

Microstructure evolution of Mg–9Gd–2Er–0.4Zr alloy during solid solution treatment

Zhao-hui WANG, Wen-bo DU, Xu-dong WANG, Ke LIU, Shu-bo LI

College of Materials Science and Engineering, Beijing University of Technology, Beijing 100124, China

Received 27 October 2011; accepted 15 February 2012

Abstract: Microstructure evolution of the cast Mg–9Gd–2Er–0.4Zr alloy during solid solution treatment at temperature of 460–520 °C for 3–12 h was investigated by using optical microscope (OM), scanning electron microscope (SEM) and transmission electron microscope (TEM). The results indicated that the grain size and the shape of second phase were obviously changed with time and/or temperature going on. At 460 °C for 3 h, the morphology of the Mg₅(GdEr) phase was changed into fragmented island morphology and the volume fraction of the phase decreased. After solution solid treatment at 460 °C for 6 h, the Mg₅(GdEr) phase was already completely dissolved, but some cuboid-shaped RE-rich phase precipitated. As the temperature increased, the morphology of the Mg₅(GdEr) phase was transformed into the same morphology as that at 460 °C for 6 h. It was suggested that the microstructure evolution of the alloy during the solid solution treatment was concluded as follows: Mg₅(GdEr) eutectic phase → Gd/Er atom diffusing into matrix → spheroidic Mg₅(GdEr) phase → cuboid-shaped RE-rich phase → grain boundary immigration.

Key words: Mg–Gd–Er–Zr alloy; microstructure evolution; solution solid treatment; eutectic phase

1 Introduction

As a result of the stricter requirement on greenhouse gas emission and fuel economy, magnesium alloys exhibit remarkable advantages to the automotive industries due to the combination of low density and high specific strength [1]. However, magnesium alloys are limited to some extent due to the lower strength. Thus, developing a new kind of Mg alloys with high mechanical performance is a significant issue [2–5].

Recently, it was found that the addition of other RE (Dy, Nd and Y) elements into the Mg–Gd based alloys is an effective way to improve strength and creep resistance of the Mg alloys at elevated temperatures [6–9]. The equilibrium solid solubility of Gd is relatively high in the Mg matrix and drops abruptly with lowering temperature [10,11]. So, it will easily lead to the formation of fine metastable precipitates during aging treatment, which is beneficial to improve mechanical properties. However, published contributions concerning the effects of solid solution treatment on the microstructure evolution and mechanical properties of the Mg–Gd–Er alloys are

limited.

Recently, the solution behavior of the Mg–15Gd–5Y–0.5Zr alloy from 500 °C to 540 °C was studied by GAO et al [12]. They found that the continuous network-like Mg₅(GdY) phase decomposed into fragmented phase and some cuboid-shaped compounds with a composition of Mg₂Y₃Gd₂ precipitated after solution solid treatment. It is suggested that the evolution of microstructure from as-cast to cast-T4 state involved α -Mg solid solution + Mg₅(GdY) eutectic phase → α -Mg solid solution + spheroidic Mg₅(GdY) phase → α -Mg supersaturated solid solution + cuboid-shaped compound Mg₂Y₃Gd₂. LI et al [13] reported that the eutectic compounds in the Mg–10Gd–3Y–1.2Zn–0.4Zr alloy dissolved gradually into the matrix with time prolonged during heat treatment at 773 K, and a new type of 14H LPSO and FCC structured cuboid-shaped RE-rich phases come into being.

As mentioned above, the microstructure evolution of the cast Mg–9Gd–2Er–0.4Zr alloy after solid solution treatment at the temperatures of 460–520 °C for 3–12 h was investigated.

