Effects of Ce addition on microstructure and mechanical properties of Mg-6Zn-1Mn alloy

ZHANG Ding-fei[1, 2], QI Fu-gang[1, 2], LAN Wei[3], SHI Guo-liang[1, 2], ZHAO Xia-bing[1, 2]

1. College of Materials Science and Engineering, Chongqing University, Chongqing 400045, China;
2. National Engineering Research Center for Magnesium Alloys, Chongqing University, Chongqing 400044, China;
3. School of Metallurgy and Materials Engineering, Chongqing University of Science and Technology, Chongqing 401331, China

Abstract: The effects of Ce addition on the microstructure of Mg-6Zn-1Mn alloy during casting, homogenization, hot extrusion, T4, T6 and T4+two-step aging were investigated. The mechanical properties of alloys with and without Ce were compared. The results showed that Ce had an obvious effect on the microstructure of ZM61-0.5Ce alloy by restricting the occurrence of dynamic recrystallization and restraining the grain growth during extrusion and heat treatment subsequently. A new binary phase $Mg_{12}Ce$ was identified in ZM61-0.5Ce alloy, which distributed at grain boundaries and was broken to small particles distributed at grain boundaries along extrusion direction during extrusion. The mechanical properties of as-extruded ZM61-0.5Ce alloy were improved with the addition of Ce. The improved tensile properties of as-extruded ZM61-0.5Ce alloy were due to the finer grain sizes as compared to ZM61 alloy. However, the UTS and YS decreased severely and the elongation increased when ZM61-0.5Ce was treated by T6 and T4+two-step aging. Brittle $Mg_{12}Ce$ phase, which was distributed at the grain boundary areas and cannot dissolve into the Mg matrix after solution treatment, became crack source under tensile stress.

Key words: Mg-6Zn-1Mn alloy; cerium; microstructure; mechanical properties

1 Introduction

As the lightest structural materials, magnesium alloys have attracted increasing interest for mass reduction in aerospace, automobile industry and transportation, but the use of magnesium alloys is still limited due to their low strength, bad deformability and high cost caused by either expensive alloying elements used or special processing technology involved[1]. To broaden the applications of magnesium alloys further, the development of wrought Mg alloys with higher strength is necessary.

Mg-6Zn-1Mn(ZM61) alloy[2−4], which is a new kind of high performance wrought magnesium alloy, has pronounced response to age-hardening, so there is a great potential to improve the strength by various heat treatments and micro-alloying. Two-step aging (high temperature aging after pre-aging at a lower temperature) was reported to be very effective to refine the microstructure of Mg-Zn-Mn alloys[4−6]. Recently, ZHANG et al[2−4,7−8] reported that the Mg-6Zn-1Mn alloy with double aging treatments exhibits higher strength values than the single-aged alloy. Further recently, microstructure and mechanical properties of twin-roll stripped Mg-6Zn-1Mn alloys which contain various Al contents and are subjected to double aging after solution heat treatment have been reported[5−6].

Another effective way to improve strength is alloying trace element to magnesium alloys. Among them, rare earth (RE) elements, such as Y, Nd, Yb, Gd, have attracted particular attention. It was proved that rare earth addition is beneficial to the mechanical properties of magnesium alloys without affecting other

Corresponding author: ZHANG Ding-fei; Tel: +86-23-65112491; E-mail: zhangdingfei@cqu.edu.cn

properties[9−13]. Conventionally, the purposes of rare earth element addition are to refine grains, and thus to improve the mechanical properties[14−17]. Up to now, few studies have been conducted about the effects of RE on microstructures or properties of Mg-Zn-Mn wrought magnesium alloys.

In this study, Ce, one of the cheapest rare earth elements, was added as a trace additive. According to Mg-Ce phase diagram[18], Ce has a little solubility in Mg. The maximum solubility of Ce in Mg at the eutectic temperature (592 °C) is 0.52%(mass fraction). The effects of Ce on the microstructure and mechanical properties of ZM61 alloy were reported.

2 Experimental

Commercial high-purity Mg(>99.9%, mass fraction), Zn(>99.95%) and two master alloys (Mg-20.82%Ce and Mg-4.10%Mn) were used to prepare the experimental alloys with nominal composition(mass fraction, %) of Mg-6Zn-1Mn (ZM61) and Mg-6Zn-1Mn-0.5Ce (ZM61-0.5Ce). All alloys were prepared by vacuum induction melting using steel crucible under an Ar atmosphere. The melt was held at 750 °C for 30 min to make sure that Ce could be completely dissolved. The chemical compositions, which were analyzed by XRF−1800 CCDE sequential X-ray fluorescence spectrometer, were Mg-5.77Zn-0.95Mn for ZM61 and Mg-5.69Zn-0.74Mn-0.39Ce for ZM61-0.5Ce.

