

Effects of minor Sr, Sn and Sc addition on as-cast microstructure and mechanical properties of ZA84 magnesium alloy

YANG Ming-bo(杨明波)^{1,2}, ZHU Yi(朱 翊)¹, PAN Fu-sheng(潘复生)², YANG Hui(杨 惠)¹

1. Materials Science and Engineering College, Chongqing University of Technology, Chongqing 400050, China;

2. National Engineering Research Center for Magnesium Alloys, Chongqing University, Chongqing 400030, China

Received 23 September 2009; accepted 30 January 2010

Abstract: The effects of minor Sr, Sn and Sc addition on the as-cast microstructure and mechanical properties of the ZA84 magnesium alloy were compared. The results indicate that addition of 0.1%Sr, 0.5%Sn or 0.3%Sc (mass fraction) to the ZA84 alloy can refine the grains of the alloy. Furthermore, addition of 0.1%Sr to the ZA84 alloy does not obviously change the morphology and distribution of $Mg_{32}(Al,Zn)_{49}$ phase. However, addition of 0.5%Sn or 0.3%Sc not only refines and modifies the $Mg_{32}(Al,Zn)_{49}$ phase but also suppresses the formation of $Mg_{32}(Al,Zn)_{49}$ phase, especially with the addition of 0.3%Sc. Furthermore, addition of 0.1%Sr, 0.5%Sn or 0.3%Sc to the ZA84 alloy improves the tensile properties at room temperature and 150 °C, especially with the addition of 0.1%Sr and 0.3%Sc. However, addition of 0.1%Sr is not beneficial to the creep properties, and addition of 0.5%Sn has no obvious influence on the creep properties. Oppositely, addition of 0.3%Sc to the ZA84 alloy greatly improves the creep properties.

Key words: magnesium alloy; ZA84 magnesium alloy; Sr; Sn; Sc

1 Introduction

Magnesium alloys are the lightest commercially available structural materials and have great potential for applications in automotive, aerospace and other industries. In recent years, improving the elevated temperature properties has become a critical issue for possible application of magnesium alloys in hot components. It was reported that the ZA84 (Mg-8Zn-4Al) alloy of the ZA (Mg-Zn-Al) system is a potential magnesium alloy due to its moderate mechanical properties and good creep resistance, which satisfies the requirement of corrosion resistance properties as compared with AZ91 alloy[1–4]. However, the castability and elevated temperature mechanical properties of the ZA84 alloy are not completely satisfying, and further enhancement in the properties for the alloy needs to be considered by alloying and/or micro-alloying. WANG et al[5] found that RE addition to the ZA84 alloy can modify the morphology, chemical compositions and stability of the precipitates and thus enhance the properties. However, RE addition to the

ZA84 alloy possibly decreases the casting fluidity due to an increase of solidification temperature range[5]. In addition, BALASUBRAMANI et al[6] reported that Sb addition to the ZA84 alloy can refine the $Mg_{32}(Al,Zn)_{49}$ phase besides forming Mg_3Sb_2 precipitate and has a little effect on the grain refinement. Strength at both room and elevated temperatures are found to increase in Sb added alloys with slight reduction in ductility. Although the above studies have been carried out to understand the effects of alloying and/or micro-alloying in the ZA84 alloy, the effects of other alloying and/or micro-alloying elements such as Sr[7–10], Sn[7,11–12] and Sc[13–14], all of which have been successfully used to improve the mechanical properties of other magnesium alloys, have not been investigated. The present work aims to investigate and compare the effects of minor Sr, Sn and Sc addition on the as-cast microstructure and mechanical properties of the ZA84 magnesium alloy.

2 Experimental

The experimental alloys were prepared from pure Mg, Al, Zn and Sn (>99.9%), Mg-10%Sr and Mg-2.91%

Sc (mass fraction) master alloys. In addition, Mn was added in the form of Mg-4.38%Mn (mass fraction) master alloy to decrease the iron content. The experimental alloys were melted in a crucible resistance furnace with flux protection. After being homogenized by mechanical stirring at 740 °C and mixed completely, the melt was held at 740 °C for 20 min and then poured into a permanent mould to obtain a casting. The tensile and creep specimens with a size reported in Ref.[10] were fabricated by wire-electrode cutting from the casting. Table 1 lists the actual chemical compositions of the experimental alloys.