2 Experimental

The alloy ingot with a nominal composition (mass fraction, %) of Mg–9Gd–2Er–0.4Zr was prepared. High purity Mg(>99.95%), Mg–30Gd(mass fraction, %) master alloy, Mg–30Er (mass fraction, %) master alloy and Mg–30Zr (mass fraction, %) master alloy were melted in a graphite crucible under mixed atmosphere of N₂ and SF₆ with a volume ratio of 20:1 in an electric resistance furnace. The melt was stirred to ensure the homogeneity, then held at 770°C for about 30 min and finally cast into a permanent mould to obtain ingots with dimensions of 33 mm×100 mm×100 mm. The ingot was cooled down in air atmosphere. The specimens for solid solution were machined from the bulk as-cast ingot. The specimens were solution treated at temperatures of 460–520 °C for 3–12 h, as listed in Table 1, and then quenched into cold water.

Table 1 Solution treatment conditions in the present study

Temperature/°C		Time/h	
460	3	6	12
490	3	6	12
520	3	6	12

The chemical compositions of the alloy were determined by an X-ray fluorescence (XRF) analyzer (Magic PW2403), as shown in Table 2. The phase compositions of the alloy were analyzed by X-ray diffraction (XRD, D8 ADVANCE) measurement in the scanning range of 20°–80° with 0.02° step size. The optical microscope (OM, ZEISS AXIO Imager A2), scanning electron microscope (SEM, HITACHI S–450) and transmission electron microscope (TEM, JEM-2100, JEOL) equipped with energy dispersive spectroscopy (EDS) were used to observe the microstructure of the alloys. The OM and SEM specimens were sliced from the same position of each casting. They were polished and etched with a solution of 5% nitric acid (volume fraction)+ethyl alcohol. The TEM specimens were prepared by electro-polishing and finally ion beam milling. The electro-polishing of the samples was conducted in a solution of 20% nitric acid and 80% methanol, using a liquid nitrogen cold region to prevent heating. The ion beam milling was performed at an incident angle less than 10°.

Table 2 Chemical compositions of investigated Mg–9Gd–2Er–0.4 alloy (mass fraction, %)

Gd	Er	Zr	Mg
9.3	1.8	0.4	Bal.

3 Results and discussion

3.1 Microstructure of as-cast alloy

The OM, SEM, TEM and corresponding SAED and EDXS results of the as-cast Mg–9Gd–2Er–0.4Zr alloy are shown in Fig. 1. The results indicate that the alloy is mainly composed of α -Mg and the network-like secondary phase which decorates the grain boundaries [14,15]. The compositions of network-like secondary phases are determined to be approximately Mg₅(GdEr) phase by energy diffraction patterns (EDXS), as shown in Fig. 1(f) and Table 3. The structure of the network-like secondary phases is identified by zone-axis selected area electron diffraction (SAED), as shown in Figs. 1(d) and (e), to be a complex structure with a large cubic cell [16].

Table 3 EDXS results of network-like secondary phases in as-cast Mg–9Gd–2Er–0.4Zr

Element	w/%	x/%
Mg	33.86	76.84
Gd	63.55	22.30
Er	2.59	0.86
Total	100.00	

3.2 DSC Study of as-cast alloy

The determination of the solution treatment temperature of the alloy was based on the DSC heating curves. Figure 2 shows the DSC curves of the Mg–9Gd–2Er–0.4Zr alloy from 200 °C to 700 °C at a scanning rate of 10 K/min. It is shown that the DSC heating curve contains two endothermic peaks. One is at 554 °C which is close to the temperature of formation of Mg₅Gd phase according to the equilibrium phase diagram of the Mg–Gd alloy. The other is at 644 °C which is close to the melting temperature of α -Mg according to the equilibrium phase diagram of the Mg–Gd alloy. This is coincided with the result in Refs. [17–19]. Therefore, the solution treatment temperatures of the Mg–9Gd–2Er–0.4Zr alloy were selected as 460, 490 and 520 °C.

3.3 X-ray diffraction study of as-cast and as-solution treated alloy

The XRD patterns of the as-cast and as-solution treated Mg–9Gd–2Er–0.4Zr alloy are presented in Fig. 3. The result indicates that the as-cast alloy is composed mainly of α -Mg together with β -phase (Mg₅(GdEr)) phase. The as-solution treated alloy is composed mainly of α -Mg, but the Mg₅(GdEr) secondary phases were dissolved into matrix after solution treatment at 460 °C for 6 h.

