

Effect of Y on age hardening response and mechanical properties of Mg–xY–1.5LPC–0.4Zr alloys

WANG Jun^{1,2}, NIE Jing-jiang¹, WANG Rong¹, XU Yong-dong¹, ZHU Xiu-rong¹, LING Guo-ping²

1. Ningbo Branch of China Ordnance Academy, Ningbo 315103, China;

2. Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China

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Abstract: Ageing hardening, microstructure and mechanical properties of Mg–xY–1.5LPC–0.4Zr ($x=0, 2, 4, 6$) alloys (LPC represents La-based rare earth metal) were investigated. It was found that the age hardening was enhanced, the grains became finer and the tensile strength was improved with the increase of Y content in Mg–Y–1.5LPC–0.4Zr alloy. The results show that the formed precipitates responsible for age hardening change from fine hexagonal-shaped equilibrium $Mg_{12}RE$ phase to metastable β' phase with orthorhombic-bc crystal structure when Y is added into Mg–1.5LPC–0.4Zr alloy, and the volume fraction of precipitate phases also increases. The cubic-shaped β - $Mg_{24}Y_5$ precipitate phases were also observed at grain boundaries in Mg–6Y–1.5LPC–0.4Zr alloy. The distribution of prismatic shaped β' phases and cubic shaped β - $Mg_{24}Y_5$ precipitate phases in Mg matrix may account for the remarkable enhancement of tensile strength of Mg–Y–LPC–Zr alloy. The Mg–6Y–1.5LPC–0.4Zr alloy exhibits maximum tensile strength at peak-aged hardness, and the values are 250 MPa at room temperature and 210 MPa at 250 °C.

Key words: magnesium alloy; rare earth; yttrium; age hardening; precipitate phases

1 Introduction

Magnesium alloys have attracted increasing interest in recent years for potential applications in the aerospace, aircraft and automotive industries due to their high specific strength [1,2]. The addition of rare earth (RE) elements including yttrium remarkably improves the mechanical properties of Mg alloys at room temperature (RT) and high temperatures due to the solution hardening and precipitation hardening [3–6].

The magnesium-based alloys containing RE elements are characterized by high strength, which is determined by the possibility of formation of a supersaturated Mg-based solid solution and its decomposition accompanied by strengthening effect [7]. The behavior of rare earths in binary alloys can be divided into two groups: the Ce group (La–Eu), and the Y group (Y and Gd–Lu). The use of rare earths enables both solid solution hardening and precipitation hardening, and the intermetallic compounds exhibit little diffusivity and a good coherent to the matrix [8]. ROKHLIN et al [9] reported that Mg alloys containing two RE metals which

belong to different subgroups can promote strengthening effectively.

Now, the RE metals are already commercially used for alloying magnesium-based alloys [9]. However, the cooperative effect of the LPC (La-based rare earth metal) and yttrium on the Mg alloy properties has rarely been studied; and their cooperative effect on the kinetics of decomposition of the Mg-based supersaturated solid solution is also studied insufficiently.

The purpose of the present work is to investigate the age hardening during isothermal ageing at 200 °C of Mg–xY–1.5LPC–0.4Zr ($x=0, 2, 4, 6$) alloys, the microstructure and tensile properties of these alloys.

2 Experimental

The Mg–Y–LPC–Zr alloys were made by melting Mg–20%LPC (85% La, 8% Ce, 7% Pr, mass fraction), Mg–20%Y, Mg–25%Zr master alloys, pure Mg in a graphite crucible with the protection of N_2 and SF_6 atmosphere. Ingots were solution treated for 10 h at 525 °C, then quenched into hot water. The hardness testing of the alloys was taken using Brinell hardness (HB) tester.

