Effect of heat treatment on the microstructures and mechanical properties of the sand-cast Mg–2.7Nd–0.6Zn–0.5Zr alloy

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Received 13 November 2013; accepted 5 January 2014
Available online 17 March 2014

Abstract

The tensile testing bars of the Mg–2.7Nd–0.6Zn–0.5Zr (wt.%) alloy were prepared by sand casting. The effect of solution temperature and aging time on the microstructures and mechanical properties were investigated. The as-cast alloy was composed of a magnesium matrix and Mg₁₂Nd eutectic compounds. After solution treatment at 500 °C for 18 h, the volume fraction of eutectic compounds decreased from ~7.8% to ~2.3%, and some small Zr-containing particles were observed to precipitate at grain interiors. As the solution temperature increased to 525 °C for 14 h, most of the eutectic compounds dissolved into the matrix. Peak-aged at 200 °C for 12 h, fine β" particles was the dominant strengthening phase. The yield strength, ultimate tensile strength and elongation in the peak-aged condition were 191 MPa, 258 MPa and 4.2%, respectively. Moreover, the Mg–2.7Nd–0.6Zn–0.5Zr alloys under different heat treatment conditions exhibited different tensile fracture modes.

Keywords: Magnesium alloy; Sand-cast; Heat treatment; Microstructure; Mechanical properties

1. Introduction

Low density, high specific strength and stiffness make Mg alloys very attractive as structural materials in applications of aircraft, space ship and ground transport, where weight saving is of great importance [1,2]. Among them, Mg alloys containing rare earth elements (RE) have received considerable interest in recent years due to their potential for achieving higher strength and better creep resistance at elevated temperatures [3,4]. Nd is one of the light rare earth element with maximum solubility in solid Mg of 3.6 wt.% at eutectic temperature 545 °C and thus offers potential for age-hardening [5]. Moreover, trace addition of Zn to Mg–Nd alloy would further increase its peak-aged hardness [6,7].

In fact, the Mg–Nd–Zn alloy is a traditionally cast Mg alloy with high strength and heat resistance. It was developed much earlier than WE54 and WE43. Especially, in China, the Mg–Nd–Zn Mg alloy has been widely used in aeronautics, such as engine box and wing rib of airplane, and is termed as ZM6 [8]. It should be noted that most of the parts are produced by sand mold casting. However, up to now, very few researches were focused on the sand mold casting with a low cooling rate of Mg–Nd–Zn alloy. In this paper, Mg–2.7Nd–0.6Zn–0.5Zr (wt.%) alloy Mg alloy were synthesized by sand mold casting. The effect of solution temperature and aging time on the microstructures and mechanical properties were investigated.

2. Experimental procedures

The Mg alloys denoted as NZ31 were examined in the present study, and its chemical composition was...
Mg$_{2.7}$Nd$_{0.6}$Zn$_{0.5}$Zr (wt.%). It was prepared with pure Mg (99.95 wt.%), Zn (99.9 wt.%), Nd (99.5 wt.%) and Mg$_{30}$Zr (wt.%) by melting under protection with an anti-oxidizing flux. Tensile testing bars with a gauge dimension of 72 mm in length and 12 mm in diameter were prepared by pouring the melt into a sand mold. Then, they were solution treated at 500°C for 18 h or at 525°C for 14 h, and were correspondingly termed as T41 and T42. The aging treatment was subsequently performed at 200°C for various periods of time.

For microstructure observations, samples were cut from the gauge part of the sand-cast tensile testing bars with the observing plane perpendicular to the tensile direction and etched in a solution of 5 vol.% HNO$_3$ in ethanol after mechanical polishing to reveal grain boundaries. The grain sizes ($L$) were determined by analyzing the optical micrographs with a line-intercept method ($d = 1.74L$). The phases were analyzed by an X-ray diffraction (XRD) (Rigaku D/max 2400 X-ray diffractometer) with Cu K$_a$ radiation, a scanning electron microscope (SEM, Philips XL30 ESEM-FEG/EDAX), and a transmission electron microscope (TEM, JEM-2100F) operating at 200 kV. Thin foil specimens for TEM were prepared by punching 3 mm diameter discs, followed by dimple grinding and Ar$^+$ ion milling in a precision ion polishing system (PIPS, Gatan) operating at 4.5 kV accelerating voltage and $\sim 8^\circ$ incident angle.