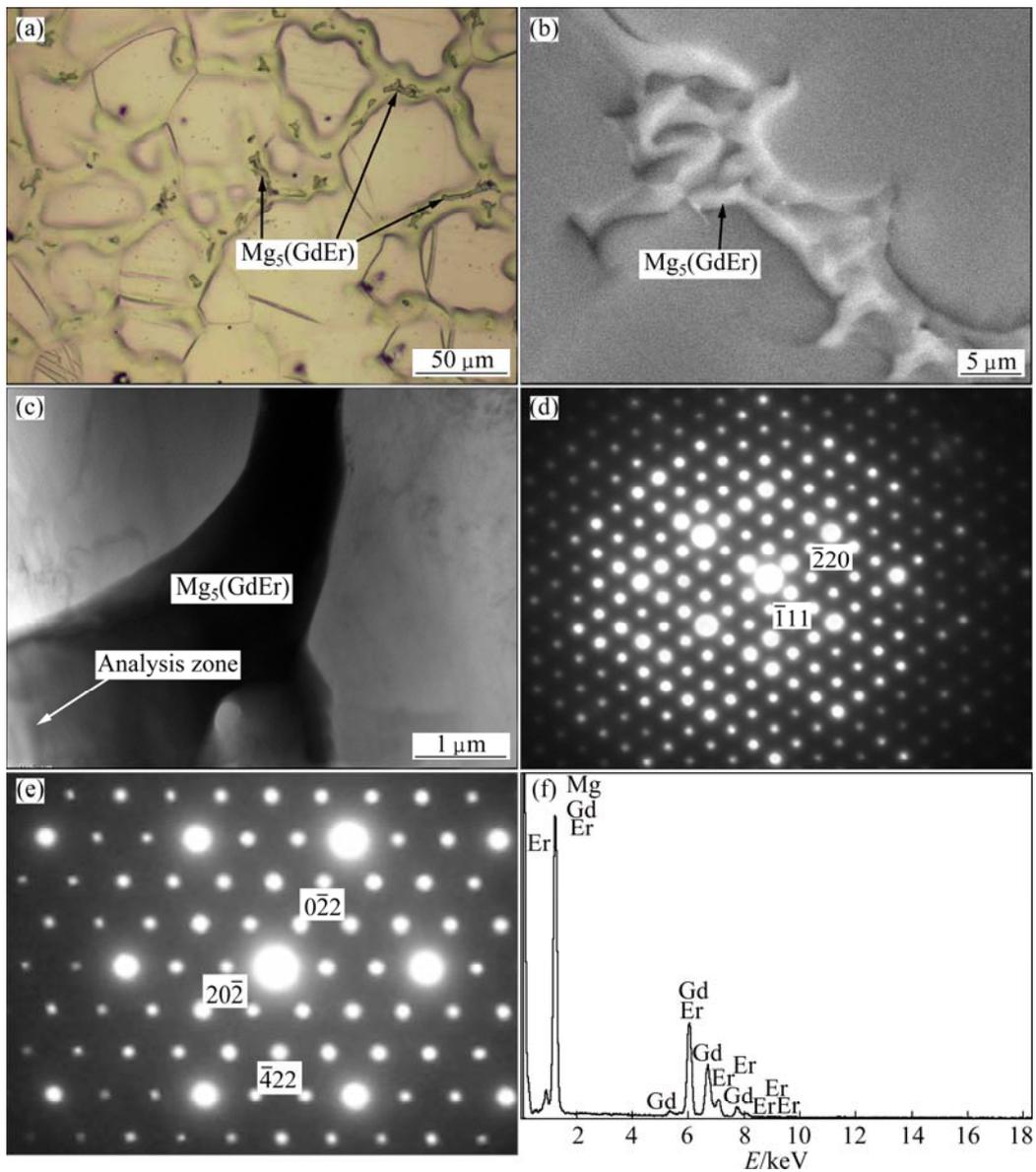


Fig. 1 OM (a), SEM (b) and TEM (c) images of network-like secondary phases in as-cast Mg-9Gd-2Er-0.4Zr alloy and corresponding SAED patterns (d, e) and EDX result (f)