Then the ingots were homogenized at 330 °C for 24 h and then under a controlled constant force by a XJ−500 horizontal extrusion machine made in China. The homogenized ingots were hot extruded to bars of 16 mm in diameter at 360 °C with the extrusion ratio of 25:1. After extrusion, the alloys were cooled in the open air. The extruded samples were solution treated (T4) at 420 °C for 2 h followed by water quenching. Subsequently, two kinds of aging treatments: single aging (180 °C for 16 h) and two-step aging (90 °C for 24 h and 180 °C for 16 h) were utilized.

Tensile tests were performed using tensile specimens with gauge length of 50 mm and gauge diameter of 5 mm at a strain rate of 2 mm/min at room temperature. Tensile property values under each condition were obtained as the average of three tests.

The microstructures of specimens were observed by NEOPHOT30 optical metallographic microscope and TESCAN VEGAⅡ scanning electron microscope equipped with an INCA Energy 350 energy dispersive X-ray spectrometer (EDS). Phase components were characterized by a Rigaku D/max 2500PC X-ray diffractometer using Cu $K_α$ radiation. Thermal analysis was carried out by using differential scanning calorimetry(DSC, a NETZSCH STA 449C system) under purified Ar atmosphere. DSC sample of around 20 mg was heated from 50 °C to 700 °C in 5 min before being cooled down to 50 °C at a controlling speed of 10 °C/min.

3 Results and discussion

3.1 As-cast microstructure

Figure 1 shows the as-cast microstructures of ZM61-Ce alloys containing no and 0.4% Ce, respectively. The two alloys exhibited similar dendritic morphologies. The grain size and dendrites of ZM61-0.5Ce alloy were slightly smaller than those of ZM61 alloy. The microstructure of ZM61 alloy was comprised of coarse equiaxed dendrites and net-work interdendritic compounds. The interdendritic coarse blocky compounds, which are indicated by arrow 'A' in Fig.2(a), were identified as Mg-Zn binary eutectic compounds, as shown Fig.2(b). Fig.2(c) shows SEM microstructure of as-cast ZM61-0.5Ce alloy. The EDS results show that no Ce was detected in the magnesium matrix, and the interdendritic compounds contain a lot of Ce apparently.
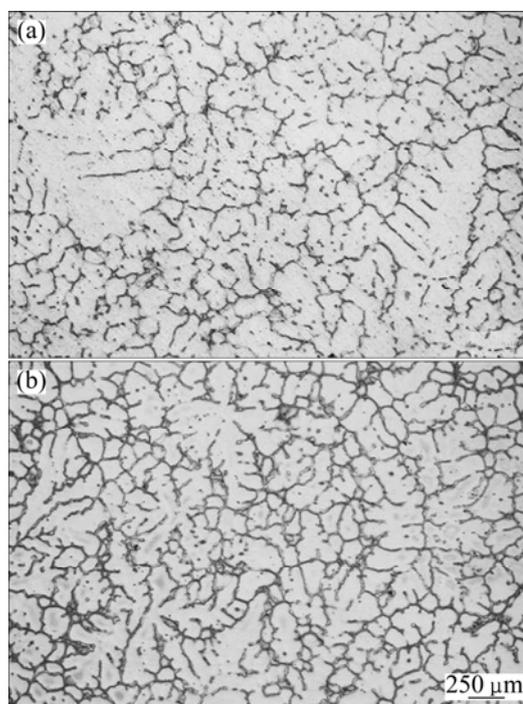
Fig.1 Optical microstructures of ZM61 (a) and ZM61-0.5Ce(b) alloys

In the present work, Ce was added to the melt in the form of Mg-20.82%Ce master alloy. The liquidus temperature of the master alloy is about 592 °C [11],

Element	Mass fraction/%	Molar fraction/%
Mg	52.24	74.63
Zn	47.76	25.37
Total	100.00	100.00

