectic compound with solution treatment. However, metal mould and sand mould cast alloys are responding differently to this heat treatment.
For the metal mould cast alloy, eutectic compounds were partly dissolved and became thinner after solution treatment at 500 °C for 4 h (Fig.7a). The average grain size increased from around 27 μm of as-cast (Fig.3a) to about 39 μm after solution treatment. After being treated for 8 h (Fig.7c), the grain size hardly changed, whereas the network of eutectic compounds were completely dissolved into Mg matrix, further some cuboid-shaped particles of 2–5 μm diameter (Fig.7c) formed and unevenly distributed in the matrix and at the grain boundary. The morphology of the particle compound resolved by high magnification SEM is shown in Fig.8, the chemistry has been quantified as having stoichiometry of Mg,Gd,Y (i.e. γ-phase). The structure of the particle was previously identified as face-centered cubic (fcc) with a = 0.56 nm by three zone-axis electron micro-diffraction patterns [10]. Obvious grain growth was observed when solution treatment was performed at a higher temperature of 535 °C, the grain size reached about 63 μm after treatment of 8 h, as shown in Fig.7(e).

The microstructural evolution of sand mould cast alloy after solution heat treatment is illustrated in Fig.7(b, d and f). Compared with the metal mould cast alloy, higher temperature and longer time are required to achieve complete solution for sand mold cast alloy. The eutectic compound became thinner and the concentration decreased obviously after solution treatment at 500 °C for 12 h (compare Fig.7b with Fig.3b), and some of the phase particles were spheroidized. The spheroidization of the eutectic compound particles developed further by increasing solution treatment temperature to 525 °C (Fig.7d), moreover some cuboid-shaped compound (γ-phase) also formed. When treated at 535 °C for 12 h, the average grain size increased to 90–100 μm.

2.3 Age hardening behavior

Figure 9 shows the age hardening response of the sand mould cast alloy aged at 225 and 250 °C, respectively. Prior to ageing, cast specimens have been solution treated for 8 and 12 h at 500 and 525 °C, and then water quenched. It can be seen from Fig. 9 that the peak hardness decreases with increasing of aging temperature (between 225 and 250 °C). It is also found that ageing time for peak hardness is 12 h if aged at 225 °C and 10 h for ageing at 250 °C, regardless of previous solution treatment. Compared with the metal mould cast alloy, which has been carefully investigated by He [11], the peak-hardness ageing time for 225 °C and 250 °C were advanced by 4 and 6 h, respectively.

2.4 Mechanical properties of Mg-10Gd-3Y-Zr alloy

Figure 10 shows the effect of solid-solution treatment on the mechanical properties of sand mould cast Mg-10Gd-3Y-Zr alloy treated at 525 °C. The TYS and Elongation decrease gradually with increasing of solution time, while the UTS seems to have an opposite tendency as a function of solution time, as shown in Fig.10(a). Figure 10(b) shows the effect of aging temperature on the mechanical properties of the alloy after peak aged. The UTS and Elongation of alloy peak-aged at 250 °C are higher than that at 225 °C, with little change in TYS.

On the other hand, the mechanical properties of metal mould
cast alloy after peak-aging are obviously better than that of sand mould cast alloy. The UTS, TYS and Elongation of as-cast alloy solution treated at 500 °C for 6 h and subsequently peak-aged at 225 °C are 370 MPa, 241 MPa and 4.1%; and the corresponding properties of cast-T4 alloy peak-aged at 250 °C are 331 MPa, 198 MPa and 11.6%, respectively.[11]

Figure 9 shows a summary of the elevated temperature tensile properties of sand mould and metal mould cast-T6 Mg-10Gd-3Y-Zr alloy. It is noted that the elongation increases consistently with testing temperature from 100 °C to 300 °C; the UTS of sand mould cast-T6 alloy increases initially from 100 °C to 200 °C and then decreases from 200 °C to 300 °C. However, the UTS of alloy under metal mould cast-T6 condition decreases slowly from 100 °C to 300 °C. The different changing tendency of UTS with temperature between sand mould and metal mould cast-T6 alloy may be related to the grain size of as-cast alloy, as shown in Fig. 3.

