Microstructure characterization and high-temperature shear strength of the Mg–10Gd–3Y–1.2Zn–0.5Zr alloy in the as-cast and aged conditions

H.R. Jafari Nodooshan a, Wencai Liu a,∗, Guohua Wu a,⁎, R. Alizadeh b, R. Mahmudi b, Wenjiang Ding a

aNational Engineering Research Center of Light Alloy Net Forming and Key State Laboratory of Metal Matrix Composite, Shanghai Jiao Tong University, Shanghai 200240, China
bSchool of Metallurgical and Materials Engineering, College of Engineering, University of Tehran, Tehran, Iran

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1. Introduction

Magnesium alloys possess a good combination of low density, high strength-to-density ratio, good castability and reasonable cost, which makes them very attractive for structural uses in aircraft, space, and ground transport applications, where weight saving is of great importance. Recently, a great deal of interest has been shown to magnesium alloys for biomaterial applications [1]. Currently, the most commonly used magnesium alloys are based on the Mg–Al–Zn system with moderate strength at room temperature, and poor mechanical properties at temperatures above 150 °C [2]. The undesirable strength drop of these alloys has been ascribed to the formation of the unstable Mg12Al17 phase that readily softens at elevated temperatures [3]. Therefore, there have been many attempts to develop new Mg-based alloys having structural stability at high temperatures. The addition of rare earth (RE) elements can significantly improve the mechanical properties of magnesium alloys especially at high temperatures due to solid solution strengthening and precipitation hardening [4–7]. Among different Mg–RE alloys, the most prominent ones are the Mg–Gd–Y–Zr series which have good mechanical properties at both room and elevated temperatures, and better creep resistances than the conventional Al and Mg alloys [8–11]. In this regard, it has been reported that Mg–10Gd–3Y–0.4Zr alloy show superior strength at elevated temperatures, with excellent creep resistance [12]. Furthermore, Liu et al. [13] reported that addition of 1% Zn to Mg–10Gd–3Y–0.5Zr alloy results in better mechanical properties and heat resistance of the alloy. Also, it has been shown that Zn additions could have significant effects on the age hardening response of these alloys [14]. The mechanical properties of Mg–Gd–Y–Zn–Zr alloys are improved mainly by two factors: (i) the formation of RE precipitates and (ii) the long period stacking ordered (LPSO) structures [14]. Different types of LPSO structures including 18R, 24R, 6H, 10H, and 14H can easily form during solidification or by thermo-mechanical treatments in the Mg–RE–Zn alloys to enhance the mechanical properties [15–17]. Zhang et al. [14] reported the presence of 14H–LPSO structure and RE precipitates in an Mg–14Gd–3Y–1.8Zn–0.5Zr alloy and found the best conditions for achieving optimum mechanical properties. Li et al. [18] also investigated the microstructure evolution of Mg–10Gd–3Y–1.2Zn–0.4Zr alloy during high-temperature heat treatment. It has been reported that stacking faults and parts of the eutectic compounds dissolve into the α-Mg matrix and the others transform to block-shaped 14H LPSO phases at grain boundaries gradually. In another investigation, the LPSO structure has proved to contribute significantly to
changing the high temperature tensile properties of the Mg–Gd–Y–Zn–Zr alloys [18]. Zr is usually added to Mg–Gd–Y alloys as a grain refining element, which can enhance both the strength and ductility of these alloys [19].

Most of the studies on the Mg–Gd–Y–Zn–Zr alloys have focused on the microstructural aspects of the solution treated alloys, with limited data on the mechanical properties such as simple hardness or tensile strength. It seems that there is a lack of comprehensive studies on the influence of LPSO structures on both microstructural evolution and high-temperature mechanical properties of the Zn-containing Mg–Gd–Y–Zr alloys. Therefore, it is the aim of this study to characterize the microstructure and mechanical properties of the as-cast and aged Mg–10Gd–3Y–1.2Zn–0.5Zr alloy at both room and high temperature. Detailed microstructural evolution was examined by SEM, TEM, and HRTEM observations. The evaluation of strength was made by using the shear-punch testing (SPT) technique, which has recently been employed for some cast magnesium alloys [20,21]. This is an efficient method that is capable of producing strength data which are well correlated with those found by the conventional tensile tests [22,23].