Element	Mass fraction/%	Molar fraction/%
Mg	28.83	56.43
Zn	49.92	36.35
Ce	21.25	7.22
Total	100.00	100.00
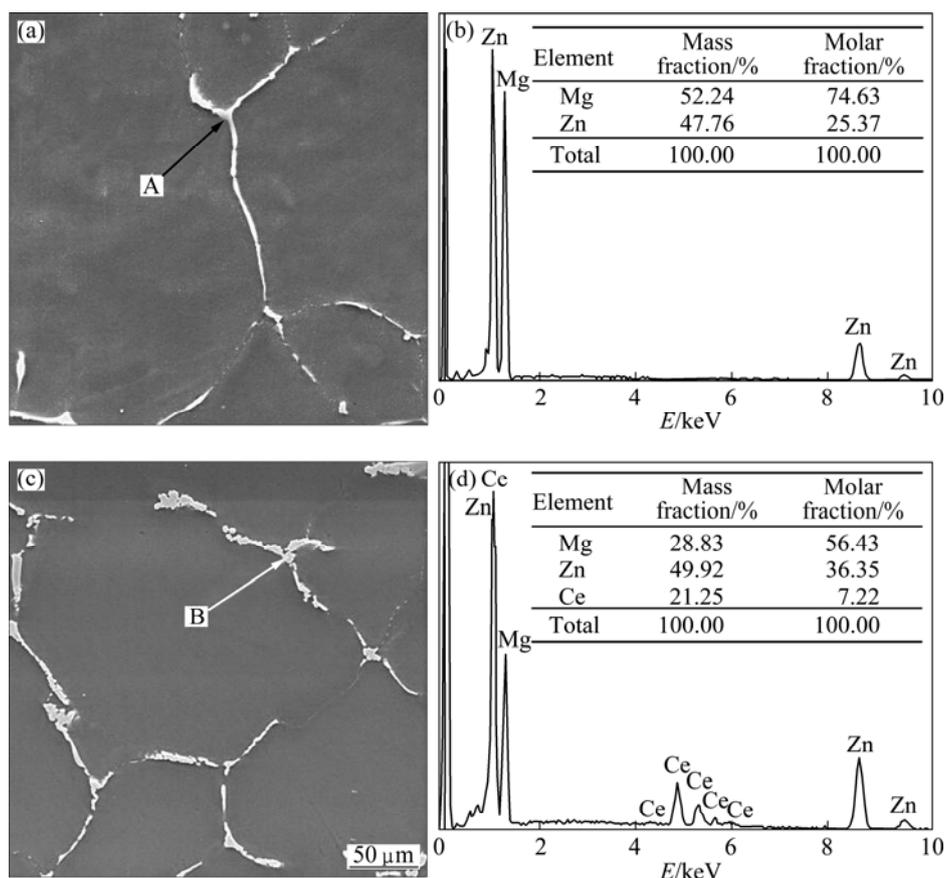
Fig.2 SEM micrographs of as-cast ZM61 alloy (a) and ZM61-0.5Ce alloy (c), EDS spectra of 'A' phase (b) and 'B' phase (d)

which is lower than the temperature of the melt. Since Ce has little solubility in Mg, little level of Ce may be soluble in Mg lattice during crystallization. Thus, the major fraction of Ce, as well as solute atom Zn, are believed to be enriched at the advancing solid-liquid interface[19], resulting in the formation of Mg-Zn and Mg-Ce intermetallics at the interdendritic areas during the last stage of solidification.

3.2 Microstructure evolution

Figures 3−7 illustrate the microstructure evolution of ZM61 and ZM61-0.5Ce alloys during homogenization, extrusion, solution, single-step aging and two-step aging. As shown in Fig.3, after homogenization at 330 °C for 24 h, some of the Mg-Zn eutectic compounds in the grain boundary dissolved into the matrix without notably difference in the two alloys. However, a lot of undissolved compounds containing a lot of Mg-Ce phases for ZM61-0.5Ce alloy still remained in the grain boundary, as shown in Fig.3(d).

Figure 4 shows the microstructures of ZM61 and ZM61-0.5Ce alloys extruded at 360 °C after homogenization at 330 °C for 24 h with the extrusion ratio of 25:1. The grains were refined severely by dynamic recrystallization (DRX) during deformation.

Blocky primary compounds were further broken into small particles. Fig.4(a) shows that complete DRX occurs in the ZM61 alloy, while incomplete DRX occurs in ZM61-0.5Ce alloy under this extrusion condition, as shown in Fig.4(b).

The phase constitutions of as-cast and as-extruded ZM61 and ZM61-0.5Ce alloys were determined by XRD analysis, as shown in Fig.8. It shows that $Mg_{12}Ce$ phase emerges in ZM61-0.5Ce as compared with ZM61 alloy. The DSC curves showed that the eutectic temperature of ZM61-0.5Ce alloy increased evidently with the addition of Ce, as shown in Fig.9. It is suggested that the rise of eutectic temperature should be attributed to the deformation of $Mg_{12}Ce$ phase which is responsible for the existence of high temperature and undissolved particles.