Tensile tests were performed at a crosshead speed of 1 mm/min at room temperature and high temperature using an Instron-type tensile testing machine. Microstructures of both as-cast and heat treated specimens were observed with an optical microscope and morphologies of secondary phase were observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

3 Results and discussion

3.1 Microstructure

Figure 1 gives the microstructures of as-cast Mg- x Y-1.5LPC-0.4Zr alloys. In the present work, the microstructure of as-cast Mg-1.5LPC-0.4Zr alloys consisted of approximately equiaxed dendrites of α -Mg solid solution surrounded by a net-shaped divorced eutectic of α -Mg solid solution and RE-rich intermetallic compounds, as shown in Fig. 1(a). An addition of 2% Y in the Mg-1.5LPC-0.4Zr alloy led to intermetallic compounds cracking and refining (Fig. 1(b)). A further increase in the Y content from 2% to 4% got the finer intermetallic compounds compared with Mg-2Y-1.5LPC-0.4Zr alloy (Fig. 1(c)). When 6% Y was added to Mg-1.5LPC-0.4Zr alloy, intermetallic compounds coarsened and increased (Fig. 1(d)). According to Mg-La-Y phase diagram [6], these RE-rich intermetallic compounds are Mg₁₂RE and Mg₂₄Y₅ compounds.

3.2 Age hardening response

Figure 2 compares the hardness curves of Mg-1.5MM-0.4Zr alloys with and without Y additions, obtained during isothermal ageing at 200 °C. The Mg-1.5LPC-0.4Zr alloy had a hardness value of about HB43 in as-quenched state, and exhibited a slight age hardening during isothermal ageing, with a maximum value of HB46. When 2% Y was added to the Mg-1.5LPC-0.4Zr alloy, a substantial increase in hardness was observed in as-quenched state. The Mg-2Y-1.5LPC-0.4Zr alloy had a hardness value of approximately HB 49 in the as-quenched state, which was about 15% higher than that of Mg-1.5LPC-0.4Zr alloy, but the increment of hardness after aging was slightly higher than that of Mg-1.5LPC-0.4Zr alloy. When 4% Y was added to the Mg-1.5LPC-0.4Zr alloy, a substantial increase in hardness was observed in both as-quenched and peak-aged states, compared with Mg-1.5LPC-0.4Zr alloy. The hardness values in the as-quenched and peak-aged condition were HB53 and HB62 respectively. With further addition of 6%Y, the Mg-6Y-1.5LPC-0.4Zr alloy exhibited a maximum hardness in as-quenched condition and the strongest age hardening. The hardness values in the as-quenched and peak-aged conditions were HB 72 and HB 83 respectively.

The microstructures of the peak-aged Mg- x Y-1.5LPC-0.4Zr alloys are shown in Fig. 3. Most of compounds have dissolved into Mg matrix, and the