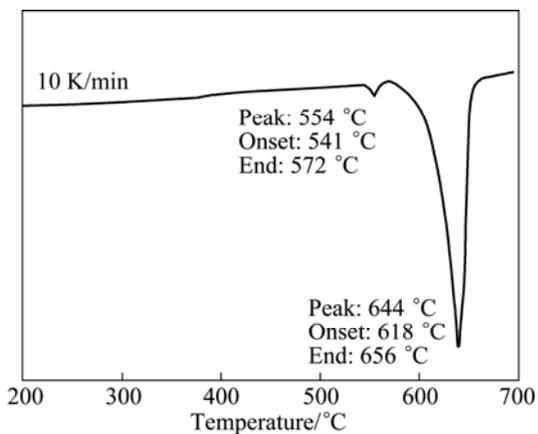


Fig. 2 DSC heating curves of Mg-9Gd-2Er-0.4Zr alloy from 200 °C to 700 °C (scanning rate: 10 K/min)

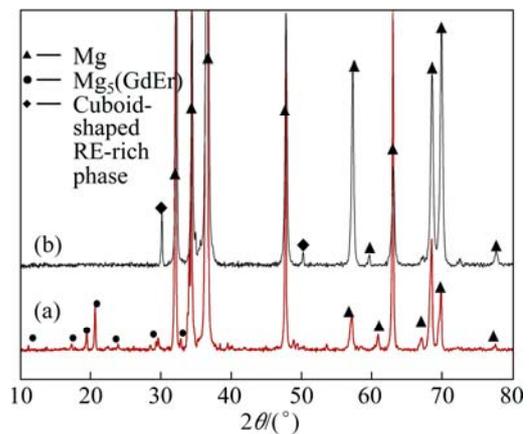


Fig. 3 XRD patterns of Mg-9Gd-2Er-0.5Zr alloy: (a) As-cast; (b) As-solution treated (460 °C for 6 h)

3.4 Microstructure of as-solution treated alloy

The microstructures of the as-solution treated alloy at different temperatures are shown in Fig. 4. The results indicate that the grain size and the shape of the second phase are obviously changed with time and/or temperature going on. At 460 °C for 3 h, the morphology of the $Mg_5(GdEr)$ phase transformed into fragmented island morphology and the volume fraction of the phase decreased, as shown in Fig. 4(a). After solid solution treatment at 460 °C for 6 h, the $Mg_5(GdEr)$ phase was completely dissolved, but some cuboid-shaped phases precipitated as time went on, as shown in Fig. 4(c). At the same temperature, the change of the morphology of the alloy has the same result with different time, as illustrated in Figs. 4(d) and Fig. 4(g) [12,20].

The SEM and TEM images of alloys are shown in Fig. 5. The SEM image of the as-solution treated alloy presents some cuboid-shaped compound with the size of 0.5–3 μm , as shown in Fig. 5(a). By the energy dispersive X-ray spectrometry, the composition is determined to be RE-rich compound and the mole ratio of Mg to Gd to Er is equal to 14.18:51.06:34.76, as shown in Fig. 5(e) and Table 4. Figure 5(b) shows TEM image of the cuboid-shaped phase and Figs. 5(c) and (d) show the corresponding two zone-axis SAED patterns.

The structure of the cuboid-shaped particles is identified as face-centered cubic (FCC) with $a=0.56$ nm [12,13]. According to the study, it is indicated that the cuboid-shaped RE-rich phase with a FCC crystal structure has been reported by several researchers, but the formation mechanism and effects on mechanical properties of the phases are still under investigation.