After solution heat treatment at 420 °C for 2 h, the dynamic recrystallized grains of the investigated alloys grew up sharply. Figure 5 shows the solutionized microstructures of both alloys. However, the grain size of ZM61-0.5Ce alloy was much smaller than that of the alloy without Ce. There were only little tiny particles dispersed in the matrix of ZM61 alloy, yet some big undissolved intermetallics still remained in the alloy with Ce, which means that the undissolved particles existing
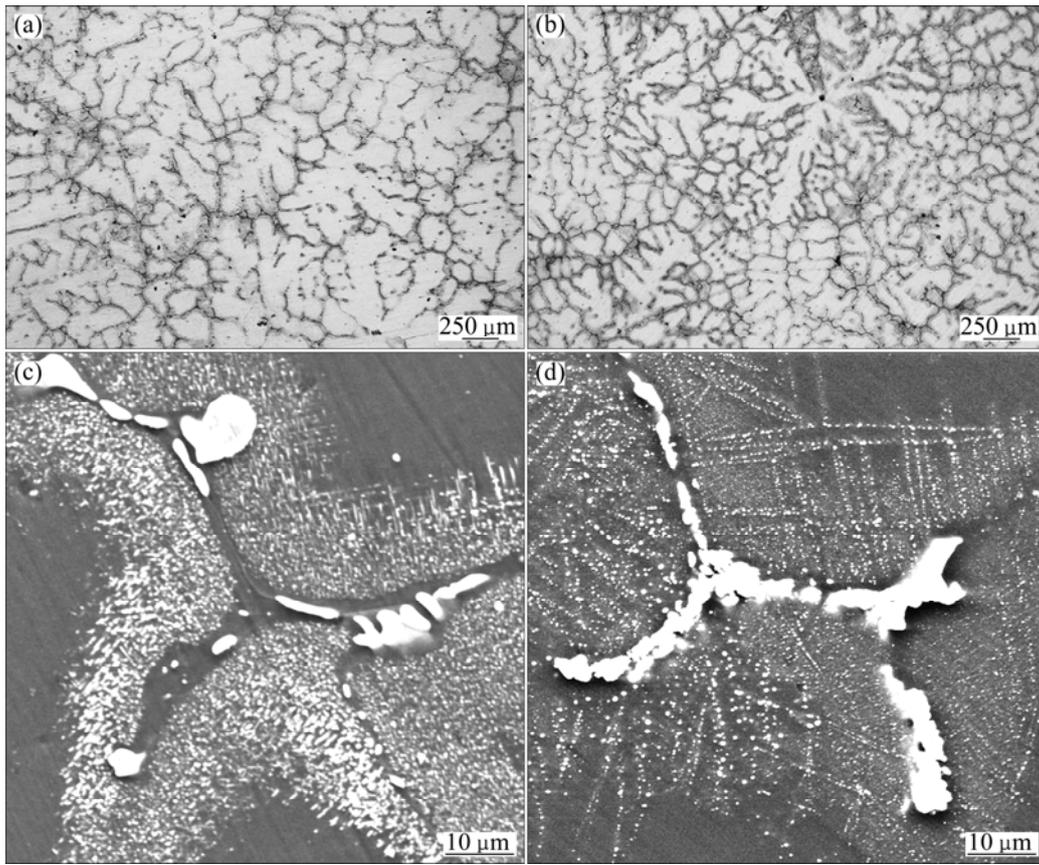
Fig.3 As-homogenized microstructures of ZM61 (a, c) and ZM61-0.5Ce (b, d) alloys at 330 °C for 24 h: (a), (b) Optical micrographs; (c), (d) SEM micrographs
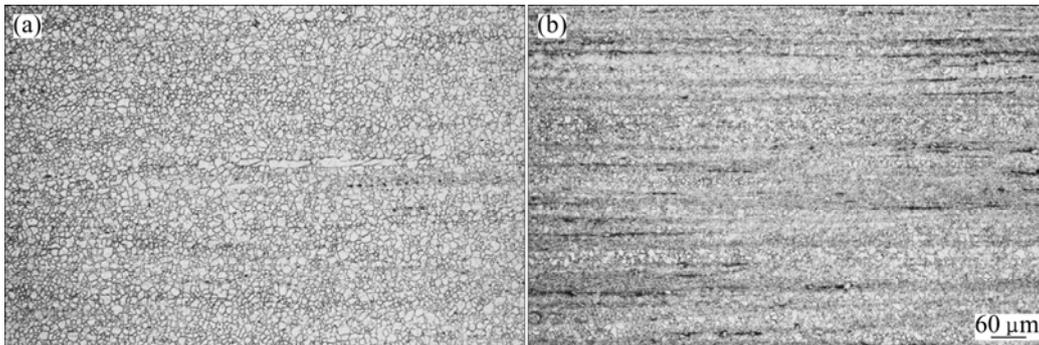