Samples for thermal analysis were cut from the as-cast ingots and machined into cylinders of 35 mm in diameter and 50 mm in length. The samples were remelted in a steel crucible in an electrical resistance furnace. Then one shielded K-type thermocouples was immersed from the top of the crucible that was insulated from the top and the bottom, and was placed at the center of the crucible. After holding 10 min at 720°C, the crucible together with the thermocouples were removed from the furnace and allowed cooling in air with a cooling rate of about 1 K/s. The temperature changes were continuously recorded during the solidification process by using a high-speed data acquisition system linked to the computer.
Vickers hardness testing was performed using 500 g load and a holding time of 10 s. Not fewer than 10 measurements were taken in each alloy. Tensile tests were performed, with an initial strain rate of $2.5 \times 10^{-4}$ s$^{-1}$ during elastic deformation and of $2 \times 10^{-3}$ s$^{-1}$ during plastic deformation, at room temperature. Three specimens were used for same test conditions to ensure the reproducibility of data.

3. Results and discussion

3.1. The as-cast NZ31 alloy

Typical microstructures of the sand-cast NZ31 alloy in as-cast condition are depicted in Fig. 1. As we can see in Fig. 1a, the sand-cast NZ31 alloy has equiaxed grain structures with an average grain size of $\sim 75 \mu m$. The grain size is $\sim 20 \mu m$ coarser than that casted by metal mold [6], due to the low cooling rate during the solidification process. A large amount of network eutectic compounds forms at the grain boundaries (Fig. 1b), and some fine spicule and rod-shaped phases are also observable mainly around the $\alpha$-Mg grain boundaries (Fig. 1c).

Fig. 2a shows the thermal analysis results for the NZ31 alloy in the as-cast condition. The first derivative of the cooling curve ($dTc/dt$) is determined to enhance slope changes that are related to the solidification reactions for the different phases, and to facilitate the determination of the critical solidification characteristics of the alloys. Two well-defined peaks are observed at 644 °C and 527 °C, which correspond to the primary Mg phase formation reaction and the non-equilibrium eutectic reaction, respectively. According to the XRD analysis (Fig. 2b), except the $\alpha$-Mg matrix, only Mg$_{12}$Nd compounds can be detected. Therefore, the coarse network phases and the spicule and rod-shaped phases around the $\alpha$-Mg grain boundaries are both belong to the Mg$_{12}$Nd compounds with a different morphology [9]. The low cooling rate doesn’t significantly change the type and the distribution of the second phases of the as-cast NZ31 alloy, and generally only leads to a low content of solute atoms in Mg Matrix [10].

3.2. The effect of heat treatment on the microstructure

Fig. 3 shows the optical and SEM microstructures of the NZ31 alloy after the solution treatment. The volume fraction of the eutectic phase and the grain size of the NZ31 alloy in as-cast and solutionized condition are summarized in Table 1. Two solution temperatures, 525 °C and 500 °C, are used. For the samples solutionized at 525 °C for 14 h (in T41 condition), the average grain size grows up to $\sim 84 \mu m$ after the solution treatment, as shown in Fig. 3a, and almost all the Mg$_{12}$Nd phase have dissolved into the matrix. Although there indeed exist a few of residual ones, especially in triple junctions at grain boundary (Fig. 3b), their volume fraction is only 0.7%. Detailed investigation reveals that three kinds of precipitates with different shapes: block-like, short rod-like, long rod-like, newly formed and gathered at grain interior (Fig. 3c). As previously reported [11,12], the block-like particle is identified

<table>
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<th>Table 1</th>
<th>The phase volume fraction and grain size of the NZ31 alloy in different conditions: as-cast (F), solution treated (T41 and T42).</th>
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<tr>
<td>Volume fraction of eutectic phase [%]</td>
<td>7.8</td>
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<tr>
<td>Grain size [µm]</td>
<td>75</td>
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as ZrH₂ phase, and the other two are Zn₂Zr₃ phase with three distinguishably different orientation relationships with the α-Mg matrix.