Table 1 Compositions of experimental alloys (mass fraction, %)

Alloy No.	Experimental	Zn	Al	Mn
1	ZA84	7.88	3.92	0.25
2	ZA84+0.1Sr	7.90	3.91	0.24
3	ZA84+0.5Sn	7.90	3.88	0.26
4	ZA84+0.3Sc	7.69	3.75	0.25

Alloy No.	Sr	Sn	Sc	Mg
1	–	–	–	Bal.
2	0.085	–	–	Bal.
3	–	0.47	–	Bal.
4	–	–	0.21	Bal.

The samples were etched in an 8% nitric acid distilled water solution, and then examined by an Olympus optical microscope (OM) and JEOL/JSM-6460LV type scanning electron microscope (SEM) equipped with an Oxford energy dispersive spectrometer (EDS). The phases in the as-cast experimental alloys were analyzed by D/Max-1200X type X-ray diffractometer (XRD) operated at 40 kV and 30 mA. The tensile properties of the as-cast experimental alloys at room temperature and 150 °C were determined from a stress–strain curve. The ultimate tensile strength (UTS), 0.2% yield strength (YS) and elongation to failure were obtained based on the average of three tests. The constant-load tensile creep tests of the as-cast experimental alloys were performed at 150 °C and 50 MPa for 100 h. The total creep strain and minimum creep rates of the experimental alloys were measured from each elongation versus time curve.

3 Results and discussion

3.1 Comparison of as-cast microstructures

Fig.1 shows the XRD patterns of the as-cast experimental alloys. In general, in the ZA84 alloy, two main ternary phases are reported in Ref.[15]. One is identified as $Mg_{32}(Al,Zn)_{49}$, and the other is $Mg_5Zn_2Al_2$

phase. As shown in Fig.1, all the as-cast experimental alloys are mainly composed of α -Mg, $Mg_{32}(Al,Zn)_{49}$ and $Mg_5Zn_2Al_2$ phases. Furthermore, it is found that adding 0.5%Sn to the ZA84 alloy results in the formation of Mg_2Sn . However, adding 0.1%Sr and 0.3%Sc to the ZA84 alloy do not cause the formation of any new phase in the alloy.

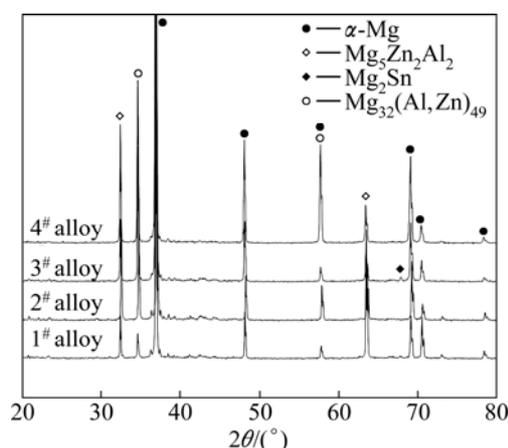


Fig.1 XRD patterns of as-cast experimental alloys

Figs.2 and 3 show the optical and SEM images of the as-cast alloys, respectively. It is found from Fig.2 that adding 0.1%Sr, 0.5%Sn or 0.3%Sc to the ZA84 alloy seems to refine the grains of the alloy. Furthermore, it is found that two types of phases showing different morphologies are present in the as-cast alloys. One is continuous and/or quasi-continuous network which mainly distributes at the grain boundaries, and the other is in an isolated shape. According to the XRD and EDS results, the continuous and/or quasi-continuous precipitates are $Mg_{32}(Al,Zn)_{49}$, and the isolated phases is $Mg_5Zn_2Al_2$. In addition, as shown in Fig.3(d), some relatively fine particles mainly contained Mg, Al, Sc and Mn are observed in the Sc-containing alloy although no Sc-containing phases are detected in the XRD results.

In addition, it is observed from Fig.3 that adding 0.1%Sr to the ZA84 alloy does not obviously influence the morphology and amount of the $Mg_{32}(Al,Zn)_{49}$ phase. However, after adding 0.5%Sn and 0.3%Sc to the ZA84 alloy, especially after adding 0.3%Sc, the morphology of the $Mg_{32}(Al,Zn)_{49}$ phase gradually changes from coarse continuous and/or quasi-continuous net to relatively fine quasi-continuous and/or disconnected shape, and the amount of the $Mg_{32}(Al,Zn)_{49}$ phase obviously decreases.