Fig.4 Microstructures in vertical section of as-extruded ZM61 (a) and ZM61-0.5Ce (b) alloys
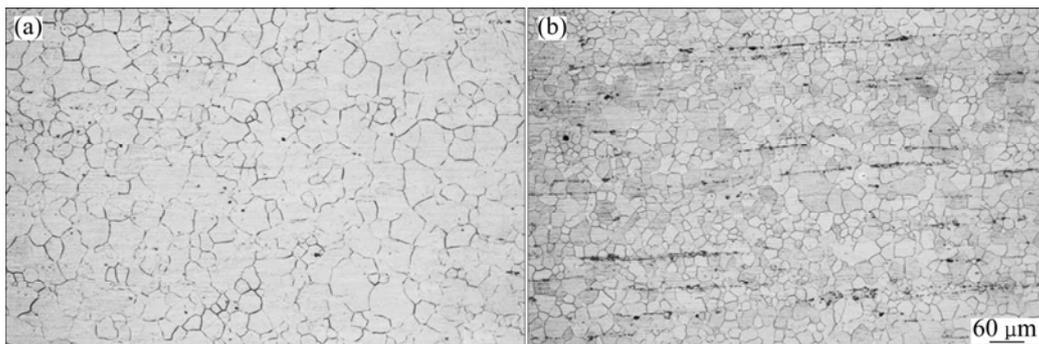
Fig.5 Microstructures in vertical section of T4 treated ZM61 (a) and ZM61-0.5Ce (b) alloys
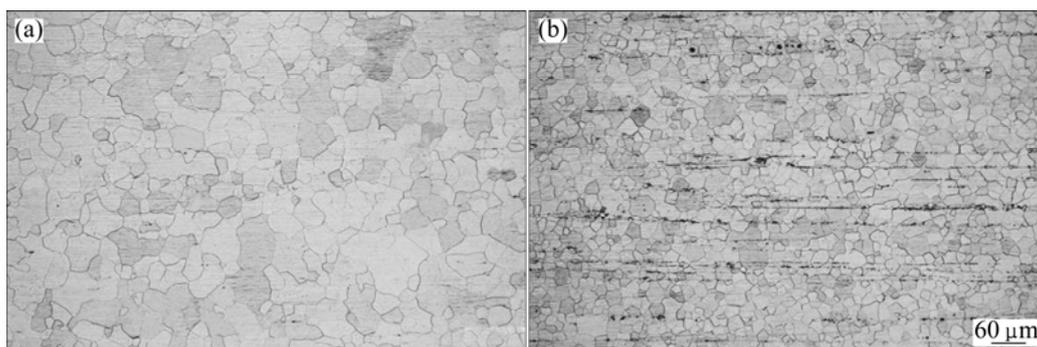
Fig.6 Microstructures in vertical section of T6 treated ZM61 (a) and ZM61-0. 5Ce (b) alloys
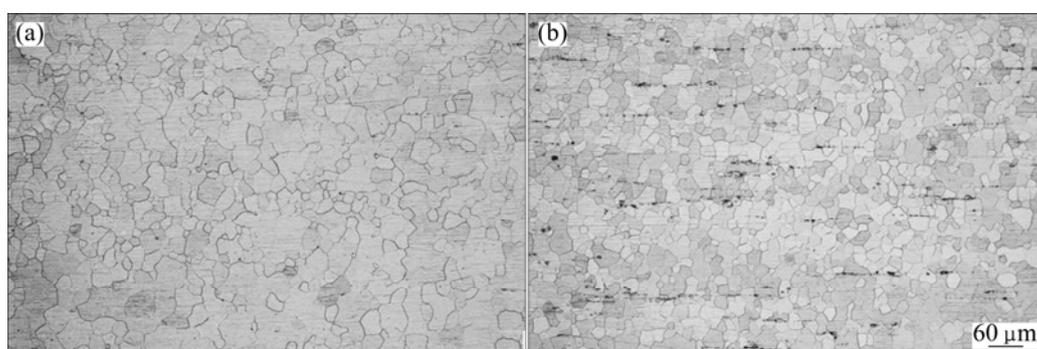
Fig.7 Microstructures in vertical section of T4+2-step aged ZM61 (a) and ZM61-0. 5Ce (b) alloys
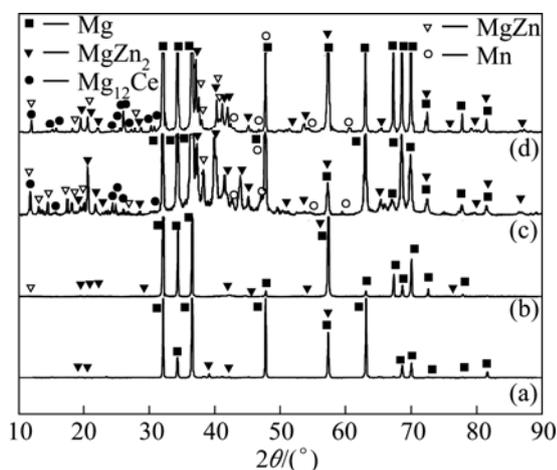
Fig.8 XRD patterns of as-cast (a, c) and as-extruded (b, d) samples: (a), (b) ZM61 alloy; (c), (d) ZM61-0.5Ce alloy
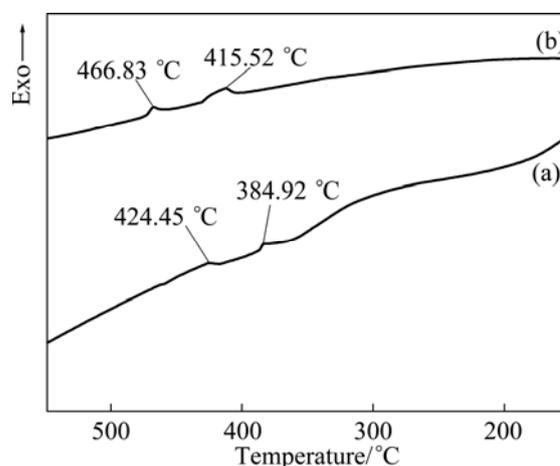
Fig.9 DSC curves of ZM61 (a) and ZM61-0.5Ce (b) alloys