Table 4 EDXS results of cuboid-shaped compound in alloy after solution treatment at 460 °C for 6 h

Element	w/%	x/%
Mg	2.43	14.18
Gd	56.59	51.06
Er	40.98	34.76
Total	100.00	

4 Conclusions

1) Microstructure evolution of the cast Mg–9Gd–2Er–0.4Zr alloy after solid solution treatment at the temperatures of 460–520 °C for 3–12 h was investigated.

2) After solid solution treatment at 460 °C for 6 h, the $Mg_5(GdEr)$ phase was completely dissolved, but

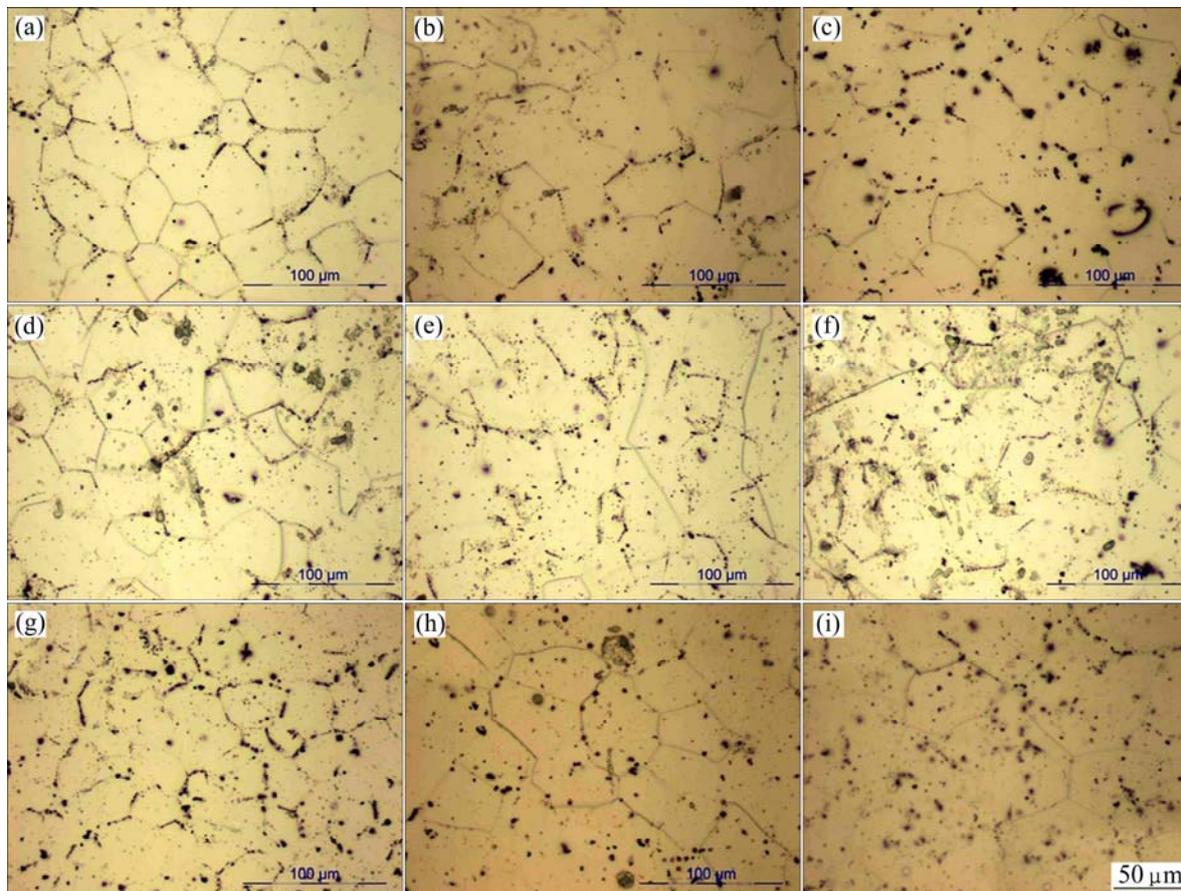


Fig. 4 Effects of solution time and solution temperature on microstructure of Mg–9Gd–2Er–0.4Zr alloy: (a) 460 °C, 3 h; (b) 460 °C, 6 h; (c) 460 °C, 12 h; (d) 490 °C, 3 h; (e) 490 °C, 6 h; (f) 490 °C, 12 h; (g) 520 °C, 3 h; (h) 520 °C, 6 h; (i) 520 °C, 12 h