2. Experimental details

2.1. Materials and processing

The material used in this study was an Mg–10Gd–3Y–1.2Zn–0.4Zr (wt%), known as the GWZK alloy. Mg–90Gd and Mg–25Y master alloys were first made by melting high-purity elemental Mg (>99.95%), Gd (>99.9%) and Y (>99.9%) in a medium-frequency vacuum induction furnace under an argon atmosphere. These together with an Mg–30Zr master alloy and pure Zn (>99.95%) were added to the molten Mg in proper fractions. Melting was carried out in an electric resistance furnace with a mild steel crucible under the protective mixed atmosphere of CO2 and SF6 with the ratio of 100:1. The Mg melt was held at 750 °C for 20 min before the addition
of Zn and master alloys. The melts were held at this temperature for 20 min and then stirred mechanically for 2 min using a stainless steel rod to provide a homogeneous composition. The molten material was poured into a steel die, preheated up to 150 °C. The real chemical composition of the cast slabs was Mg–10.46Gd–2.62Y–1.14Zn–0.51Zr (wt%), determined by an inductively coupled plasma analyzer (ICP, Perkin Elmer, Plasma-400). Based on the experimental results in Ref. [10], GWZK specimens cut from the ingot were solution treated at 525 °C for 36 h, quenched into cold water, and then aged at 225 °C for 16 h in an oil bath.

Microstructures of the specimens were analyzed by optical microscopy (OM) and the FEI SIRION 200 scanning electron microscope (SEM) equipped with an Oxford energy dispersive X-ray spectrometer (EDS). Constitutive phases were characterized by D/Max-IIIA X-ray diffractometer using Ni-filtered Cu Kα radiation. Characterization of phases was performed in a JEOL-2010 transmission electron microscope (TEM), operating at 200 kV. Thin foils for the TEM observations were prepared by twin jet electro polishing in a solution of 25% HNO₃ and 75% methanol cooled down to −20 °C. Further thinning was carried out using low energy ion beam milling.

2.2. Mechanical property measurements

The 1 mm thick slices of the material were ground to a thickness of 0.7 mm, from which disks of 10 mm in diameter were punched for the SPT. A shear punch fixture with a 3.175 mm diameter flat cylindrical punch and 3.225 mm diameter receiving-hole, the schematic view of which is shown elsewhere [23], was used for this experiment. Shear punch tests were performed at RT, 150, 175, 200, 225, 250 and 300 °C using a screw driven 150 kN MTS 30/ MH material testing system. After application of the load, the load P was measured automatically as a function of punch displacement; the data were acquired by a computer so as to determine the shear stress (τ) of the tested material using the relationship [24]:

\[ τ = \frac{P}{\pi d h} \]  

where \( t \) is the specimen thickness and \( d \) is the average of the punch and die hole diameters. SPT curves, were plotted as shear stress against normalized punch displacement (\( \delta = h/t \), where \( h \) is the punch displacement).

3. Results

3.1. Microstructural evolution

Optical micrographs of the studied alloys in the as-cast and aged conditions are shown in Fig. 1a and b, respectively. The microstructure of the as-cast condition consists of a network-like phase in the α-Mg grains. As can be seen in Fig. 1b, the microstructure of the aged alloy consists of at least three components; (i) equi-axed grains, (ii) some needle-like phases, and (iii) intermetallic particles formed inside the grains. Needle-like phases are elongated from the grain boundaries toward the inside of grains.