in as-extruded ZM61-0.5Ce alloy cannot be dissolved considerably into matrix.

The microstructures in vertical section of ZM61 and ZM61-0.5Ce alloys in T6 and T4+two-step aging condition are shown in Figs.6 and 7. The grain size of ZM61-0.5Ce alloy is much smaller than that of ZM61 alloy. For ZM61 alloy, the effect of pre-aging at a lower temperature below 100 °C of two-step aging on the optical microstructure is inappreciable. Nano-sized G.P.

zones which precipitate during the pre-aging process can act as heterogeneous nucleation sites for the high-temperature-aging transition phases, resulting in more multiplied and denser coherent metastable phases than single aging. Such G.P. zones can only be observed by transmission electron microscope(TEM), so the optical micrographs of two-step aged alloys just indicate the same principles as those of one-step aged alloys[6, 20]. For ZM61-0.5Ce alloy, big undissolved Mg-Ce intermetallics cannot dissolve into the matrix and

distribute at the extrusion streamlines parallel to the extrusion direction.

3.3 Mechanical properties

Table 1 shows the tensile results of as-extruded, T6 and T4+two-step aged alloys with and without Ce addition. It is interesting to note that the yield strength and elongation of as-extruded ZM61-0.5Ce increased compared with those of ZM61, while the tensile strength values of both alloys were almost the same. For ZM61 alloy, the T6, especially the T4+two-step aging can obviously increase the ultimate tensile strength and yield strength, while decrease the elongation. However, the yield strength and tensile strength decreased and the elongation increased with the addition of Ce for T6 and T4+two-step aged alloys.

Table 1 Tensile properties of as-extruded, T6 and T4+two-step aged ZM61 alloys with and without Ce addition

Alloy	State	YS/ MPa	UTS/ MPa	Elongation/ %
ZM61	As-extruded	209	305	11.5
	T6	314	352	7.9
	T4+two-step aged	338	366	5.2
ZM61-0.5Ce	As-extruded	232	304	14.7
	T6	267	297	9.3
	T4+two-step aged	287	308	10.4

The improvement of the whole mechanical properties of the as-extruded ZM61-0.5Ce is the result of refined grain sizes by $Mg_{12}Ce$ particles, which is present at the grain boundary areas and can restrict the growth of recrystallized grains[21].

For ZM61 alloy, Mg-Zn phase particles precipitated during air cooling after extrusion almost dissolve again into the α-Mg matrix during the T4 treatment, then strengthening β' precipitates form in α-Mg matrix during T6 and T4+two-step aging. The reason why T4+two-step aging could remarkably increase the yield and tensile strengths is that in the first step aging at a lower temperature, a large amount of GP zones and metastable phases are formed, which could act as nucleation sites for β' precipitates in the second step aging, resulting in finer and more dispersive β' particles[4, 20, 22−24].

The phenomenon that the tensile properties of T6 and T4+two-step aged ZM61-0.5Ce alloy are severely deteriorated by adding Ce is conflictive with our previous expectation for alloy design. Figure 10 shows the SEM images of the tensile fracture surfaces for both alloys tested at room temperature. Huge amounts of

cleavage planes and steps(arrow 'A' in Fig.10(a)) are present and some minute lacerated ridges can also be observed in the local areas of tensile fracture surfaces for ZM61 alloy, which have mixed characteristics of cleavage and quasi-cleavage fractures. However, a lot of cracks (arrow 'B' in Fig.10(b)), which originate in brittle $Mg_{12}Ce$ phase with 20 μm in diameter, are found in the fracture surface of ZM61-0.5Ce alloy. According to