3.2 Comparison of mechanical properties

The tensile properties, including ultimate tensile strength (UTS), 0.2% yield strength (YS), elongation, and creep properties of the as-cast experimental alloys are listed in Table 2. It is observed that the tensile properties of the 2[#]–4[#] alloys at room temperature and

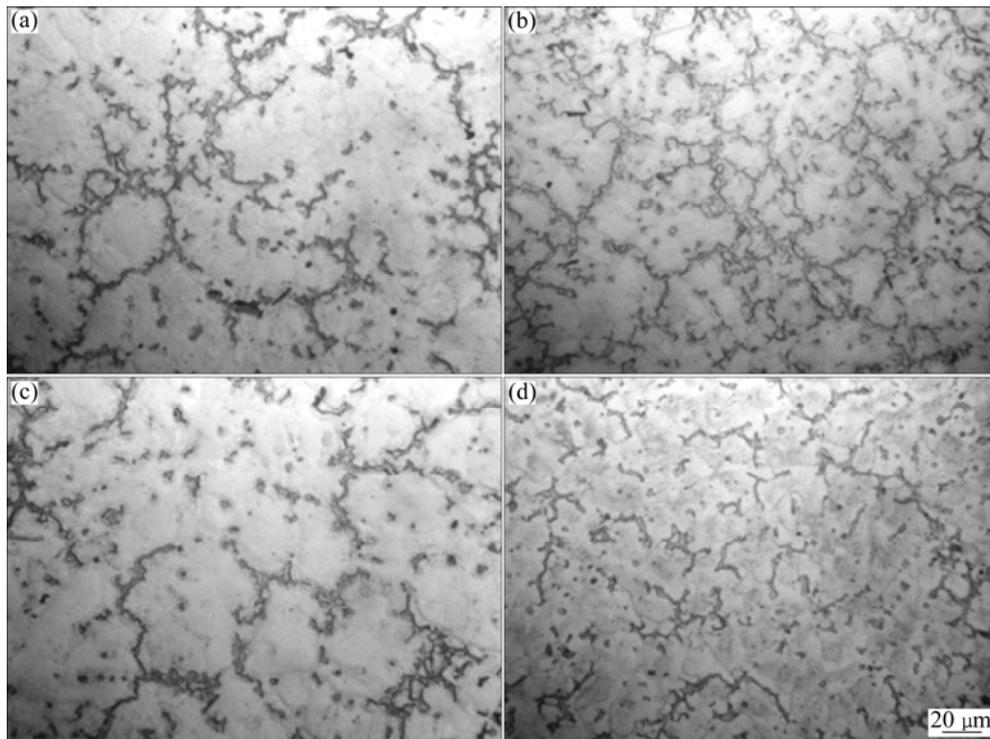


Fig.2 Optical images of as-cast alloys: (a) 1[#]; (b) 2[#]; (c) 3[#]; (d) 4[#]

