

Effect of zinc addition on microstructure and mechanical properties of Mg–7Y–3Sm–0.5Zr alloy

ZHAO Yang¹, WANG Qu-dong^{1,2}, GAO Yan¹

1. National Engineering Research Center of Light Alloy Net Forming,
Shanghai Jiao Tong University, Shanghai 200240, China;

2. State Key Laboratory of Metal Matrix Composites, Shanghai Jiao Tong University, Shanghai 200240, China

Received 10 November 2011; accepted 31 May 2012

Abstract: The effect of zinc addition on the microstructure and mechanical properties of Mg–7Y–3Sm–0.5Zr casting alloy was investigated. Creep test was carried out at 200–300 °C under 50–120 MPa. Within the limits of the creep test conditions used in this study, the creep activation energy of the investigated alloys was in the range of 156–221 kJ/mol. The microstructure evolution during creep was characterized by optical metallography, SEM and TEM. The results show that the creep life of the alloy is increased from 52.2 to 152.8 h at 300 °C under 50 MPa by only 1% addition of Zn, though both the alloys have similar creep behaviors below 250 °C, which suggests that the thermally stable compound and lamellar structure can improve the high temperature creep resistance of the alloy with the addition of Zn.

Key words: Mg–Y–Sm–Zr alloy; zinc; microstructure; mechanical properties; creep behavior

1 Introduction

Magnesium alloys are being rapidly developed as alternative lightweight materials to ferrous and aluminum alloys due to their remarkable effort to cut exhaust emission of automobiles through mass reduction [1]. In the automobile industry, however, the use of magnesium alloys has been limited in thermally mild applications, such as instrument panel, steering wheel and cylinder head cover, owing to their poor high temperature performances, not capable of more thermally severe environment like powertrain parts that could get more significant mass savings. Therefore, there is a strong demand for the improvement in the high temperature properties, especially creep resistance of the magnesium alloys.

It is reported that the addition of rare earth elements (RE) could remarkably improve the mechanical properties of magnesium, especially at elevated temperatures, since the solubility of the RE elements

rapidly decreases with decreasing temperature, and dispersive precipitation takes place to enhance the mechanical properties of the alloys [2,3]. A number of binary and ternary Mg–RE alloys have been developed in recent decade [4–6]. For instance, Mg–Y–Sm–Zr alloy has considerable precipitation hardening with mechanical properties superior to the commercial WE54 alloy [7]. In 2001, Mg–2Y–1Zn alloy with extremely high yield strength of 610 MPa and reasonable elongation of 5% was developed by rapid solidification powder metallurgy process [8]. The coexistence of an HCP (2H)-Mg fine grain matrix with 100–200 nm in size and a long period stacking order (LPSO) phase, which is basically constructed by ABCBCB stacking (6H-type) of closed-packed planes of the Mg crystal, is contributed to the excellent performance. Moreover, LPSO structure prevents the growth of $\{10\bar{1}2\}$ deformation twins. It is very interesting that such very small additives like 1%–2% Zn and Y into pure Mg dramatically change its microstructure and mechanical properties. In 2003, AMIYA et al [9] and MATSUURA et al [10]

Foundation item: Project (51074106) supported by the National Natural Science Foundation of China; Project (2009AA033501) supported by the National High-Tech Research and Development Program of China; Projects (2011BAE22B01-5, 2006BAE04B01-2) supported by the National Science and Technology Pillar Program during the 12th Five-Year Plan Period; Project (06SR07104) supported by the International Cooperation Fund of Shanghai Science and Technology Committee, Shanghai/Rhone-Alpes Science and Technology Cooperation Fund, China

Corresponding author: WANG Qu-dong; Tel: +86-21-54742715; E-mail: wangqudong@sjtu.edu.cn
DOI: 10.1016/S1003-6326(11)61409-X

subsequently reported that Y and Zn elements were enriched in the long-period region and the periodicity changed from 6H-type to 14H-type with increasing cooling rate in melt spinning (melt-spun) Mg₉₇Zn₁Y₂. ITOI et al [11] reported that a LPSO structure with 18R-type was observed in Mg₉₇Zn₁Y₂ alloy prepared by Cu-mold casting and induction melting methods. After annealing at 773 K for 5 h, the 18R-type LPS structure transformed to a 14H-type LPSO structure. Considering the special role of Zn with RE elements, the addition of Zn was introduced into Mg–Gd–Y–Zr alloys to improve their mechanical properties [12–14]. LPSO phases along grain boundaries were clearly observed by optical microscopy. However, little study on the microstructures and mechanical properties especially creep resistance of Mg normal casting alloy with the addition of Zn and RE has been reported so far.