For the parts with complex or thin-walled structure, high temperature may result in distortion during the solution treatment. So, we try to lower the solution temperature to 500 °C. As depicted in Fig. 3d, although we have extend the solution time to 18 h, there still exist lots of network eutectic compounds left at grain boundary. The volume fraction of the Mg₁₂Nd compound is only reduced from 7.8% in as-cast condition to 2.3% in T42 condition. Some small Zr-containing particles are also observed at grain interiors.

Fig. 4 shows two hardness curves of the NZ31 alloy during isothermal aging at 200 °C, corresponding to the two kinds of solution treatment (T41: 525 °C 14 h and T42: 500 °C 18 h). It can be seen that the samples in the two conditions both exhibit an obvious age-hardening behavior. The hardness starts to increase rapidly after an incubation period of about 0.5—1 h. For the sample in T41 condition, the peak hardness (HV 82) attains at about 12 h. Further aging leads to a little drop in hardness and then shows a wide hardness plateau from 18 h to 48 h with a Vickers hardness of about HV 78, followed by a rapid decline. For the sample in T42 condition, it only takes about 4—8 h to reach a peak hardness plateau, yet the peak hardness (HV 73) is much lower than that of the sample in T41 condition. Since the lower solution temperature leaves a lots of eutectic Mg₁₂Nd compound at grain boundary, resulting in a low content of solute atoms in the Mg matrix of sample in T42 condition. So, during isothermal aging at 200 °C, in peak-aging condition, the precipitate density of sample in T42 condition should be lower than that of sample in T41 condition, corresponding to a lower peak hardness.

The samples, of the NZ31 alloy solutionized at 525 °C for 12 h and subsequently aged at 200 °C for various periods of time, were selected for microstructure investigation. The optical microstructure of aged samples is similar to that of solutionized one and the grain size does not change during aging. Fig. 5 shows the TEM bright field image and corresponding selected area electron diffraction (SAED) pattern with the incident electron beam approximately parallel to [110]ₐ. For the sample in T61 condition (200 °C 3 h), it can be observed in Fig. 5a that the microstructure contained a uniform distribution of very fine precipitates in the Mg matrix. The fine precipitation and corresponding diffraction pattern showing precipitates, of the NZ31 alloy solutionized at 525 °C for 14 h and subsequently aged at 200 °C for (a) 3 h, (b) 6 h, (c) 12 h and (d) 48 h, along [110]ₐ zone axis.
precipitates lay on \{100\}_a and extend along [0001] direction. As the aging time extend to 6 h (T62 condition in Fig. 5b), the size of the fine prismatic precipitates changes little, while the density obviously increases. Thus, the hardness goes with a sharply increase from HV 57 in T41 condition to HV 76. After aged at 200 °C for 12 h, the sample in T63 condition gets a peak hardness. Compared with those in under-aged condition, the precipitates in peak-aged condition grow up and have an average size of about 30–50 nm in length along [0001]_a direction and 2–5 nm in thickness. The morphology, size and orientation investigation indicates that most of the precipitates here should be the \(β^0\) phase, consistent with those reported in Mg–Nd alloy without or with trace addition of Zn [7,13]. Continuously aged to 48 h, the sample transits to over-aged condition. The \(β^0\) precipitates become larger in size, while still keep a high density. So, the hardness of the sample in T64 condition also maintains in a high level, only ~HV 10 less than that in peak-aged condition.

### 3.3. The effect of heat treatment on the mechanical properties

Fig. 6 shows the typical engineering stress—engineering strain curves of the sand-cast NZ31 alloy in different conditions. The average values for TYS, UTS and elongation-to-failure are summarized in Table 2. Compared to the as-cast alloy, solution treatment, whether at 525 °C or at 500 °C, may result in a great enhancement in elongation and ultimate tensile strength (UTS). But the yield strength (YS) drops a little. Solution treatment may result in lots of the eutectic phase dissolving into the Mg matrix. The increased content of solute atoms indeed benefits its YS [14]. However, after solution treatment, the grain size also increases, as indicated above. According to the Hall–Petch relationship, the YS should decrease [15]. In solution treated alloy, besides pure Mg, only solid solution strengthening and grain boundary strengthening contribute to the strength. Here, the later one obviously mainly operates in the sand-cast NZ31 alloy in solutionized condition.