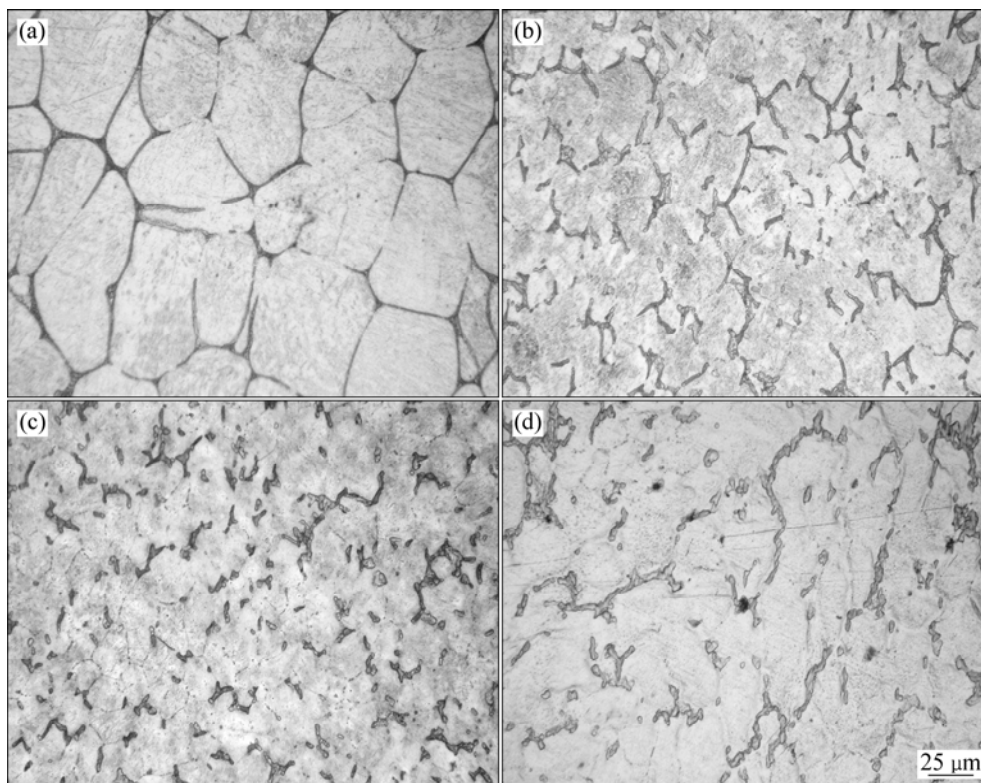


Fig. 1 Optical micrographs of as-cast Mg- x Y-1.5LPC-0.4Zr: (a) $x=0$; (b) $x=2$; (c) $x=4$; (d) $x=6$

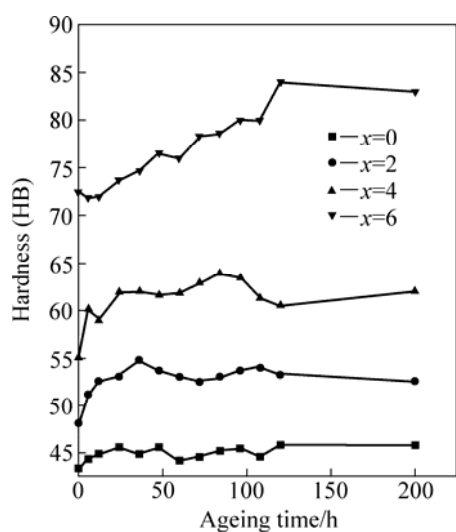


Fig. 2 Aging hardening curve of Mg- x Y-1.5LPC-0.4Zr alloys at 200 °C

average grain sizes are 70, 40, 26 and 22 μm , respectively. It was indicated that Y had a remarkable effect on grain refinement. A few block-shaped intermetallic particles still remained at/near grain boundaries in all alloys, and EDS analysis revealed that the typical chemical composition of the intermetallic particles is approximately 92.14Mg-6.38La-0.66Ce-0.82Y (mole fraction, %), which corresponds to the Mg_{12}RE type compound in peak-aged Mg-6Y-1.5LPC-

0.4Zr alloy shown in Fig. 4. Some fine cuboid-shaped intermetallic particles formed at grain boundaries in peak-aged Mg-6Y-1.5LPC-0.4Zr alloy, as shown in Fig. 5(a). The structure of the particles was also identified by electron diffraction pattern, as shown in Fig. 5(d), to be body-centred cubic (BCC). The composition of these particles was determined to be approximately Mg_{24}Y_5 by EDS. According to the above analysis, it is also indicated that LPC can dissolve into Mg_{24}Y_5 phase, and Y can also dissolve into Mg_{12}RE phase.

TEM micrograph of the peak-aged Mg-1.5LPC-0.4Zr alloy is shown in Fig. 6. As shown in Fig. 6(a), fine hexagonal-shaped precipitates were observed when viewed in an $[001]_{\text{Mg}}$ direction. Those precipitates seemed to be Mg_{12}RE phases [9]. The structure of the hexagonal-shaped phase was also identified by electron diffraction pattern, as shown in Fig. 6(b), to be BCT crystal structure of Mg_{12}RE . Fig. 7(a) shows bright field image recorded from the Mg-6Y-1.5LPC-0.4Zr alloy sample at peak-aged condition, with the incident electron beam approximately parallel to $[10\bar{1}0]_{\alpha}$. They revealed the presence of fine precipitates with prismatic plate-like morphology. The size of plate-shaped precipitates was typically 30–50 nm in length, with a thickness of <30 nm. The SAED pattern indicates that the peak-aged microstructure was predominantly metastable β' phase with BCO crystal structure, as shown in Fig. 7(b). However, the hexagonal-shaped Mg_{12}RE precipitates