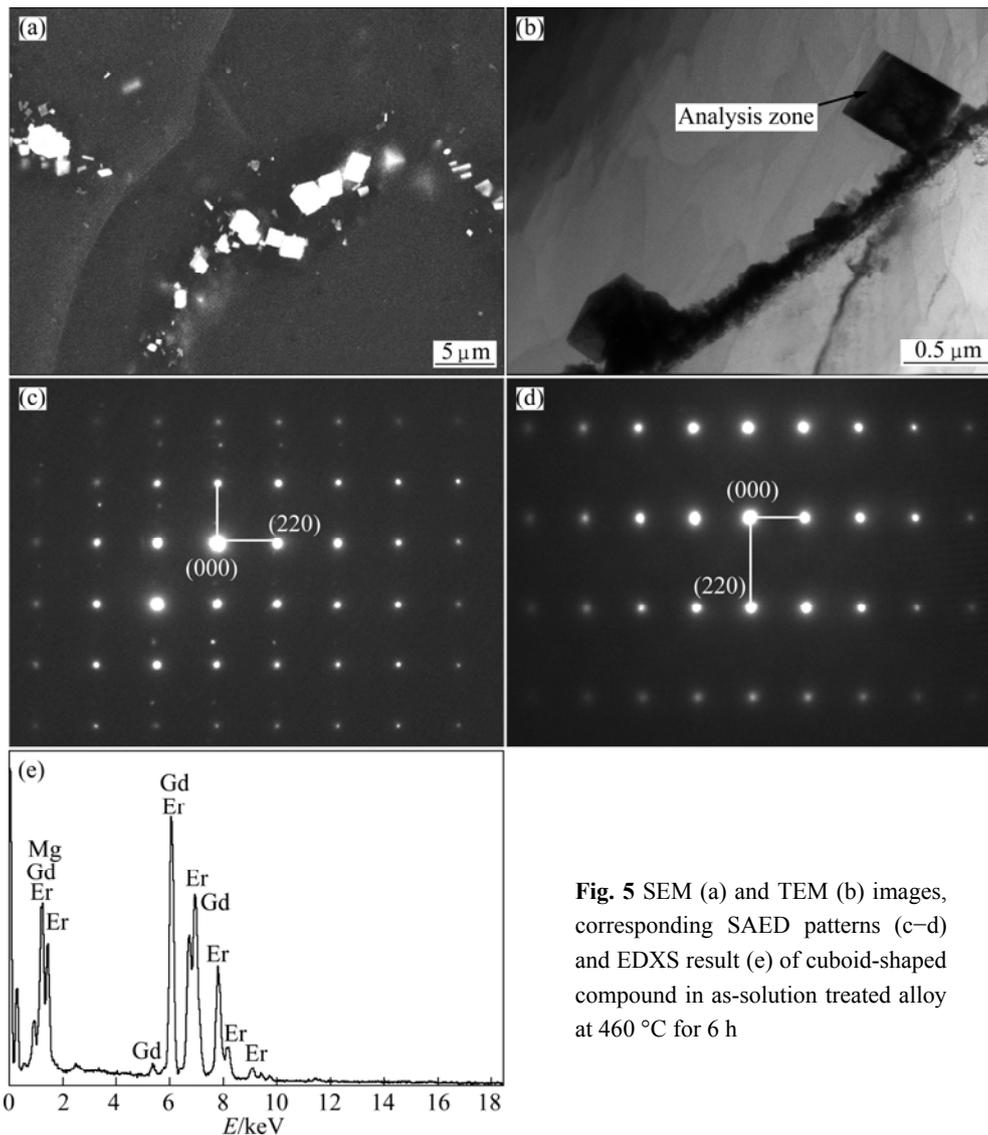


Fig. 5 SEM (a) and TEM (b) images, corresponding SAED patterns (c–d) and EDXS result (e) of cuboid-shaped compound in as-solution treated alloy at 460 °C for 6 h