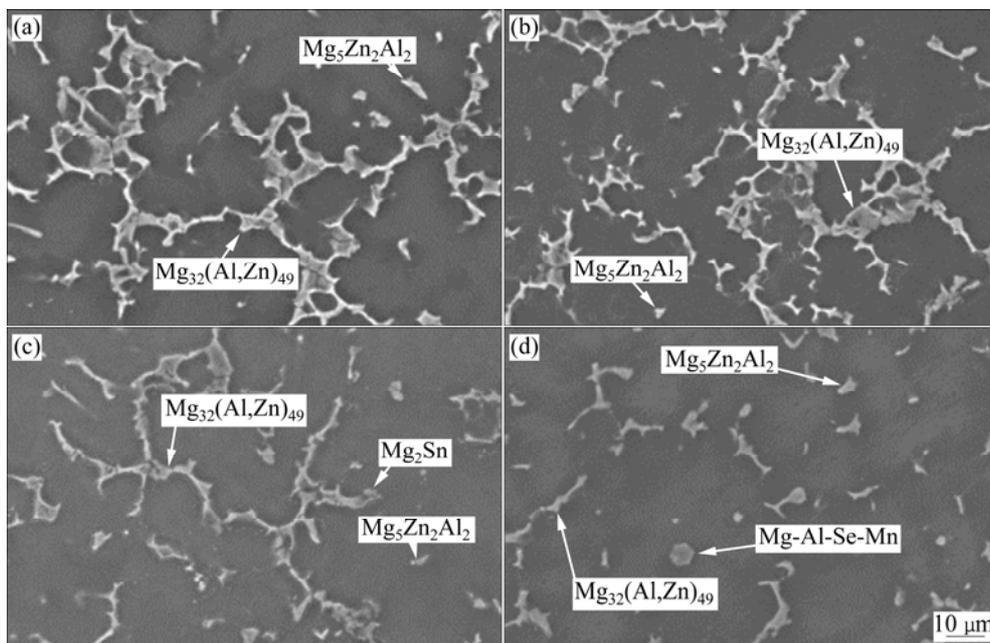


Fig.3 SEM images of as-cast alloys: (a) 1[#]; (b) 2[#]; (c) 3[#]; (d) 4[#]

150 °C are higher than those of the 1[#] alloy, indicating that adding 0.1%Sr, 0.5%Sn and 0.3%Sc to the ZA84 alloy can improve both the tensile strength and elongation of the alloy. This situation is possibly related to the effects of Sr, Sn and Sc additions on the as-cast microstructure of the ZA84 alloy. Furthermore, it is observed from Table 2 that among the Sr-, Sn- and Sc-containing ZA84 alloys, the tensile properties of the

Sr- and Sc-containing alloys at room temperature and 150 °C are relatively high. In addition, it is observed from Table 2 that the 4[#] alloy exhibits higher creep properties than the 1[#] alloy while the creep properties of the 2[#] alloy are lower than those of the 1[#] alloy, and the creep properties of the 3[#] alloy are similar to those of the 1[#] alloy. The above results indicate that adding 0.1%Sr to the ZA84 alloy is not beneficial to the creep properties of

Table 2 Tensile and creep properties of as-cast experimental alloys

Experimental alloy	Tensile properties						Creep properties	
	Room temperature			150 °C			150 °C and 50 MPa for 100 h	
	UTS/MPa	YS/MPa	δ /%	UTS/MPa	YS/MPa	δ /%	Total creep strain/%	Minimum creep rate/ 10^{-8} s^{-1}
1 [#]	174	125	3.85	156	116	11.4	0.68	1.89
2 [#]	190	152	4.91	174	136	15.8	1.03	2.86
3 [#]	185	137	4.05	164	120	12.2	0.62	1.72
4 [#]	191	140	4.35	173	131	14.2	0.48	1.33

the alloy, and adding 0.5%Sn to the ZA84 alloy has no obvious influence on the creep properties of the alloy. However, adding 0.3%Sc to the ZA84 alloy can greatly improve the creep properties of the alloy. At present, the reason for the difference of the effects of minor Sr, Sn and Sc additions on the creep properties of the ZA84 alloy is not clear. Further investigation still needs to be considered.

3.3 Discussion

The above results indicate that adding 0.1%Sr, 0.5%Sn or 0.3%Sc to the ZA84 alloy can effectively refine the grains of the alloy. In addition, adding 0.5%Sn or 0.3%Sc to the ZA84 alloy can also modify and refine the $\text{Mg}_{32}(\text{Al,Zn})_{49}$ phase in the alloy. In general, the grain refinement in industrial applications usually involves adding nucleates and/or solute elements into a melt before casting, and the effect of a solute element is explained in terms of the growth restriction factor (GRF) [16]. According to the GRF mechanism, the larger the GRF value is, the higher the refinement efficiency of a solute element is. Obviously, the grain refinement of the ZA84 alloy added with 0.1%Sr can easily explained by the GRF mechanism. Furthermore, the reason for the refinement and/or modification of grains and $\text{Mg}_{32}(\text{Al,Zn})_{49}$ phases in the ZA84 alloy added with 0.5%Sn is possibly related to the Sn enrichment of the liquid during solidification, which induces a constitution undercooling at the solidification interface front. Of course, it is one of the possible reasons that the Mg_2Sn compound which has high thermal stability possibly inhibits the growth of grains and $\text{Mg}_{32}(\text{Al,Zn})_{49}$ phases during solidification. In addition, the reason for the refinement and/or modification of grains and $\text{Mg}_{32}(\text{Al,Zn})_{49}$ phases in the ZA84 alloy added with 0.3%Sc is possibly related to the Sc enrichment. It is well known that Sc atom has larger atomic radius than Al and Zn atoms. After the addition of Sc to the ZA84 alloy, the Sc element is rich in the solid/liquid interface during solidification, and the enrichment hinders the diffusion of Zn and Al atoms and induces the constitution undercooling at the solidification interface front. Accordingly, the grains and $\text{Mg}_{32}(\text{Al,Zn})_{49}$ phase are

refined.