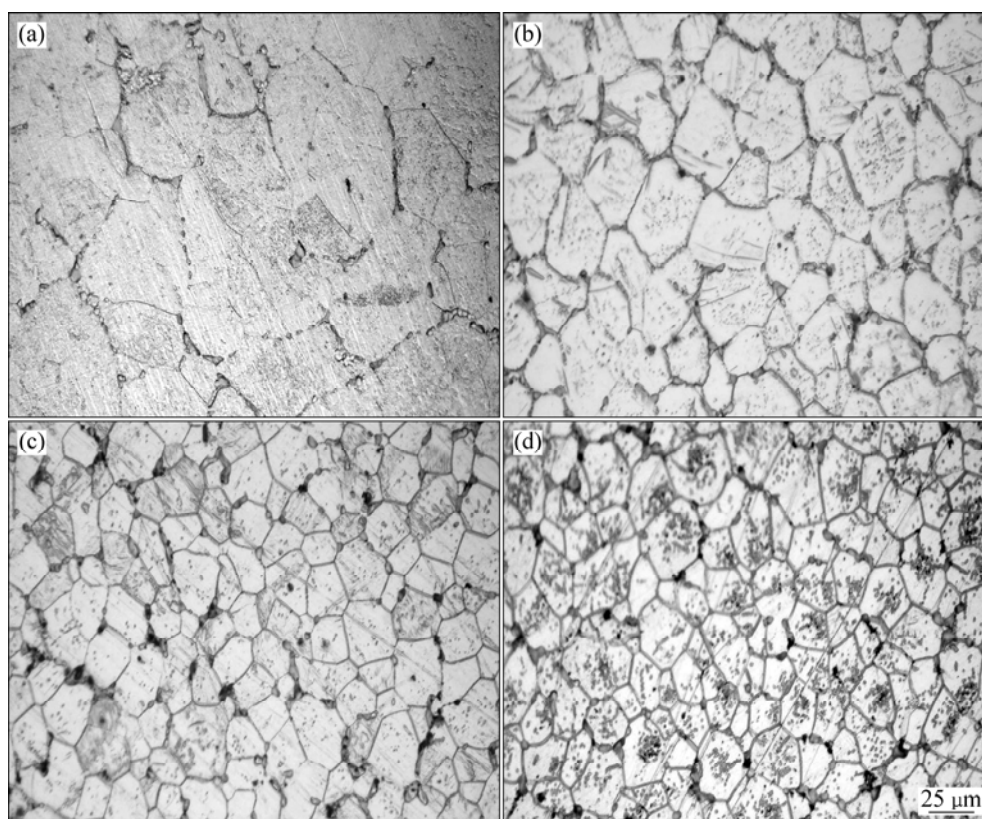


Fig. 3 Optical micrographs of peak-aged Mg- x Y-1.5LPC-0.4Zr alloys: (a) $x=0$; (b) $x=2$; (c) $x=4$; (d) $x=6$

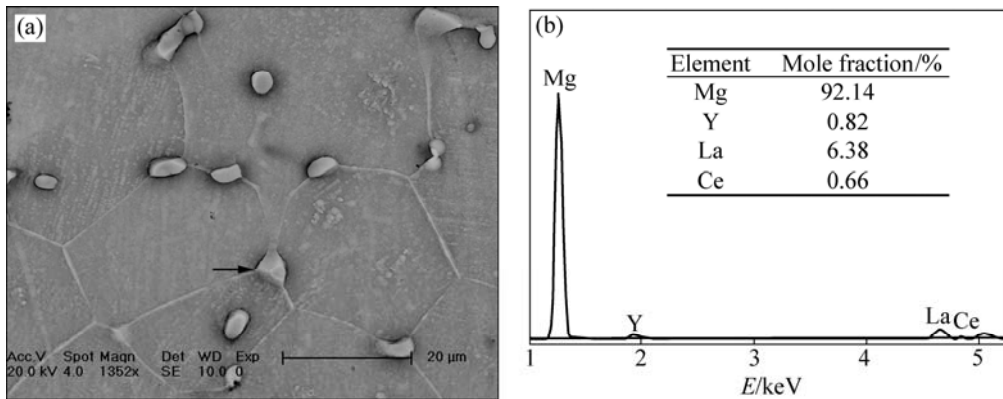


Fig. 4 SEM image of peak-aged Mg-6Y-1.5LPC-0.4Zr alloy (a) and corresponding EDS spectrum (b) of point indicated in Fig. 4(a)