In the present work, the microstructures, mechanical properties at room temperature and elevated temperatures and creep behaviors of Mg–7Y–3Sm–*x*Zn–0.5Zr alloys were investigated to develop a novel heat-resistant magnesium alloy system.

2 Experimental

Four alloys with nominal compositions of Mg–7Y–Sm–0.5Zr (WS73K), Mg–7Y–3Sm–0.5Zn–0.5Zr (WSZ7305K), Mg–7Y–3Sm–1Zn–0.5Zr (WSZ731K) and Mg–7Y–3Sm–2Zn–0.5Zr (WSZ732K) were investigated. The alloy ingots were prepared from high-purity Zn (99.99%), Mg–25%Y, Mg–25%Sm and Mg–30%Zr master alloys in a steel crucible by an electric resistance furnace under an anti-oxidizing flux of 1% SF₆ and 99% CO₂. The chemical compositions of these alloys analyzed by inductive coupled plasma (ICP) technique are listed in Table 1.

Table 1 Chemical compositions of investigated alloys (mass fraction, %)

Alloys	Composition/%				
	Y	Sm	Zn	Zr	Mg
WS73K	6.90	2.75	–	0.35	Bal.
WSZ7305K	6.67	2.78	0.55	0.36	Bal.
WSZ731K	6.80	2.73	1.05	0.31	Bal.
WSZ732K	6.51	2.61	2.00	0.41	Bal.

The ingots were solution treated at 525 °C for 10 h (T4-treatment), and then quenched into water at about 60 °C. A subsequent aging treatment was performed at 225 °C for 20 h (T6-treatment). The tensile test was

performed using standard tensile testing machine at room temperature, 200, 250 and 300 °C, and the samples were held for 30 min to get uniformly distributed temperature before tensile tests. Creep resistances of the alloys were evaluated at 200–300 °C and 50–120 MPa by a CSS–3902 multifunction material tester using plate specimens with dimensions of 2 mm×10 mm. The microstructures of the alloys were studied by optical microscopy (OM), scanning electron microscopy (SEM) and transmission electron microscope (TEM). Double-jet electropolisher was used to prepare thin foils for TEM observation (Philips CM20). The thinning was carried out in an electrolyte consisting of one-third nitric acid and two-thirds methanol at –30 °C and 15 V. The phase structures of the alloys were characterized by X-ray diffractometry (XRD) in a scanning range of 20°–80°.

3 Results and discussion

3.1 Microstructure of alloys

The microstructures of the as-cast Mg–7Y–3Sm–*x*Zn–0.5Zr alloys are shown in Fig. 1. The microstructure of the as-cast WS73K alloy is mainly composed of α -Mg, semi-continuous network-shaped eutectic compound distributed at the α -Mg grain boundaries and very few granular phase in the α -Mg grain (Fig. 1(a)). The average grain size of the WS73K alloy is about 40 μ m. The average grain sizes of the other three alloys with Zn addition appear to be similar to that of the WS73K alloy. However, the morphologies of the second phases are different and a few amount of lamellar-shaped phases are observed in WSZ7305K, WSZ731K and WSZ732K alloys, as shown in Figs. 1(b), (c) and (d). The lamellar-shaped phase appears to grow from grain boundaries to the inside of grains and has the same growing direction in one grain, implying that the lamellar-shaped phase has specific orientation relationship with Mg matrix. Its volume fraction increases with increasing Zn content. The similar phase was reported in as-cast Mg–Gd–Y–Zn–Zr alloy [14].