some cuboid-shaped RE-rich phase precipitated.

3) The evolution of the microstructure from as-cast to as solid solution state involved $Mg_5(GdEr)$ eutectic phase \rightarrow Gd/Er atom diffusing into matrix \rightarrow spheroidic $Mg_5(GdEr)$ phase \rightarrow cuboid-shaped RE-rich phase \rightarrow grain boundary immigration.

References

- [1] COLE G S, SHERMAN A M. Light weight materials for automotive applications [J]. *Mater Charact*, 1995, 35: 3–9.
- [2] LI Ji-lin, CHEN Rong-shi, KE Wei. Microstructure and mechanical properties of Mg–Gd–Y–Zr alloy cast by metal mould and lost foam casting [J]. *Transactions of Nonferrous Metals Society of China*, 2011, 21(4): 761–766.
- [3] YANG Ming-bo, QIN Cai-yuan, PAN Fu-sheng, ZHOU Tao. Comparison of effects of cerium, yttrium and gadolinium additions on as-cast microstructure and mechanical properties of Mg–3Sn–1Mn magnesium alloy [J]. *J Rare Earth*, 2011, 29(6): 550–557.
- [4] ZHANG Kui, LI Xing-gang, LI Yong-jun, MA Ming-long. Effect of Gd content on microstructure and mechanical properties of Mg–Y–RE–Zr alloys [J]. *Transactions of Nonferrous Metals Society of China*, 2011, 18: s12–s16.
- [5] LIU Xi-bo, GUAN Xun, CHEN Rong-shi, HAN En-hou. Creep behavior of ageing hardened Mg–10Gd–3Y alloy [J]. *Transactions of Nonferrous Metals Society of China*, 2010, 20: s545–s549.
- [6] ZHANG Jing-huai, ZHE Leng, LIU Shu-juan, LI Ji-qing, ZHANG Mi-lin, WU Rui-zhi. Microstructure and mechanical properties of Mg–Gd–Dy–Zn alloy with long period stacking ordered structure or stacking faults [J]. *J Alloys Compd*, 2011, 509: 7717–7722.
- [7] LIU Ke, ROKHLIN L L, ELKIN F M, TANG Ding-xiang, MENG Jian. Effect of ageing treatment on the microstructures and mechanical properties of the extruded Mg–7Y–4Gd–1.5Zn–0.4Zr alloy [J]. *Mater Sci Eng A*, 2010, 527: 828–834.
- [8] LIN Dan, WANG Lei, MENG Fan-qiang, CUI Jian-zhong, LE Qi-chi. Effects of second phases on fracture behavior of Mg–10Gd–3Y–0.6Zr alloy [J]. *Transactions of Nonferrous Metals Society of China*, 2010, 20: s421–s425.
- [9] WANG Jie, YANG Yuan-sheng, TONG Wen-hui. Effect of purification treatment on corrosion resistance of Mg–Gd–Y–Zr alloy