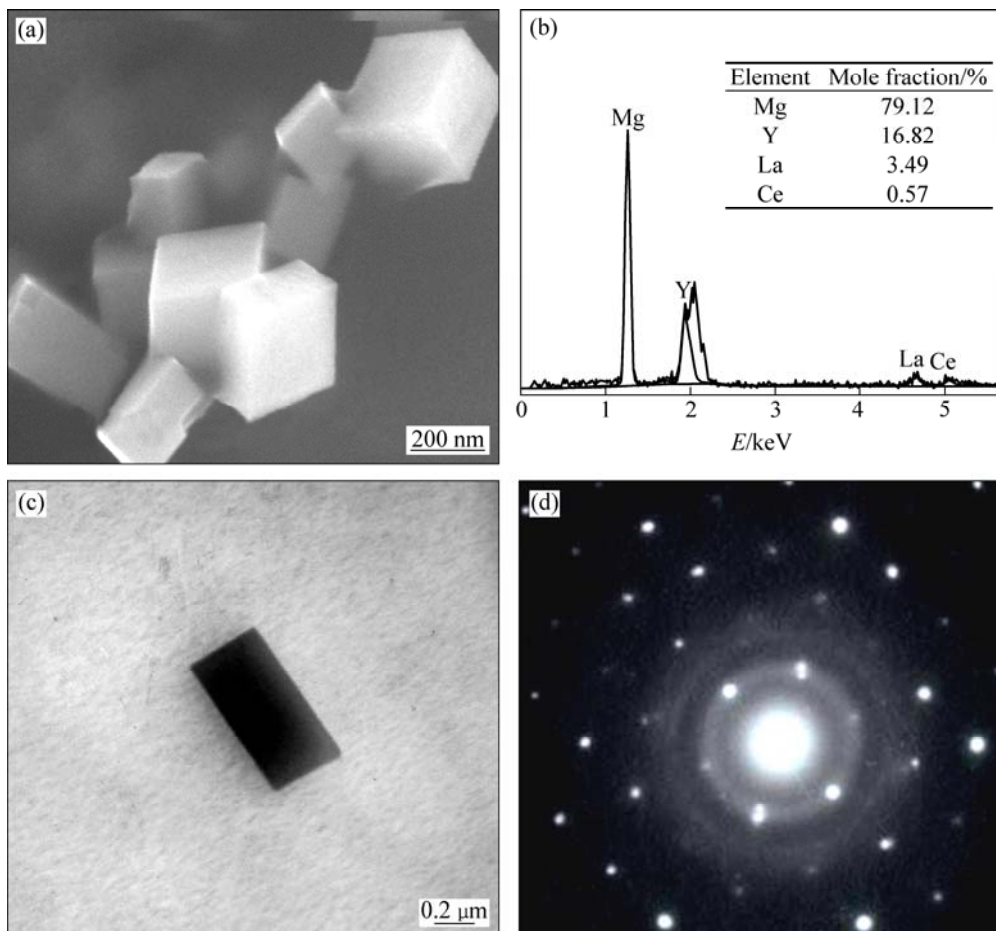


Fig. 5 SEM (a) and TEM (c) images and corresponding EDS (b) and SAED (d) patterns of cuboid-shaped precipitates in peak-aged Mg-6Y-1.5LPC-0.4Zr alloy

were not observed in the Mg-6Y-1.5LPC-0.4Zr alloy.

Mg-1.5LPC-0.4Zr alloy exhibited the least as-quenched hardness and the weakest age hardening in the present experiment. It is known that the solubility of La in solid Mg is quite small [5], and then the increase of hardness of Mg-La alloy during isothermal ageing condition is quite limited. It is indicated that the weak age hardening of Mg-1.5LPC-0.4Zr alloy is also associated with quite small solubility of LPC in solid Mg,

though fine hexagonal-shaped $Mg_{12}RE$ phases have marked effect on age hardening in Mg-1.5LPC-0.4Zr alloy.