Figure 2 shows the microstructures of the alloys after T4 treatment, indicating that almost all the eutectic compounds in WS73K alloy are dissolved into α -Mg at 525 °C for 10 h. The average grain size is about 75 μ m, which is much larger than that of the as-cast WS73K alloy, and a few small granular phases can be observed near the grain boundaries (Fig. 2(a)). It is also seen that the eutectic compounds in WSZ7305K, WSZ731K and WSZ732K alloys are partly dissolved into the Mg matrix, and more distinct straight lamellar-shaped phases with a specific grain orientation are generated at grain boundaries, as shown in Figs. 2(b), (c) and (d). The size,

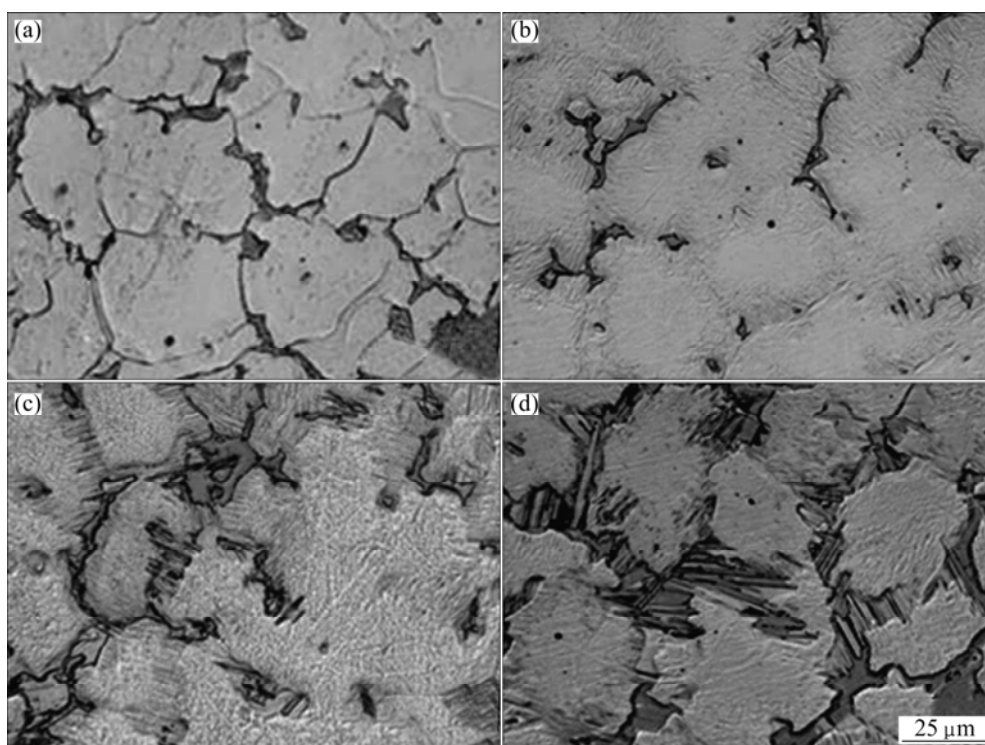


Fig. 1 OM images of as-cast alloys: (a) WS73K; (b) WSZ7305K; (c) WSZ731K; (d) WSZ732K