Further aging leads to a significant improvement in UTS and TYS. After aged at 200 °C for 3 h, the NZ31 alloy in T61 condition exhibits the high strength, and the UTS and YS are 227 and 179 MPa, respectively. Unfortunately, the elongation-to-failure is greatly decreased from 9.5% in solution treated condition to 3.2%. It is worth noting that the NZ31 alloy in T62 condition (200 °C 6 h) gets the highest YS, which is inconsistent with the results of aging hardening curves. In peak-aged condition (T63), the YS falls by 5 MPa, in comparison with that in T62 condition, while the UTS reaches to the highest one (258 MPa). As the aging time increases from 14 h to 48 h, there seems no significant change for the mechanical properties of the sand-cast NZ31 alloy. In general, the hardness of Mg alloy corresponds to its YS during the aging process [16]. Throughout the aging process of the sand-cast NZ31 alloy, from 3 h to 48 h at 200 °C, the variation in the strength is obviously weaker than that in hardness. This should be connected to the casting surface. By a short aging process (~3 h), the casting surface may quickly get a high strength and dominate the mechanical properties of the tensile testing bars up to an over-aged condition (~48 h). The detailed relationship between the casting surface and the mechanical properties need to be studied further.

The secondary electron (SE) SEM micrographs of the fracture surfaces perpendicular or parallel to the tensile axis of the sand-cast NZ31 alloy in different conditions are illustrated in Fig. 7.
fracture surfaces consist of cleavage planes, which is in accordance with its limited elongation of 2.8%. The fracture model of as-cast NZ31 alloy is quasi-cleavage. When the alloy is subjected to solution treatment at 525 °C, the fracture surfaces are mainly composed of ductile trans-granular cleavage planes of coarse dimples (river pattern) and tear ridges (Fig. 7c), which is in accordance with its high elongation of 9.5%. The fracture mode is trans-granular cleavage. As already mentioned, some residual eutectic compounds can be observed on the fracture surface of the solutionized samples. The micro-cracks may first initiate around the residual eutectic compounds, and then propagate trans-granularly, remaining a lot of cleavage planes. Moreover, some cracks residing inside the grains are also found. Followed by being peak-aged at 200 °C for 12 h, fine prismatic β′′ phases precipitate and strengthen the alloy. In this condition, the alloy has highest UTS of 258 MPa. Throughout the aging process of the sand-cast NZ31 alloy, from 6 h to 48 h at 200 °C, the YS of the NZ31 alloy all keeps in a high level (no less than 190 MPa), on account of the tensile bars tested with casting surface. The NZ31 alloy in different conditions shows different fracture behaviors: in as-cast alloy, cracks form by the fracture of eutectics along the grain boundaries and propagate trans-granularly; after solution treatment and peak-aged at 200 °C, the alloy exhibits a trans-granular cleavage fracture.

4. Summary

The sand-cast NZ31 alloy in as-cast condition contains Mg matrix and Mg12Nd eutectic compounds. Solution treatment may result in the dissolution of the Mg12Nd phase into the Mg matrix, and a higher YS and elongation. The fall of solution temperature from 525 °C to 500 °C means more eutectic phase left in the matrix, while there seems no influence to mechanical properties. Peak-aged at 200 °C for 12 h, fine prismatic β′′ phases precipitate and strengthen the alloy. In this condition, the alloy has highest UTS of 258 MPa. Throughout the aging process of the sand-cast NZ31 alloy, from 6 h to 48 h at 200 °C, the YS of the NZ31 alloy all keeps in a high level (no less than 190 MPa), on account of the tensile bars tested with casting surface. The NZ31 alloy in different conditions shows different fracture behaviors: in as-cast alloy, cracks form by the fracture of eutectics along the grain boundaries and propagate trans-granularly; after solution treatment and peak-aged at 200 °C, the alloy exhibits a trans-granular cleavage fracture.
Acknowledgments

This work was funded by the National Basic Research Program of China (973 Program) through project No. 2013CB632202, and National Natural Science Foundation of China (NSFC) through projects No. 51105350 and No. 51301173, respectively.

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