The addition of Y to Mg-1.5LPC-0.4Zr alloy resulted in an increase of as-quenched hardness and significantly enhanced the age hardening. The increase of as-quenched hardness was likely attributed to the solid solution strengthening. The remarkable increase of peak hardness appeared to be associated with β' phases. We

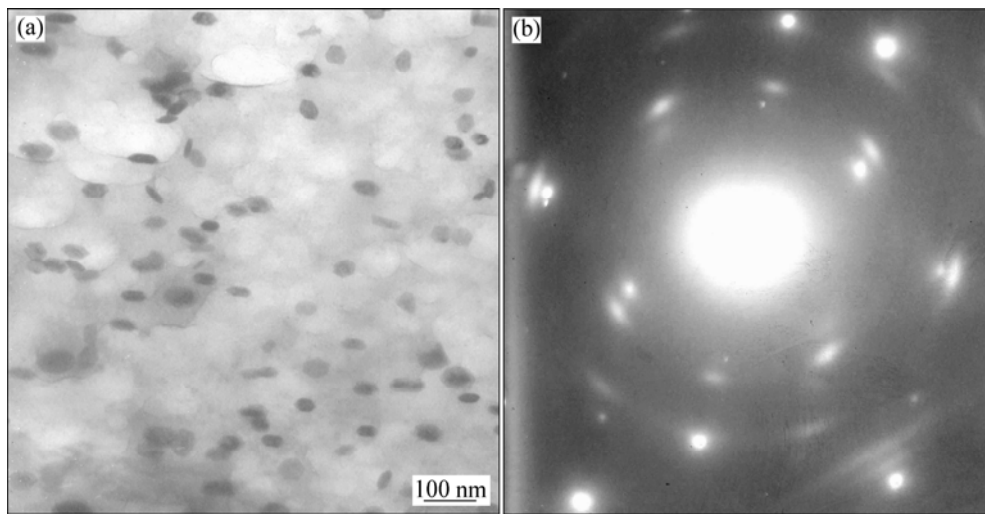


Fig. 6 TEM micrograph (a) and SAED pattern (b) of peak-aged Mg-1.5LPC-0.4Zr alloy

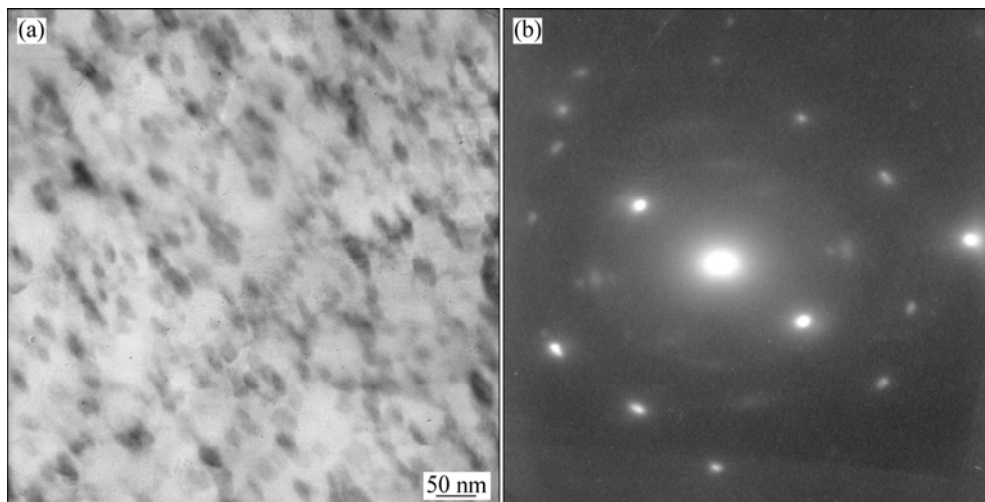


Fig. 7 TEM micrograph (a) and SAED pattern (b) of peak-aged Mg-6Y-1.5LPC-0.4Zr alloy

consider that the following factor is ascribed to improving the age hardening response. It is known that the atomic radius of LPC and Y is similar, which confirms that atom position of LPC and Y can be easily substituted each other when Y is added to Mg-1.5LPC-0.4Zr alloy. Accordingly, the solid solubility of Y changes. It was reported that the response of ageing was proved to be quite little for Mg-(3%–6%)Y at high temperature [10,11]. In the present experiment, when Y was added to Mg-1.5LPC-0.4Zr alloy, only the decomposition of the supersaturated solid solution of typical Mg-Y alloy was found. The experimental result indicated that La-based rare earth metal was dissolved into the decomposition products of the supersaturated solid solution in the Mg-Y alloy, which led to an increase in the amount of particles precipitating upon the decomposition and to an acceleration of diffusion process. Some similar