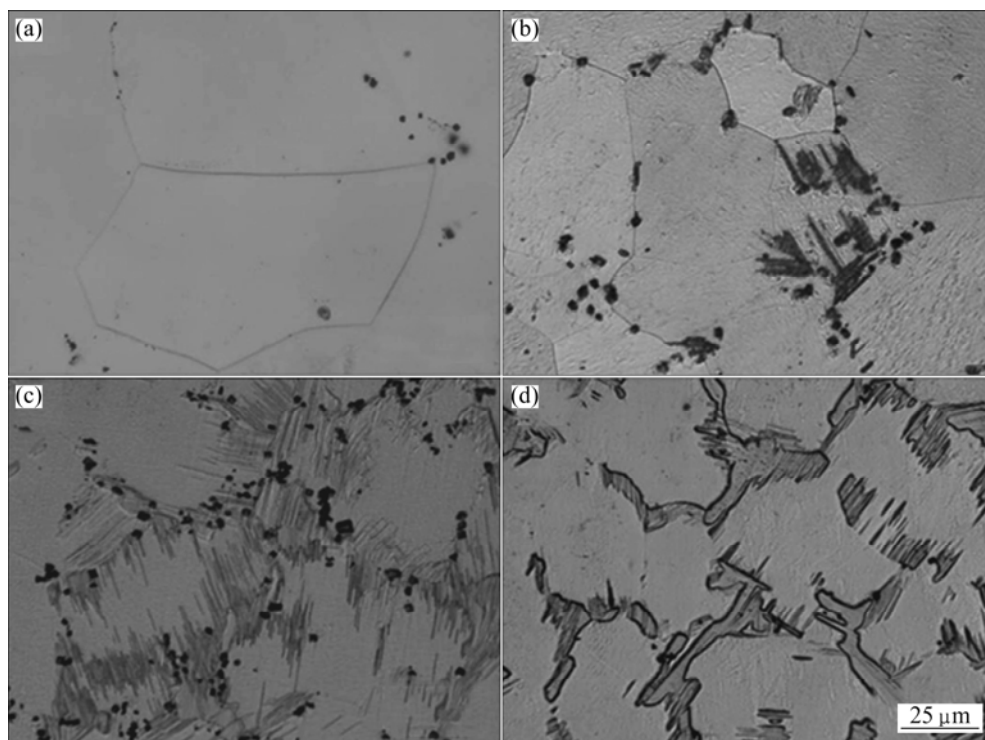


Fig. 2 OM images of solution-treated alloys: (a) WS73K; (b) WSZ7305K; (c) WSZ731K; (d) WSZ732K

volume fraction and morphology of these lamellar-shaped phases are different from those of the as-cast specimens. The average grain sizes of the alloys with Zn addition, however, have no significant change. It seems that the alloys with Zn addition have better stability at high temperature. On the other hand, it can be seen that

the higher the Zn content is, the more the undissolved compounds remain after T4 treatment, implying that the solubility of Y and Sm atoms in Mg decreases with the addition of Zn, and these second phases have good thermal stability. More small granular phases can be seen near the grain boundaries or inside the grains of the

T4-treated alloys, especially for WSZ731K alloy. It seems that these phases mainly form during high temperature heat-treatment. It was reported that similar microstructures were observed in T4-treated Mg–10Gd–3Y–1.2Zn–0.4Zr alloy [14], and it was believed that the fine lamellar phase was 14H LPSO phase decomposed from the block-shaped 14H LPSO phase at grain boundaries that was transformed from $\text{Mg}_5(\text{Gd,Y,Zn})$ eutectic compounds during heat treatment.

The XRD patterns of the as-cast and T4-treated WS73K and WSZ732K specimens are shown in Fig. 3. Only two phases can be recognized in the as-cast alloys, α -Mg and $\text{Mg}_5(\text{Y,Sm})$, which means no different crystal structures come out with the addition of Zn. After T4-treatment, only the peaks of α -Mg can be seen since the eutectic compound of $\text{Mg}_5(\text{Y,Sm})$ has dissolved into the Mg matrix. The extra peaks designated as $\text{Mg}_{12}(\text{Y,Sm})\text{Zn}$ can be observed in the T4-treated WSZ732K alloy.

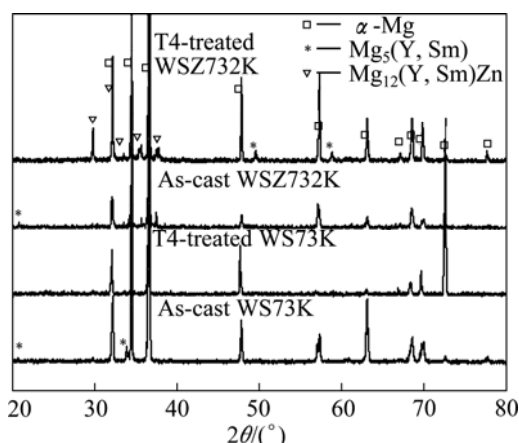


Fig. 3 XRD patterns of as-cast and T4-treated WS73K, as-cast and T4-treated and WSZ732K alloys

3.2 Mechanical properties at elevated temperatures

The tensile properties of Mg–7Y–3Sm–xZn–0.5Zr alloys at room and elevated temperatures are shown in Fig. 4. It shows that the ultimate tensile strength (UTS) decreases with increasing Zn additions at room temperature. This is probably due to the consumption of Y and Sm to form compounds with Zn, therefore the precipitation density decreases during the aging treatment. At elevated temperatures, the UTS of WS73K alloy decreases rapidly from 330 MPa at room temperature to 190 MPa at 300 °C with a 43% reduction. For Zn-added alloys, however, the UTS loss at elevated temperatures are much less than that of the Zn-free WS73K alloy, which are 22%, 20% and 10%, respectively. The loss of UTS decreases with increasing Zn content, indicating that Zn can improve the thermal stability of the alloy. At 300 °C, the UTS of WSZ7305K alloy is still 228 MPa, better than that of the other alloys.