To have a better understanding of the morphology of the present phases, SEM micrographs of the tested alloys are shown in Fig. 2. It can be depicted from Fig. 2a that the network-like phase in the as-cast condition is a lamellar eutectic compound. Some fine particles can also be detected in the microstructure. Another important feature of the as-cast alloy is the presence of some needle-like phases, elongated from the grain boundaries toward the inside of the grains. This needle-like phase, both in the as-cast and aged alloys (Fig. 2a and b), seems to possess a specific orientation in each grain, indicating the existence of some crystallographic relationships between the needle-like phase and α-Mg matrix. This relationship would be discussed in more details with the help of TEM observations in the following parts. Fig. 2c shows a higher magnification image of the intermetallic particles formed in the aged condition. It seems that the fine particles are clustering around some central points, to form a Chinese scripts morphology.
Average chemical composition of the selected points in Fig. 2, obtained by EDS analysis, is given in Table 1. The composition (at.%) of the eutectic compound in the as-cast condition (point A) is approximated as 86.79Mg–8.15Gd–1.48Y–3.54Zn, in accordance with previous findings [10]. Because of the small size of the particles, it was not possible to determine chemical composition of the lamellar particles separately. The composition of the matrix (point B) shows that there exists a cooperative contribution in solid solution strengthening of Zn, Gd and Y elements in Mg. Composition of point C indicates that there exist some Zr-rich particles in the as-cast condition, which formed during solidification and can act as nucleation sites for precipitation of particles during aging, forming a clustered like morphology (Fig. 2c). Finally, points D, E and F in the microstructure of the aged alloy show the chemical composition of LPSO structure, matrix, and Zr rich particles, respectively.

XRD analysis was performed on the as-cast and aged specimens to identify the phases existing in the alloy at different conditions and the results are shown in Fig. 3. It confirms the presence of $\alpha$-Mg, $\text{Mg}_5(\text{Gd},\text{Y})$, $\text{Mg}_{24}\text{Y}_5$, and $\text{Mg}_4\text{Zn}_7$ phases in the diffraction patterns of the as-cast alloy. On the other hand, the phase constituents of the aged alloy are mainly composed of $\alpha$-Mg, $\text{Mg}_5(\text{Gd},\text{Y})$, and $\text{Mg}_4\text{Zn}_7$ type phases.

In order to examine the microstructure of the tested alloys in more details, and to study the very fine particles and their orientation relationships, TEM observations were made. TEM microstructure, selected-area electron diffraction (SAED) pattern, and HRTEM image of the needle-like phase in the as-cast condition are shown in Fig. 4. The incident electron beam was parallel to the $[1\bar{1}2\bar{0}]_a$ direction. As can be seen in Fig. 4a, the needle-like phase consists of some layers with a width of several nanometers elongated parallel to each other, forming a needle-like phase in a specific crystallographic orientation in each grain. A 2H–Mg crystal structure is identified from the corresponding diffraction pattern (Fig. 4b), where the strong streaks between the diffraction spots along the $c$-axis confirm basal plane stacking faults (SF) for these phases. Fig. 4c shows the HRTEM image of the lamellar structure with width less than 5 nm.

![Fig. 5. TEM image and the corresponding SAED pattern of the aged alloy (B)//[0001]$_a$.](image)

![Fig. 6. TEM image and the corresponding SAED pattern of the aged alloy (B)//[1\bar{1}2\bar{0}]_a.](image)
To have a better understanding of the morphology of the particles, TEM BF images observed from the $\{1\bar{1}20\}_a$ zone axis are shown in Fig. 6. It can be seen that some $b_0$ phases with ellipsoidal shapes together with some parallel lines are detectable. From the observations on the $\{0001\}_a$ and $\{1\bar{1}20\}_a$ zone axes, the morphology of the $b_0$ phases appears to be cylindrical with an ellipsoidal cross-section. The inserted SAED pattern in Fig. 6b shows diffraction streaks along $(0002)_a$ diffraction spot. This corresponds to the needle-shaped precipitates formed near the grain boundaries as stacking faults. Like the needle-like phase in as-cast state, these stacking faults can be considered as segments of the 14H phase, which have not been well developed yet.

The peak-aged microstructure is confirmed to be composed of the $\alpha$-Mg matrix, the 14H–LPSO structure, and the $b_0$ and $b_1$ RE precipitates. Fig. 7 shows the TEM images and SAED patterns ($B = [1\bar{1}20]_a$) for the microstructure of the RE precipitates and 14H–LPSO structure in the matrix of the aged alloy. According to the corresponding SAED pattern given in Fig. 7b, besides the diffraction spots caused by the $b_0$ phase, extra diffraction spots appeared at the positions $n/14$ (where $n$ is an integer) of the $(0002)_{\alpha\text{-Mg}}$ fundamental diffraction, indicating that the lamellar-shaped phase should be 14H type LPSO phase [28]. It has been reported [29,30] that a four-stage precipitation sequence of $\alpha$-Mg (SSS) $\rightarrow b''$ (D0$_{19}$) $\rightarrow b'$ (cbo) $\rightarrow b_1$ (fcc) as well as an Mg(SSS) $\rightarrow$ 14H LPSO phase takes place in Mg–Gd–Y(–Zn) alloys at 225 °C. Fig. 8 shows LPSO structure located at grain boundaries in the peak aged alloy. Many researchers reported the formation of LPSO structure in the grain boundaries [22,31,32].