characters were reported for Mg-Ce-Y alloy containing two rare earth metals belonging to two different (cerium and yttrium) subgroups [10]. It was indicated that the solid solubility of Y would be decreased relatively in Mg-LPC-Y-Zr alloys. According to the previous result, NIE and MUDDLE [13] reported that the peak-aged microstructure contained predominantly the phases β' , β_1 and β in WE54 alloy. In the present experiment, it was possible that the metastable β' with BCO crystal structure was mainly attributed to the improvement of ageing hardening in Mg-Y-LPC-Zr alloys.

3.3 Tensile properties

Tensile properties of peak-aged samples of Mg-xY-1.5LPC-0.4Zr alloys ($x=0, 2, 4, 6$) are provided in Fig. 8. At both room temperature and 250 °C, the ultimate tensile strength (UTS), yield strength (YS) and ductility of Mg-2Y-1.5LPC-0.4Zr alloy were all higher

than those of the Y-free alloy. The yield strength of Mg–2Y–1.5LPC–0.4Zr alloy was about 19% and 34% higher than that of Y-free alloy at room temperature and 250 °C, respectively. A further increase in Y content to 4% in the alloy only led to a slightly increase in ultimate tensile strength and yield strength, compared with Mg–2Y–1.5MM–0.4Zr alloy. When 6% Y was added to the Mg–1.5LPC–0.4Zr alloy, the alloy exhibited the maximum ultimate tensile strength and yield strength at peak-aged hardness, and the values were 250 MPa and 140 MPa at room temperature, and 210 MPa and 130 MPa at 250 °C respectively, and the ductility had a slight decrease.

The tensile results demonstrated that adding Y into the Mg–1.5LPC–0.4Zr alloy can improve the mechanical properties, especially the stability of the alloy at high temperature (250 °C). According to the TEM observation, it can be confirmed that the precipitate phases changed from equilibrium $Mg_{12}RE$ phase to metastable β' phase when Y was added to Mg–1.5LPC–0.4Zr alloy, and the volume fraction of intermetallic phases also increased. According to the diagrams of Mg with La, Ce, Pr and Nd [7], the solid solubility of LPC in Mg matrix is quite small. It is difficult to assume that an adequate amount of intermetallic compounds of Mg–1.5LPC–0.4Zr alloy can be formed during isothermal ageing. For Mg–Y–LPC–Zr

alloys, the LPC accelerates the decomposition of these alloys during isothermal ageing, and an adequate amount of metastable β' phases are formed. These β' phases in grains have also high melting point and good thermal stability, which is related with the low diffusion speed of Y and LPC elements in the α -Mg matrix. It can effectively prevent gliding of dislocation and deformation of grain at room and elevated temperatures. It was reported that the β' or β phase plays a positive role in strengthening by providing effective barriers to gliding of dislocation in Mg–Y–Nd alloy [13,14]. It was known that high dense precipitate plates formed on habit plane of the matrix phase provide the least effective barrier to gliding of dislocations. Compared with $Mg_{12}RE$ phases, the increment in yield stress produced by prismatic precipitate plates is invariably larger [15]. In addition to precipitate strength in Mg matrix, $Mg_{24}Y_5$ phases and $Mg_{12}RE$ phases which were observed to exist as relatively large particles and have good thermal stability can still strengthen boundary at room and elevated temperatures. These particles can effectively pin grain boundaries and prevent gliding of grain boundaries. Accordingly, these particles play an important role in strengthening alloy.

Besides the precipitates strengthening, the change of grain size is also an important factor affecting the yield strength. As shown in Fig. 3, the grain sizes were reduced greatly. According to the Hall-Petch equation [16]:

$$\sigma = \sigma_0 + kd^{-1/2}$$

where σ is the 0.2% yield strength, d is the average grain size, and σ_0 and k are parameters determined for the polycrystalline material, the 0.2% yield strength should increase with increasing Y content. It was indicated that this result was well consistent with the experimental result in Fig. 8.