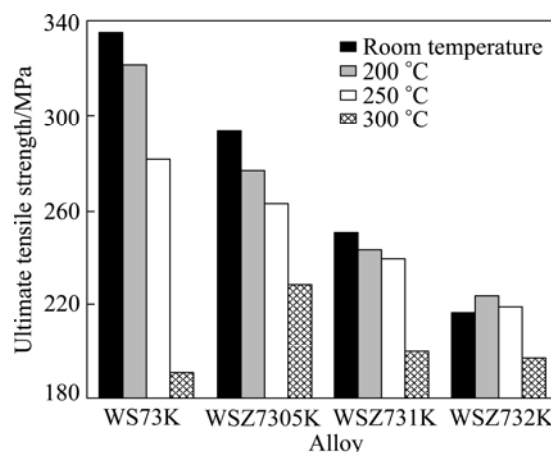


Fig. 4 Tensile properties of alloys at room and elevated temperatures

3.3 Creep resistance

Figure 5 shows the typical creep curves for the Mg–7Y–3Sm–xZn–0.5Zr alloys obtained at 300 °C and 50 MPa. After 50 h creeping under this investigated environment, the alloys without the addition of Zn, T6 treated WS73K and as-received WE54, all rapidly rupture. With increasing Zn addition, the creep life of the alloys extends significantly. The Zn-added WSZ7305K and WSZ731K alloys have creep life of 125.1 and 152.8 h, respectively, much better than that of the commercial alloy WE54. With the addition of 2% Zn, however, the creep life of WSZ732K is about 80 h less than that of lower Zn content alloys, but remarkably superior to Zn-free alloys in this study. This is most likely due to the coarse secondary phase along the grain boundary.

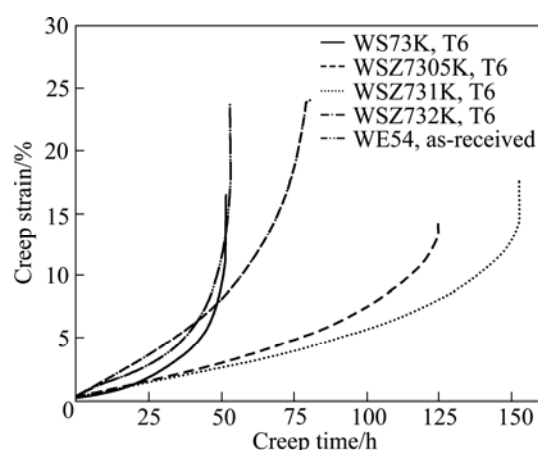


Fig. 5 Creep curves of studied alloys at 300 °C and 50 MPa

The activation energies for the creep of the investigated alloys can be calculated from the slope of the graphs in Fig. 6, which are higher than that of the self-diffusion of magnesium varies from 81 to 135 kJ/mol [15–17]. Two temperature regions can be recognized from the difference in the activation energy at 250 °C.

The activation energy is influenced by the slip planes of dislocations, i.e. basal and prismatic planes, which are controlled by the amount and kind of precipitates and solute atoms [17]. Two different creep deformation mechanisms are proposed, the cross slips of dislocations from basal to prismatic planes and the drag of jogs by screw dislocations to leave a trail of interstitials [18].