Element	Mass fraction/%	Molar fraction/%
Mg	41.71	74.72
Zn	20.13	13.41
Ce	38.16	11.86
Total	100.00	100.00
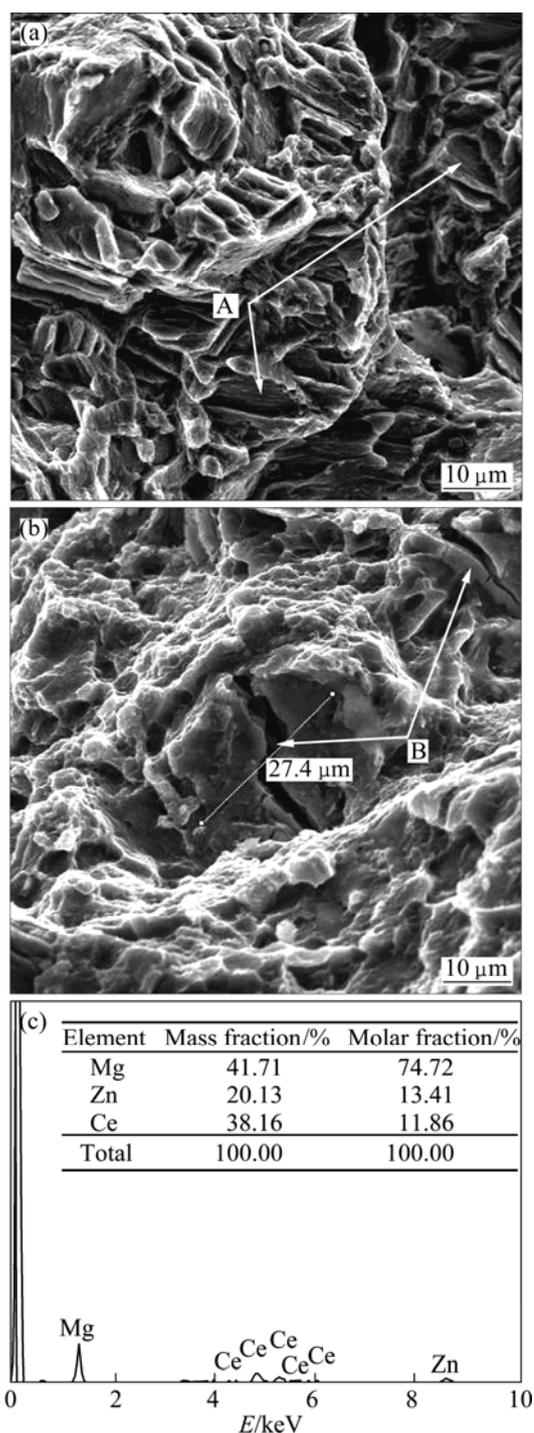
Fig.10 SEM images of fracture surface of T6 aged alloys tested at room temperature: (a) ZM61; (b) ZM61-0.5Ce; (c) EDS spectrum of 'B' phase in Fig.10(b)

above analysis of microstructure evolution, the major cause of the deterioration comes from the residual coarse $Mg_{12}Ce$ particle clusters which cannot thoroughly dissolve into matrix during solution treatment and may act as crack sources under tensile stress.

4 Conclusions

1) Ce has obvious refining effects on the grain sizes of ZM61 alloys in as-cast, as-extruded, T4, T6 and T4+two-step aged states. The addition of Ce can restrain the grain growth of DRX during extrusion and various heat treatment process.

2) For as-extruded alloy, the mechanical properties are improved by the addition of Ce, while for T6 and T4+two-step aged alloys the UTS and YS decrease severely and the elongation increases by the addition of Ce. The $Mg_{12}Ce$ high temperature phases, which are distributed at the grain boundary area and cannot dissolve into the Mg matrix during T4, become crack source of fracture under tensile strength.

References

[1] YANG Z, LI J P, ZHANG J X, LORIMER G W, ROBSON J. Review on research and development of magnesium alloys [J]. Acta Metallurgica Sinica, 2008, 21(5): 313−328.

[2] ZHANG Ding-fei, DING Pei-dao, YUAN Wei, PENG Jian, SHI Guo-liang. Mg-Zn-Mn magnesium alloy with high Zn content: China, 200710078329.X.[P]. 2007. (in Chinese)

[3] ZHANG Ding-fei, DING Pei-dao, YUAN Wei, SHI Guo-liang, DUAN Hong-ling. Heat treatment process of Mg-Zn-Mn wrought magnesium: China, 200710092859.X.[P]. 2008. (in Chinese)

[4] ZHANG Ding-fei, SHI Guo-liang, DAI Qing-wei, YUAN Wei, DUAN Hong-ling. Microstructures and mechanical properties of high strength Mg-Zn-Mn alloy [J]. Transactions of Nonferrous Metals Society of China, 2008, 18: 59−63.

[5] PARK S S, BAE G T, KANG D H, JUNG I H, SHIN K S, NACK J KIM. Microstructure and tensile properties of twin-roll cast Mg-Zn-Mn-Al alloys [J]. Scripta Materialia, 2007, 57: 793−796.

[6] PARK S S, BAE G T, KANG D H, JUNG I H, SHIN K S, NACK J KIM. Superplastic deformation behavior of twin-roll cast Mg-6Zn-1Mn-1Al alloy [J]. Scripta Materialia, 2009, 61: 223−226.

[7] YUAN Wei. Researches on microstructure and mechanical properties of the new Mg-6Zn-1Mn alloy [D]. Chongqing: Chongqing University, 2007. (in Chinese)

[8] DAI Qing-wei, ZHANG Ding-fei, YUAN Wei, SHI Guo-liang, DUAN Hong-ling. Researches on extrusion, microstructure and mechanical properties of new Mg-Zn-Mn alloy [J]. Materials Engineering, 2008, 4: 38−42.

[9] ZHOU Hai-tao, ZENG Xiao-qin, LIU Liu-fa, ZHANG Ya, ZHU Yan-ping, DING Wen-jiang. Effect of cerium on microstructures and mechanical properties of AZ61 wrought magnesium alloy [J]. Journal of Materials Science, 2004, 39: 7061−7066.