4 Conclusions

1) The age hardening of Mg–Y–LPC–Zr alloys can be significantly enhanced, the grain sizes became finer and the tensile strength was improved with increasing Y contents.

2) The precipitate phases changed from equilibrium $Mg_{12}RE$ phase to metastable β' phase with BCO crystal structure when Y was added to Mg–1.5LPC–0.4Zr alloy, and the volume fraction of precipitate phases also increased. The remarkable improvement in strength for Mg–Y–LPC–Zr alloy is associated with the distribution of prismatic-shaped β' phases and cubic-shaped β - $Mg_{24}Y_5$ precipitate phases in Mg matrix.

3) The Mg–6Y–1.5LPC–0.4Zr alloy exhibited a maximum tensile strength at peak-aged hardness, and the values were 250 MPa at room temperature and 210 MPa at 250 °C respectively.

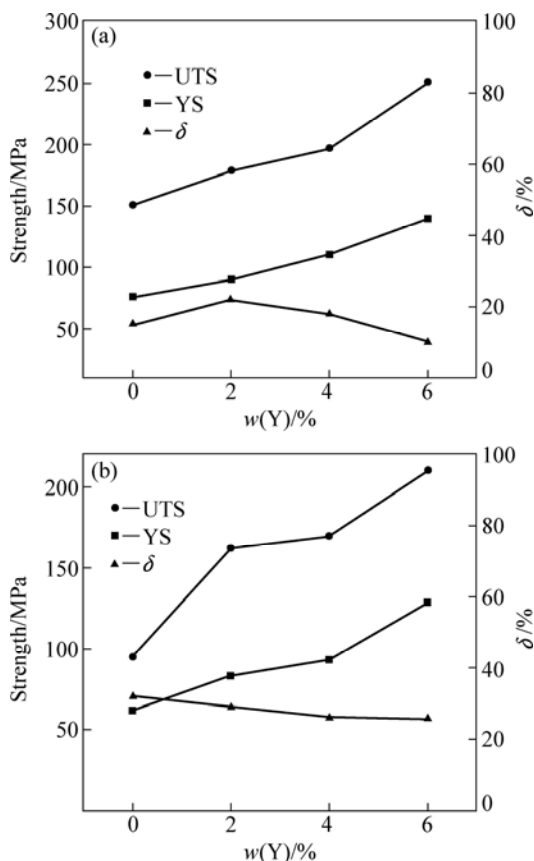


Fig. 8 Tensile properties of peak-aged Mg–xY–1.5LPC–0.4Zr alloys at room temperature (a) and 250 °C (b)

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钇含量对 Mg–xY–1.5LPC–0.4Zr 合金的时效硬化和力学性能的影响

王 军^{1,2}, 聂景江¹, 王 荣¹, 徐永东¹, 朱秀荣¹, 凌国平²

1. 中国兵器科学研究院宁波分院, 宁波 315103;

2. 浙江大学 材料科学与工程系, 杭州 310027

摘 要: 研究钇含量对 Mg–xY–1.5LPC–0.4Zr 镁合金的时效硬化、显微组织和力学性能的影响(其中 LPC 代表富镧混合稀土金属)。当将 Y 加入 Mg–1.5LPC–0.4Zr 时, 随着 Y 含量的增加, 合金的时效硬化反应相应增强, 晶粒尺寸变小, 强度增加。当将 Y 添加到 Mg–1.5LPC–0.4Zr 合金中时, 时效析出相发生改变, 由 Mg–LPC 基合金的稳态 Mg₁₂RE 相转变为 Mg–Y 基合金的亚稳态 β' 相, 且随着 Y 含量的增加, β' 相的数量也相应增多。在合金晶界上还发现了稳态立方形的 β–Mg₂₄Y₅ 相。对于 Mg–Y–LPC–Zr 合金, 拉伸性能的改善主要归功于均匀、弥散分布的 β' 相, 在晶界上的 β–Mg₂₄Y₅ 相对合金的晶界也有明显的强化作用。当 Y 含量达到 6% 时, 合金的拉伸强度最大, 合金在室温和 250 °C 的抗拉强度分别是 250 MPa 和 210 MPa。

关键词: 镁合金; 稀土; 钇; 时效硬化; 沉淀相

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