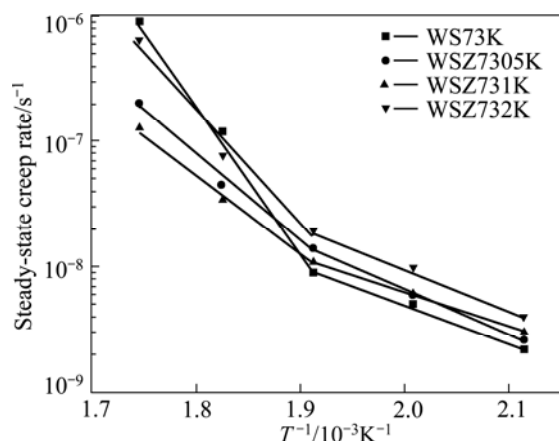


Fig. 6 Relationship between steady-state creep rate of alloys and reciprocal of test temperature under 50 MPa

Figure 7 shows the TEM image and corresponding selected areas electron diffraction pattern of peak-aged WS731K alloy. These plate-shaped β' precipitates, formed on prismatic planes $\{11\bar{2}0\}$ of the Mg matrix with the body centered orthorhombic structure ($a=0.640$ nm, $b=2.223$ nm, $c=0.521$ nm), effectively control the dislocation motion on the basal planes [7]. It is also seen that the lamellar precipitated LPSO is distributed uniformly in the grains. The result of TEM observation is similar to that reported by HONMA et al [13] for the Mg–Gd–Y–Zn–Zr alloys. The significant improvement

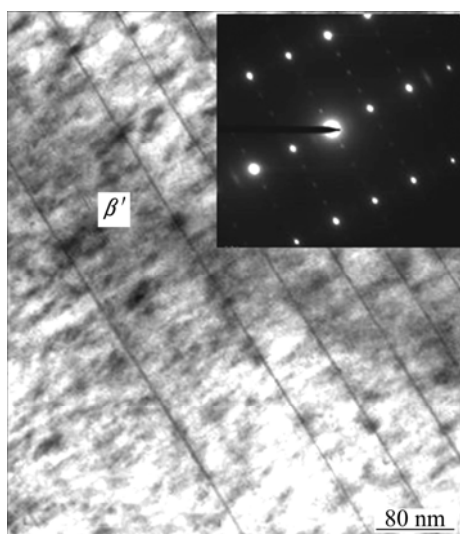


Fig. 7 TEM image and SAED pattern of peak-aged WS731K alloy with beam direction $[2\bar{1}\bar{1}0]_{\alpha}([100]_{\beta'})$

in creep resistance of Mg–Y–Sm–Zr alloys with Zn addition is considerably attributed to the co-existing precipitates of β' phase and LPSO structure.

4 Conclusions

1) The microstructure of the as-cast WS73K alloy is mainly composed of α -Mg and intermetallic compound $Mg_{12}(Y,Sm)$. After T4-treatment, almost all the eutectic compounds are dissolved into α -Mg. The microstructure of the as-cast Zn-added alloy also consists of α -Mg and $Mg_{12}(Y,Sm)$. However, $Mg_{12}(Y,Sm)Zn$ phase is formed after T4-treatment.

2) The Zn-containing alloys have better tensile properties at 300 °C and excellent creep resistance at 300 °C and 50 MPa, superior to the Zn-free WS73K alloy and commercial heat resistant WE54 alloy.

3) The co-existing precipitates of β' phase and LPSO structure in Zn-added alloys are effective strengthening phases at high temperature.

Acknowledgments

The authors would like to thank the members of Mg research groups both in Shanghai Jiao Tong University, China, and the University of Auckland, New Zealand.

References

- [1] ROKHLIN L L. Magnesium alloys containing rare earth metals [M]. London: Taylor & Francis, 2003: 22–50.
- [2] HE Shang-ming. Study on the microstructural evolution, properties and fracture behavior of Mg–Gd–Y–Zr(–Ca) alloys [D]. Shanghai: Shanghai Jiao Tong University, 2007: 23–24. (in Chinese)
- [3] NIE J F, MUDDLE B C. Characterisation of strengthening precipitate phases in a Mg–Y–Nd alloy [J]. Acta Mater, 2000, 48: 1691–1703.
- [4] MORDIKE B L. Creep-resistant magnesium alloys [J]. Mater Sci Eng A, 2002, 324: 103–112.
- [5] HE S M, ZENG X Q, PENG L M, GAO X, NIE J F, DING W J. Microstructure and strengthening mechanism of high strength Mg–10Gd–2Y–0.5Zr alloy [J]. J Alloys Compd, 2007, 427: 316–323.
- [6] ANYANWU I A, KAMADO S, KOJIMA Y. Aging characteristics and high temperature tensile properties of Mg–Gd–Y–Zr alloys [J]. Mater Trans, 2001, 42: 1206–1211.
- [7] LI D Q, WANG Q D, DING W J. Characterization of phases in Mg–4Y–4Sm–0.5Zr alloy processed by heat treatment [J]. Mater Sci Eng A, 2006, 428: 295–300.
- [8] KAWAMURA Y, HAYASHI K, INOUE A, MASUMOTO T. Rapidly solidified powder metallurgy Mg97Zn1Y2 alloys with excellent tensile yield strength above 600 MPa [J]. Mater Trans, 2001, 42: 1171–1176.
- [9] AMIYA K, OHSUNA T, INOUE A. Long-period hexagonal structures in melt-spun Mg97Ln2Zn1 (Ln=Lanthanide Metal) alloys [J]. Mater Trans, 2003, 44: 2151–2156.
- [10] MATSUURA M, SAKURAI M, AMIYA K, INOUE A. Local structures around Zn and Y in the melt-quenched Mg97Zn1Y2 ribbon [J]. J Alloys Compd, 2003, 353: 240–245.
- [11] ITOI T, SEIMIYA T, KAWAMURA Y, HIROHASHI M. Long