### 3.2. Mechanical properties

To investigate shear strength behavior of the material, SPT curves at different test temperatures from room temperature to 300 °C are shown in Fig. 9 for both as-cast and aged alloys. It can be observed that, similar to a conventional tensile stress–strain
curve, after a linear elastic behavior the curve deviates from linearity before it reaches a maximum point. Finally, after undergoing a short post uniform deformation, the specimen experiences fracture. The deviation point from linearity is taken as the shear yield stress (SYS) and the stress corresponding to the maximum point is referred to as the ultimate shear strength (USS). It can also be inferred that increasing the test temperature from 25 to 300 °C results in variation of SYS and USS values in both alloys. To have an overall view on the variations of strength with temperature, the SYS and USS data are summarized in Fig. 10a and b, respectively.

There are some important features that can be inferred from this figure. First, the general trends of variations with temperature are similar for the SYS and USS data. Secondly, the strength of the as-cast alloy decreases with increasing temperature up to 150 °C, after which it passes through a maximum at 250 °C and then decreases again. This behavior is in contrast to that of the aged alloy, in which the strength continually decreases with increasing temperature from RT to 300 °C. Finally, strength of the aged condition shows higher values at all test temperatures. The observed shear strength behavior of the alloy and the microstructural changes occurring during the high temperature exposure will be discussed in the following section.

4. Discussion

In this part, it is tried to rationalize the observed shear behavior of the material by the use of microstructural observations and thermal analysis for a better understanding of the high temperature deformation behavior of the material. DSC curves, obtained by heating in the temperature range of 25–400 °C and with a scanning rate of 10 °C/min with a commercial system (Netzsch STA 449), are shown in Fig. 11 for both of the as-cast and aged alloys. As can be deduced from this figure, both conditions show endothermic events, with the peak temperature at 138 °C and 129 °C for the as-cast and aged alloys, respectively. The endothermic peaks can be caused by the dissolution of one or some of the phases present in both conditions with increasing temperature. However, the distinct difference is that the endothermic event continues in the aged condition to temperatures near 300 °C, meaning that the dissolution is occurring in a broad temperature range. Precipitates in the aged condition tend to transform to more stable phases to reduce the free energy of the whole system, whenever the temperature is increased to temperatures higher than the aging temperature (the samples were aged at 225 °C in this study). For the as-cast material, however, the situation becomes different, where an exothermic event, with the peak temperature at about 230 °C, overcomes the endothermic reaction. This means that, at temperatures higher than 150 °C, an exothermic reaction starts and finally overcomes the dissolution process. This exothermic event can be a precipitation process, since some saturated regions certainly exist locally in the as-cast condition, and precipitation can occur in these regions, whenever the temperature is increased. The occurrence of the precipitation peak is in agreement with the peaks observed at 250 °C in the SYS and USS curves, indicating the role of precipitates in the strengthening of the cast alloy.

One can use combinations of both DSC and XRD analyses to describe better the events that occur during high-temperature deformation. According to the obtained XRD and DSC results, it
can be concluded that the precipitation process in both conditions can be attributed to the precipitation of Mg₃(Gd,Y) particles which tend to be formed from the saturated regions during aging treatment, as the temperature increases. Formation of these particles could be the main reason for the observed increase in strength of the as-cast alloy at high temperatures. These particles can act in the opposite direction of matrix softening that occurs normally with increasing the test temperature, resulting in an overall increase in strength of the as-cast alloy. However, at temperatures higher than 270°C (according to the DSC results), the precipitation phenomenon slowdowns and cannot compete the matrix softening and this results in a decrease in strength of the as-cast material at 300°C (Fig. 9). On the other hand, it seems that the precipitates, which exist primarily in the microstructure of the aged alloy before deformation, tend to be over-aged at high temperatures according to the DSC results. Therefore, an overall decrease in strength of the alloy can be observed with increasing the test temperature. An important point which has to be mentioned is that although some overaging or dissolution occurs at high temperatures, the strength of the aged alloy is higher than that of the as-cast condition at all investigated temperatures.