In addition, the above results indicate that adding 0.1%Sr to the ZA84 alloy has no obvious influence on the amount of the $\text{Mg}_{32}(\text{Al,Zn})_{49}$ phase in the alloy. However, after adding 0.5%Sn or 0.3%Sc to the ZA84 alloy, especially after adding 0.3%Sc, the amount of the $\text{Mg}_{32}(\text{Al,Zn})_{49}$ phase is obviously decreased, indicating that adding minor Sn or Sc to the ZA84 alloy can suppress the formation of $\text{Mg}_{32}(\text{Al,Zn})_{49}$ phase. Based on the Mg-Zn-Al phase diagram and the investigation of ZHANG et al[17], during the solidification of Mg-Zn-Al alloys, the primary α -Mg phases first nucleate and grow until the temperature reaches about 343 °C, where a binary eutectic reaction $L_1 \rightarrow \alpha\text{-Mg} + \text{Mg}_5\text{Zn}_2\text{Al}_2$ occurs followed by a ternary quasi-peritectic reaction $L_2 + \text{Mg}_5\text{Zn}_2\text{Al}_2 \rightarrow \alpha\text{-Mg} + \text{Mg}_{32}(\text{Al,Zn})_{49}$. Finally, the binary eutectic reaction $L_3 \rightarrow \alpha\text{-Mg} + \text{Mg}_{32}(\text{Al,Zn})_{49}$ takes place. In this case, if the amount of $\text{Mg}_5\text{Zn}_2\text{Al}_2$ phase was relatively large, it would not be used up in the ternary quasi-peritectic reaction. Accordingly, the final microstructure consists of α -Mg, $\text{Mg}_{32}(\text{Al,Zn})_{49}$ and $\text{Mg}_5\text{Zn}_2\text{Al}_2$ phases as the studied ZA84 alloys in this work. Therefore, it is inferred that the decrease of the amount for the $\text{Mg}_{32}(\text{Al,Zn})_{49}$ phase in the Sn- and Sc-containing ZA84 alloys might be related to the effects of Sn and Sc additions on the eutectic reaction of the ZA84 alloy during solidification. In spite of the above analysis, the reason for the effects of Sr, Sn and Sc additions on the amount of the $\text{Mg}_{32}(\text{Al,Zn})_{49}$ phase in the ZA84 alloy is not completely clear. Further investigation needs to be considered.

4 Conclusions

1) The difference for the effects of minor Sr, Sn and Sc addition on the as-cast microstructure of the ZA84 alloy is relatively obvious. Adding 0.5%Sn to the ZA84 alloy results in the formation of Mg_2Sn , while adding 0.1%Sr or 0.3%Sc to the ZA84 alloy does not cause the formation of any new phase in the alloy. Furthermore, adding 0.1%Sr, 0.5%Sn or 0.3%Sc to the ZA84 alloy can refine the grains of the alloy, and adding 0.1%Sr has no obvious influence on the morphology and amount of the

Mg₃₂(Al,Zn)₄₉ phase in the alloy. However, after adding 0.5%Sn or 0.3%Sc to the ZA84 alloy, especially after adding 0.3%Sc, the morphology of the Mg₃₂(Al,Zn)₄₉ phase in the alloy gradually changes from coarse continuous and/or quasi-continuous net to relatively fine quasi-continuous and/or disconnected shape, and the amount of the Mg₃₂(Al,Zn)₄₉ phase obviously decreases.

2) Adding 0.1%Sr, 0.5%Sn and 0.3%Sc to the ZA84 alloy can improve both the tensile strength and elongation of the alloy. Among the Sr-, Sn- and Sc-containing ZA84 alloys, the tensile properties of the Sr- and Sc-containing alloys at room temperature and 150 °C are relatively high. In addition, adding 0.1%Sr to the ZA84 alloy is not beneficial to the creep properties, and adding 0.5%Sn to the ZA84 alloy has no obvious influence on the creep properties. However, adding 0.3%Sc to the ZA84 alloy can greatly improve the creep properties.