- [J]. Transactions of Nonferrous Metals Society of China, 2011, 21(4): 949–954.
- [10] HU Yao-bo, DENG Juan, ZHAO Chong, WANG Jing-feng, PAN Fu-sheng. Microstructure and mechanical properties of as-quenched Mg–Gd–Zr alloys [J]. Transactions of Nonferrous Metals Society of China, 2011, 21: 732–738.
- [11] APPS P J, KARIMZADEH H, KING J F, LORIMER G W. Precipitation reactions in magnesium–rare earth alloys containing yttrium, gadolinium or dysprosium [J]. Scripta Materialia, 2003, 48: 1023–1028.
- [12] GAO X, HE S M, ZENG X Q, PENG L M, DING W J, NIE J F. Microstructure evolution in a Mg–15Gd–0.5Zr (wt.%) alloy during isothermal aging at 250 °C [J]. Mater Sci Eng A, 2006, 431: 322–327.
- [13] LI D H, DONG J, ZENG X Q, LU C, DING W J. Characterization of β'' precipitate phase in a Mg–Dy–Gd–Nd alloy [J]. Materials Characterization, 2007, 58: 1025–1028.
- [14] HE S M, ZENG X Q, PENG L M, GAO X, NIE J F, DING W J. Precipitation in a Mg–10Gd–3Y–0.4Zr (wt.%) alloy during isothermal ageing at 250 °C [J]. J Alloys Compd, 2006, 421: 309–313.
- [15] HONMA T, OHKUBO T, HONO K, KAMADO S. Chemistry of nanoscale precipitates in Mg–2.1Gd–0.6Y–0.2Zr (at.%) alloy investigated by the atom probe technique [J]. Mater Sci Eng A, 2005, 395: 301–306.
- [16] FORNASINI M L, MANFRINETTI P. GdMg₅: A complex structure with a large cubic cell [J]. Acta Cryst, 1986, C42: 138–141.
- [17] WANG Xu-dong, DU Wen-bo, WANG Zhao-hui, LI Shu-bo. Microstructures and mechanical properties of the Mg–xGd–Er (x=5, 7, 9 and 11wt%) alloys [J]. Adv Mater Res, 2011, 146–147: 1080–1085.
- [18] GAO Yan, WANG Qu-dong, GU Jin-hai, ZHAO Yang, TONG Yan. Behavior of Mg–15Gd–5Y–0.5Zr alloy during solution heat treatment from 500 to 540 °C [J]. Mater Sci Eng A, 2007, 459: 117–123.
- [19] LI D J, ZENG X Q, DONGA J, ZHAI C Q, DING W J. Microstructure evolution of Mg–10Gd–3Y–1.2Zn–0.4Zr alloy during heat-treatment at 773 K [J]. J Alloys Compd, 2009, 468: 164–169.
- [20] PENG Qiu-ming, DONG Han-wu, WU Yao-ming, WANG Li-min. Age hardening and mechanical properties of Mg–Gd–Er alloy [J]. J Alloys Compd, 2008, 456: 395–399.

固溶处理中 Mg–9Gd–2Er–0.4Zr 合金的组织演变

王朝辉, 杜文博, 王旭东, 刘 轲, 李淑波

北京工业大学 材料科学与工程学院, 北京 100124

摘 要: 利用 OM、SEM 和 TEM 研究了固溶处理过程中 Mg–9Gd–2Er–0.4Zr 铸造镁合金的微观组织演变, 其固溶处理温度和时间范围分别为 460~520 °C 和 3~12 h。结果表明, 随着固溶时间的延长和(或)温度的升高, 合金的晶粒尺寸和第二相形态均有显著变化。当固溶温度和时间分别为 460 °C 和 3 h 时, Mg₅(GdEr)相的体积分数降低并转变为破碎的岛状。当固溶温度和时间分别为 460 °C 和 6 h 时, Mg₅(GdEr)相已经完全溶解, 但是析出了少量的立方状富 RE 相。随着固溶温度的升高, Mg₅(GdEr)相的形貌演变与固溶温度 460 °C 和时间 6 h 时的相似。在固溶处理过程中合金的组织演变为: Mg₅(GdEr)共晶相→Gd/Er 原子向基体扩散→类球形 Mg₅(GdEr)相→立方状富 RE 相→晶界迁移。

关键词: Mg–Gd–Er–Zr 合金; 组织演变; 固溶处理; 共晶相

(Edited by Hua YANG)