[10] LIU Wen-juan, CAO Fa-he, CHANG Lin-rong, ZHANG Zhao, ZHANG Jian-qing. Effect of rare earth element Ce and La on corrosion behavior of AM60 magnesium alloy [J]. Materials Science and Engineering A, 2008, 474: 317−322.

[11] WANG Ying-xin, GUAN Shao-kang, ZENG Xiao-qin, DING Wen-jiang. Effects of RE on the microstructure and mechanical properties of Mg-8Zn-4Al magnesium alloy [J]. Materials Science and Engineering A, 2006, 416: 109−118.

[12] ZHANG Jing, MA Qi, PAN Fu-sheng. Effects of trace Er addition on the microstructure and mechanical properties of Mg-Zn-Zr alloy [J]. Materials and Design, 2010, 31: 4043−4049.

[13] YU Wen-bin, LIU Zhi-yi, HE Hong, CHENG Nan-pu, LI Xue-lian. Microstructure and mechanical properties of ZK60-Yb magnesium alloys [J]. Materials Science and Engineering A, 2008, 478: 101−107.

[14] XU D K, LIU L, XU Y B, HAN E H. The effect of precipitates on the mechanical properties of ZK60-Y alloy [J]. Materials Science and Engineering A, 2006, 420: 322−332.

[15] 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 Materialia, 2007, 56: 137−140.

[16] ZOU Hong-hui, ZENG Xiao-qin, ZHAI Chun-quan, DING Wen-jiang. Effects of Nd on the microstructure of ZA52 alloy [J]. Materials Science and Engineering A, 2005, 392: 229−234.

[17] LI Z F, DONG J, ZENG X Q, LU C, DING W J. Influence of strong static magnetic field on intermediate phase growth in Mg-Al diffusion couple [J]. Journal of Alloys and Compounds, 2007, 440: 132−136.

[18] NAYEB-HASHEMI A A, CLARK J B. Phase diagrams of binary magnesium alloys [M]. Metals Park, USA: ASM International, 1999: 353.

[19] DAVIS S H. Theory of solidification [D]. Cambridge: Cambridge University Press, 2001.

[20] SINGH A, TSAI A P. Structural characteristics of β_1' precipitates in Mg-Zn-based alloys [J]. Scripta Materialia, 2007, 57(10): 941−944.

[21] OH-ISHI K, MENDIS C L, HOMMA T, KAMADO S, OHKUBO T, HONO K. Bimodally grained microstructure development during hot extrusion of Mg-2.4Zn-0.1Ag-0.1Ca-0.16Zr(at.%) alloys [J]. Acta Materialia, 2009, 57: 5593−5604.

[22] GAO X, NIE J F. Characterization of strengthening precipitate phases in a Mg-Zn alloy [J]. Scripta Materialia, 2007, 56(8): 645−648.

[23] O-ISHI K, HONO K, SHIN K S. Effect of pre-aging and Al addition on age-hardening and microstructure in Mg-6wt%Zn alloys [J]. Materials Science and Engineering A, 2008, 496(1−2): 425−433.

[24] GAO X, NIE J F. Structure and thermal stability of primary intermetallic particles in an Mg-Zn casting alloy [J]. Scripta Materialia, 2007, 57(7): 655−658.

Ce 元素对 Mg-6Zn-1Mn 变形镁合金显微组织和
力学性能的影响

张丁非 [1, 2], 齐福刚 [1, 2], 兰 伟 [3], 石国梁 [1, 2], 赵霞兵 [1, 2]

1. 重庆大学 材料科学与工程学院，重庆 400045；
2. 重庆大学 国家镁合金材料工程技术研究中心，重庆 400044；
3. 重庆科技学院 冶金与材料工程学院，重庆 401331

摘　要：利用光学显微镜、X 射线衍射、扫描电镜和差热分析等手段研究添加 Ce 对 Mg-6Zn-1Mn 镁合金在不同状态下的微观组织和相组成的影响，并对合金的室温力学性能进行测试和比较。结果表明：添加的 Ce 元素以 $Mg_{12}Ce$ 相存在于合金中，主要分布在晶界和枝晶间，铸态晶粒得到细化；添加 Ce 元素能够明显地提高挤压态 Mg-6Zn-1Mn 合金的屈服强度和伸长率，这是由于热挤压过程中弥散分布在晶界上的 $Mg_{12}Ce$ 相能够有效钉扎晶界，抑制再结晶晶粒长大，从而得到更加细小的热变形晶粒组织；然而，添加 Ce 元素恶化了时效态 Mg-6Zn-1Mn 合金的力学性能，这是因为热处理不能使这些 $Mg_{12}Ce$ 相固溶于基体中，在拉伸断裂时 $Mg_{12}Ce$ 相表面形成微裂纹，导致力学性能下降。
关键词：Mg-6Zn-1Mn 合金；铈；显微组织；力学性能

(Edited by YUAN Sai-qian)