- period stacking structures observed in Mg₉₇Zn₁Y₂ alloy [J]. Scripta Mater, 2004, 51: 107–111.
- [12] LI J P, YANG Z, LIU T, GUO Y C, XIA F, YANG J M, LIANG M X. Microstructures of extruded Mg–12Gd–1Zn–0.5Zr and Mg–12Gd–4Y–1Zn–0.5Zr alloys [J]. Scripta Mater, 2007, 56: 137–140.
- [13] HONMA T, OHKUBO T, KAMADO S, HONO K. Effect of Zn additions on the age-hardening of Mg–2.0Gd–1.2Y–0.2Zr alloys [J]. Acta Mater, 2007, 55: 4137–4150.
- [14] LI D J, ZENG X Q, DONG 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.
- [15] VIGARALI S S, LANGDON T G. Deformation mechanism in HCP metals at elevated temperatures (1). Creep behavior of magnesium [J]. Acta Metall, 1981, 29: 1969–1982.
- [16] ASHBY M F, JONES D R H. Engineering materials (1): An introduction to their properties and applications [M]. Oxford, UK: Butterworth Hernemann, 1996: 183–186.
- [17] ANYANWU I A, KAMADO S, KOJIMA Y. Creep properties of Mg–Gd–Y–Zr alloys [J]. Materials Transactions, 2001, 42: 1212–1218.
- [18] HENNING W, MORDIKE B L. Creep in magnesium-rare earth alloys [C]//McQUEEN H J, BAILON J P, DICKSON J I, JONAS J J, AKBEN M G. Proc of 7th Int Conf on Strength of Metals and Alloys. Strength of Metals and Alloys. Oxford: Pergamon Press, 1986: 803–808.

Zn 元素对 Mg–7Y–3Sm–0.5Zr 合金 显微组织和力学性能的影响

赵 阳¹, 王渠东^{1,2}, 高 岩¹

1. 上海交通大学 轻合金精密成型国家工程研究中心, 上海 200240;
2. 上海交通大学 金属基复合材料国家重点实验室, 上海 200240

摘 要: 研究添加 Zn 元素对铸造 Mg–7Y–3Sm–0.5Zr 合金的显微组织和力学性能的影响。蠕变测试的温度范围为 200–300 °C, 应力范围为 50–120 MPa。在本研究的蠕变测试条件下, 合金的蠕变激活能为 156–221 kJ/mol。采用光学显微镜、扫描电镜和透射电镜观察合金在蠕变过程中显微组织的演化。结果表明: 尽管合金在 250 °C 以下有着相似的蠕变行为, 仅添加 1% 的 Zn 元素就能使合金在 300 °C 和 50 MPa 蠕变条件下的蠕变寿命从 52.2 h 提高到 152.8 h, 表明 Zn 元素能够提高合金的高温抗蠕变性能。加入 Zn 元素后, 合金中形成的高温稳定相和片层状结构相是合金高温抗蠕变性能提高的根本原因。

关键词: Mg–Y–Sm–Zr 合金; 锌; 显微组织; 力学性能; 蠕变行为

(Edited by FANG Jing-hua)