References

- [1] ZHANG Z, COUTUNE A, LUO A. An investigation of the properties of Mg-Zn-Al alloys [J]. *Scripta Mater*, 1998, 39(1): 45–53.
- [2] XIAO W L, JIA S S, WANG J L, YANG J, WANG L M. The influence of mischmetal and tin on the microstructure and mechanical properties of Mg-6Zn-5Al-based alloys [J]. *Acta Mater*, 2008, 56(5): 934–941.
- [3] CHEN J H, CHEN Z H, YAN H G, ZHANG F Q, LIAO K. Effects of Sn addition on microstructure and mechanical properties of Mg-Zn-Al alloys [J]. *J Alloys Compds*, 2008, 461(1/2): 209–215.
- [4] YANG Ming-bo, PAN Fu-sheng, CHENG Ren-ju, SHEN Jia. Effects of holding temperature and time on semi-solid isothermal heat-treated microstructure of ZA84 magnesium alloy [J]. *Transactions of Nonferrous Metals Society of China*, 2008, 18(3): 566–572.
- [5] WANG Y X, GUAN S K, ZENG X Q, DING W J. Effects of RE on the microstructure and mechanical properties of Mg-8Zn-4Al magnesium alloy [J]. *Mater Sci Eng A*, 2006, 416(1/2): 109–118.
- [6] BALASUBRAMANI N, SRINIVASAN A, PILLAI U T S. Effect of antimony addition on the microstructure and mechanical properties of ZA84 magnesium alloy [J]. *J Alloys Compds*, 2008, 455(1/2): 168–173.
- [7] YANG M B, PAN F S, CHENG R J, SHEN J. Comparison about effects of Sb, Sn and Sr on as-cast microstructure and mechanical properties of AZ61-0.7Si magnesium alloy [J]. *Mater Sci Eng A*, 2008, 489(1/2): 413–418.
- [8] YANG M B, PAN F S, CHENG R J, TANG A T. Effect of Mg-10Sr master alloy on grain refinement of AZ31 magnesium alloy [J]. *Mater Sci Eng A*, 2008, 491(1/2): 440–445.
- [9] GUAN Sao-kang, ZHU Shi-jie, WANG Li-guo, YANG Qing, CAO Wen-bo. Microstructures and mechanical properties of double hot-extruded AZ80+xSr wrought alloys [J]. *Transactions of Nonferrous Metals Society of China*, 2007, 17(6): 1143–1151.
- [10] YANG Ming-bo, SHEN Jia, BAI Liang, PAN Fu-sheng. Effects of Sr on the microstructure, tensile and creep properties of AZ61-0.7Si magnesium alloy [J]. *Inter J Minerals, Metallurgy and Materials*, 2009, 16(1): 89–95.
- [11] XIANG Q, WU R Z, ZHANG M L. Influence of Sn on microstructure and mechanical properties of Mg-5Li-3Al-2Zn alloys [J]. *J Alloys Compds*, 2009, 477(1/2): 832–835.
- [12] CHEN J H, CHEN Z H, YAN H G, ZAI F Q, CHEN Y L. Effects of Sn and Ca additions on microstructure, mechanical properties, and corrosion resistance of the as-cast Mg-Zn-Al-based alloy [J]. *Materials and Corrosion*, 2008, 59(12): 934–941.
- [13] YAO S J, YI D Q, YANG S. Effect of Sc on the microstructure and corrosion properties of AZ91 alloy [J]. *Mater Sci Forum*, 2007, 546/549: 139–142.
- [14] WANG S C, CHOU CP, FANN Y C. Microstructures and mechanical properties of modified AZ31-Zr-Sc alloys [J]. *Mater Sci Eng A*, 2008, 485(1/2): 428–438.
- [15] BALASUBRAMANI N, PILLAI U T S, PAI B C. Optimization of heat treatment parameters in ZA84 magnesium alloy [J]. *J Alloys Compds*, 2008, 457(1/2): 118–123.
- [16] LEE Y C, DAHLE A K, SJOHN D H. The role of solute in grain refinement of magnesium [J]. *Metal Mater Trans A*, 2000, 31(11): 2895–2906.
- [17] ZHANG Z, TREMBLAY R, COUTUNE A. Solidification microstructure of ZA102, ZA104 and ZA106 magnesium alloys and its effect on creep deformation [J]. *Canadian Metall Quarterly*, 2000, 39(4): 503–512.

(Edited by FANG Jing-hua)