The precipitation sequence of sand mould cast-T4 Mg-10Gd-3Y-Zr alloy during isothermal ageing at 250 °C has been analyzed by XRD, as shown in Fig. 12. The noticeable four-stage successive precipitation sequence involving S.S. → β″ → β′ → β1 → β (fcc) is similar to that reported for metal mould cast Mg-10Gd-3Y-Zr alloy.[10] The XRD analysis indicates that the β″ forms at the beginning of...
ageing treatment (around 0.5 h); subsequently a small quantity of \( \beta' \) appears after ageing of 2 h. The amount of \( \beta' \) grows continuously with time and becomes the dominant phase in the alloy upon 10 h, which is responsible for the peak hardness. The metastable \( \beta' \) phase will partly disappear and transform into \( \beta \) phase during over ageing, e.g. over 20 h.

![Fig.12: X-ray diffraction spectra of sand mould cast-T4 specimens aged at 250 °C for different times](image)

### 3 Discussions

It is well known that mould materials significantly impact the microstructure of as-cast Mg-10Gd-3Y-Zr alloy by altering the cooling rate during solidification process. It is noted that the grain size and second phase in the sand mould cast alloy are larger than that in metal mould cast alloy, as shown in Fig.3. Due to the facts that Zr does not influence the phase transition \(^{12,13}\) and that the atomic radius of Gd and Y are similar, the solidification process of Mg-Gd-Y-Zr alloy can be treated as equivalent to that of Mg-Gd binary alloy, whose phase diagram is shown in Fig.13. The line of \( 1 \) stands for the composition of GW103K alloy, and the curves of \( ab \) and \( ac \) indicates the non-equilibrium solidification of sand mould and metal mould cast Mg-10Gd-3Y-Zr alloy, respectively. The amount of second phases can be calculated approximately from the diagram. The ratio of second phases of sand mould and metal mould cast alloy in as-cast condition is about \( h/bg \) and \( ef/eg \), respectively. Since \( ef/eg > h/bg \), it can be concluded that \( ef/eg > h/bg \), which indicates that the relative amount of second phases in metal mould cast alloy are much more than that in sand mould cast alloy.

XRD analysis (Fig.4) shows that the microstructures of sand mould and metal mould cast Mg-10Gd-3Y-Zr alloy are similar. The microstructure of as-cast alloy is mainly consisted of \( \alpha \)-Mg solid solution and \( \gamma \)-phase. The only microstructural difference between sand mould and metal mould cast alloy is the grain size and shape of second phase, the former has slower solidification rate and the eutectic reaction takes place with relatively a larger amount of melting liquid to transformation which results in large size of second phase, however the latter represents the opposite tendency and obtains finer crystal grains.

High temperature solution treatment usually results in high vibration energy and diffusion coefficient of solutes (increases exponentially with temperature), and high concentration of vacancies in the alloys. The solutes will dissolve into the matrix, causing the decomposition of the intermetallic compounds \(^{134}\), remaining phases and their concentration can be predicted by phase diagram under equilibrium condition. During solution treatment, defects, such as dislocation and vacancies, are important for the kinetics of atom diffusion. Compared with sand mould, the metal mould cast alloy has higher density of defects, which play an important role during the morphological change of Mg-Gd-Y-Zr, during subsequent solution treatment.

As mentioned above, defects will be in favor of the dissolving of second phase at solution treatment, so the metal mould cast alloy is easier to homogenize than that of sand mould cast alloy. As shown in Fig.7, the heat treatment temperature and time of absolute solution of the eutectic phase under metal mould cast condition is 8 h at 500 °C, however sand mould cast alloys needs 12 h at 525 °C for a full solution treatment. It should also be noted that small grain size in the metal mould alloy physically reduced the distance of atoms’ diffusion from the grain boundary to the dendrite center and the rare earth atoms tended to distribute homogeneously, all these contributed to a speedy solution treatment compared with sand mould cast alloy. Solution treatment also caused the formation of cuboid-shaped compound \( \gamma \) (Fig.8), and \( \gamma \) phases continued to exist during subsequent aging treatment (Fig.12). The existence of stable \( \gamma \) phases impinges dislocation motion during deformation and might contribute to the superior tensile properties of this alloy at elevated temperatures.