In order to study the shear deformation behavior of the material, SEM micrographs of both conditions after shear punch tests are shown in Fig. 12. Comparing the microstructures of the alloy after low-temperature (25°C) and high-temperature (300°C) deformation, it is clear that limited deformation has occurred at low temperatures. As can be seen in Fig. 12c, the grains have been remained equiaxed after deformation at low temperature. This micrograph also shows that a crack has been passed through both the LPSO and the grain boundary in the aged alloy. Thus, the LPSOs in the aged condition seem to have some contributions in strengthening of the material through resisting deformation and decreasing the energy of cracks. Fig. 12b and d shows the microstructure of the material after SPT at 300°C in the as-cast and aged alloys, respectively. An important feature in these figures is that the lamellar eutectic compound has been elongated along the deformation direction, an effect which shows that these particles do not have sufficient thermal stability to resist plastic deformation at high temperatures. On the other hand, the fine particles in the aged alloy (Fig. 12d), which were clustering around some central points before deformation, have been distributed more uniformly in the deformation direction. This distribution of particles implies that they have resisted against deformation of the matrix at high temperatures and thus have played their role as strengthening particles, resulting in increased strength of the aged alloy in comparison with the as-cast alloy.

Another important fact which can affect the strengthening capability of particles in hcp metals, in addition to their thermal stability and shape, is the orientation relationship between the particles and the Mg matrix. In this regard, the particles or phases, which are aligned parallel to the basal planes, can impede dislocation movements on the matrix basal planes. However, these particles cannot have their main contribution to strengthening at high temperatures, due to the activation of pyramidal and prismatic slip planes. In this condition, particles which lay not parallel in relation to the basal planes can be considered as dislocation hinders at high temperatures in hcp metals. Accordingly, the LPSOs, in both the as-cast and aged conditions, cannot be considered to play a critical
role in high temperature strengthening, since they have been formed parallel to basal planes (Figs. 4 and 7). However, the \( \beta_1 \) and \( \beta \) precipitates, with their broad faces parallel to the \( \{1120\}_{\parallel} \) direction (Figs. 5 and 6), can impede dislocation movement on the other slip systems at high temperatures [30]. Thus, the precipitates which form in the aged condition, with sufficient thermal stability and favorable orientation relationship with the Mg matrix, enhance the high temperature mechanical properties of the material in comparison with the cast condition, resulting in higher strength of the aged condition at all investigated test temperatures.

5. Conclusions

Microstructure evolution and high temperature shear behavior of the Mg–10Gd–3Y–1.2Zn–0.4Zr alloy in as-cast and T6 aged conditions were investigated using shear punch tests. The main achievements can be summarized as follows:

(1) Microstructure of the as-cast condition consists of \( \alpha \)-Mg, \( \mathrm{Mg_5(Gd,Y)} \), \( \mathrm{Mg_2Zn_5} \), and \( \mathrm{Mg_2Zn_7} \) phases, while the aged condition mainly contains \( \alpha \)-Mg, \( \mathrm{Mg_5(Gd,Y)} \), and \( \mathrm{Mg_2Zn_7} \) phases.

(2) The T6 heat treatment can greatly improve the shear properties of as-cast alloy at all test temperatures. LPSO structure located at the grain boundaries in the aged alloy has some contributions to the strengthening of the alloy.

(3) The as-cast and aged alloys exhibit different shear behavior with increasing test temperature. For the as-cast alloy, the shear strength decreases up to 150°C and then increases to reach a maximum value at 250°C. The obtained strengthening is due to the precipitation from saturated cast structure. This is in contrast to the aged condition, in which the strength decreases monotonically with test temperature.

(4) The orientation relationship between the precipitates and the Mg matrix in the aged condition was such that they could enhance high-temperature mechanical properties of the material, in contrast to the LPSOs which were more effective in low-temperature strengthening.

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References