As a high strength and heat resistance magnesium alloy, Mg-10Gd-3Y-Zr exhibits higher specific strength at elevated temperatures, tensile properties at temperatures ranging from 100 to 300°C, as shown in Fig.11. Such property may be attributed to the increasing diffusion of Gd and Y atoms as well as other deformation mechanisms activated at high temperatures. The diffusion of Gd and Y releases partial stress and decreases the brittleness, resulting in the increase of
strength.

Precipitation reaction sequence in Mg-Gd-Y-Zr alloy has been previously investigated by Kamado et al.\(^{[1]}\) It was reported that the precipitation sequence follows the order of S.S.S. \(\rightarrow \beta'\)\((D0_1)_\alpha\) \(\rightarrow \beta'(cbo)\rightarrow \beta'(bcc)\), this is similar to that reported for Mg-Y alloys\(^{[2]}\). However, recent research indicated that the precipitation sequence of Mg-10Gd-3Y-0.5Zr alloy involves four stages: S.S.S. \(\rightarrow \beta'\)\((D0_1)_\alpha\) \(\rightarrow \beta'(cbo)\rightarrow \beta'(bcc)\).\(^{[1]}\) The reduced peak-aged time for sand mould cast alloy, as compared with metal mould cast alloy, can be attributed to the appearance of large numbers of \(\beta'\) after 10 h at 250 \(^\circ\)C as shown in Fig.12. \(\beta'\) has a hexagonal \(D0_{19}\) structure (typically found in Mg-RE alloys\(^{[13,18]}\)) with lattice parameters \(a = 2 \times a_{\alpha-Mg} = 0.64 \text{ nm}, c = c_{\alpha-Mg} = 0.52 \text{ nm}\) and an orientation relationship of \([0001]_{\beta'}\parallel[0001]_{\alpha}, (2\overline{1}10)_{\beta'}\parallel(2\overline{1}10)_{\alpha}\). The peak-aged microstructure contained predominantly metastable \(\beta'\) phase, whose lattice parameters are \(a = 2 \times a_{\alpha-Mg} = 0.64 \text{ nm}, b = 8 \times a_{\alpha-Mg} = 2.22 \text{ nm}, c = c_{\alpha-Mg} = 0.52 \text{ nm}\).\(^{[19]}\) The \(\beta'\) precipitates formed in present Mg-Gd-Y-Zr alloy have a convex morphology, which is different from the globular shape reported in WE54\(^{[19]}\). In addition, the \(\beta'\) phase formed in the Mg-Gd-Y-Zr alloy is more thermally stable than that in the WE54 alloy, since it still dominates the microstructure after ageing of 193 h, and exists with a minor fraction in the microstructure after ageing for 2,400 h. He et al.\(^{[1]}\) proposed that the transition of \(\beta'\) into equilibrium \(\beta\) phase takes much longer time, so it is almost impossible to observe the \(\beta\) phase in the sand mould cast-T4 alloy aged after only ageing of 20 h (Fig.10).

In summary, the control of the shape, quantity and distribution of \(\beta'\) becomes a major challenge for increasing the strength of Mg-10Gd-3Y-Zr alloy.

### 4 Conclusions

A systematically comparative study of Mg-10Gd-3Y-Zr alloy cast by sand mould and metal mould was reported in this paper. The as-cast microstructure, ageing response and mechanical properties at various temperatures of the alloy were compared and following conclusions were made:

1. The composition of metal mould and sand mould cast Mg-10Gd-3Y-Zr alloy is similar. The as-cast microstructure mainly consists of \(\alpha\)-Mg solid solution and \(\alpha\)-Mg\(_{\alpha}\)(Gd,Y) eutectic compound.

2. The complete dissolution of the eutectic compound of metal mould and sand mould cast Mg-10Gd-3Y-Zr alloy is 8 h at 500 \(^\circ\)C, and 12 h at 525 \(^\circ\)C, respectively.

3. In contrast to metal mould cast alloy, the peak time aged at 225 \(^\circ\)C and 250 \(^\circ\)C of sand mould cast alloy were advanced by 4 h and 6 h, respectively.

4. The precipitation sequence in sand mould cast Mg-10Gd-3Y-Zr alloy during isothermal ageing at 250 \(^\circ\)C involves S.S.S.

Reference


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