JOURNAL OF MATERIALS SCIENCE **39** (2004) 7061 – 7066

Effect of cerium on microstructures and mechanical properties of AZ61 wrought magnesium alloy

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The effects of Cerium (Ce) addition on microstructures and mechanical properties of hot-extruded AZ61 alloy were investigated. It is found that Ce refines $Mg_{17}Al_{12}$ particles and brings about precipitation of a new rod-like phase that is identified as Al_4Ce by X-ray diffraction. During hot deformation, Al_4Ce particles can refine dynamic recrystallized grains by impeding grain growth. For Ce additions up to 1.0 wt%, the recrystallized grain size decreases; When Ce addition is more than 1.0 wt%, grain size increases inversely. Strength and elongation of extruded or annealed specimens at room temperature increase along with Ce addition up to 1.0 wt%, then decrease. Optimal mechanical properties are correspondent to 1.0 wt% Ce addition. © *2004 Kluwer Academic Publishers*

1. Introduction

Magnesium alloys are the lightest metallic structural materials with high specific strength. They are likely to be applied in such industries as automotive, railway and aerospace [1]. However, strength of magnesium is generally lower compared with aluminum and ferrous alloys. The ductility of magnesium is not good either because of its h.c.p structure [2]. These disadvantages are substantial obstacles against their utilities in antecedent applications. To meet the property demands of such applications, magnesium alloys with high mechanical properties must be developed. As one of the most fundamental and effective methods, alloying with elements like Ca and rare earth metals have been frequently practiced. It has been proved that rare earth (RE) metals are beneficial to the mechanical properties of magnesium alloys without affecting other properties [3, 4]. Conventionally, the purposes of rare earth element are to refine grains, and thus to improve the mechanical properties. Wang [5] suggests that RE can increase the yield strength of Mg alloys. Mukai [6] suggests that the ductility in WE43 alloy can be improved by RE addition. Objective alloys in these researches have all been casting magnesium alloys. Up to now, few studies have been conducted about the effects of RE on microstructures or properties of wrought magnesium alloys.

In this work, we prepared several kinds of alloys by adding different amounts of Ce into a wrought magnesium alloy, viz. AZ61. We clarified the effects of Ce addition by studying and comparing the microstructure and mechanical properties of as-cast, annealed and hot-extruded alloys.

2. Experimental procedure

Four kinds of alloys (Table I) were prepared by adding different amount of Ce into melt of commercial AZ61 alloy. Alloys were melted in a milled steel crucible under protection of a mixed shield gas composed of SF_6(1 vol.%) and CO_2 (BAL). At 750°C, the melt was purged for about 5 mins. After purging, the melt was held for 15 min so that inclusions could settle to the melt bottom. The melt was then poured into a steel mold to make ingot of $\Phi 90 \times 150$ mm. Solution processes were conducted at 400°C for 10 h. Hot extrusion was carried out at 350°C to make long rods of $\Phi 15$ mm. We used an extrusion ratio of 10:1. Some rods were annealed at 320°C for 1 h. Tensile specimens had a 5-mm diameter and 66-mm gage length. Tensile tests with strain rate of $5 \times 10^{-4}\ s^{-1}$ were performed at room temperature. Microstructure was analyzed by OM (Optical Microscopy, LEICA MEF4M), SEM (Scanning Electron Microscopy) and EPMA (Electron Probe Micro Analyzer, JCXA-733). Phase analyses were conduced by means of a D/MAS-IIIA X-ray diffractometer (XRD). The specimens for observations were etched with 4% HNO_3 in alcohol.

3. Results

3.1. Effect of Ce on microstructures of as-cast alloys

Fig. 1 shows the microstructure of the alloys with different content of Ce. As Fig. 1a shows, the microstructure of the Alloy I, i.e., the conventional AZ61 alloy is composed of the primary α(Mg) matrix, and a secondary

TABLE I Chemical compositions of the experimental alloys

Alloy no.	Ce	Al	Zn	Mn	Fe	Cu	Ni	Mg
I	0.0	5.546	1.008	0.33	0.012	0.004	0.0015	Bal
II	0.5	5.504	1.009	0.33	0.012	0.004	0.0015	Bal
III	1.0	5.582	0.9163	0.31	0.012	0.004	0.0015	Bal
IV	1.5	5.415	0.9604	0.32	0.012	0.004	0.0015	Bal

phase that exists in two kinds of morphologies, i.e., a discontinuous network of coarse particles along grain boundaries, and many spherical particles that distribute both inside grains and at grain boundaries. In Alloy III, i.e., the alloy with 1.0% Ce (Fig. 1b), there is much less secondary particles and the particle size becomes much smaller. Beside some spherical particles can be observed either in grains or along grain boundaries (Mn enrich), there are still some rod-shaped precipitates at grain boundaries. However, when the Ce addition was increased from 1.0 to 1.5%, precipitation of secondary particles increased again, and the size of particles became much larger.

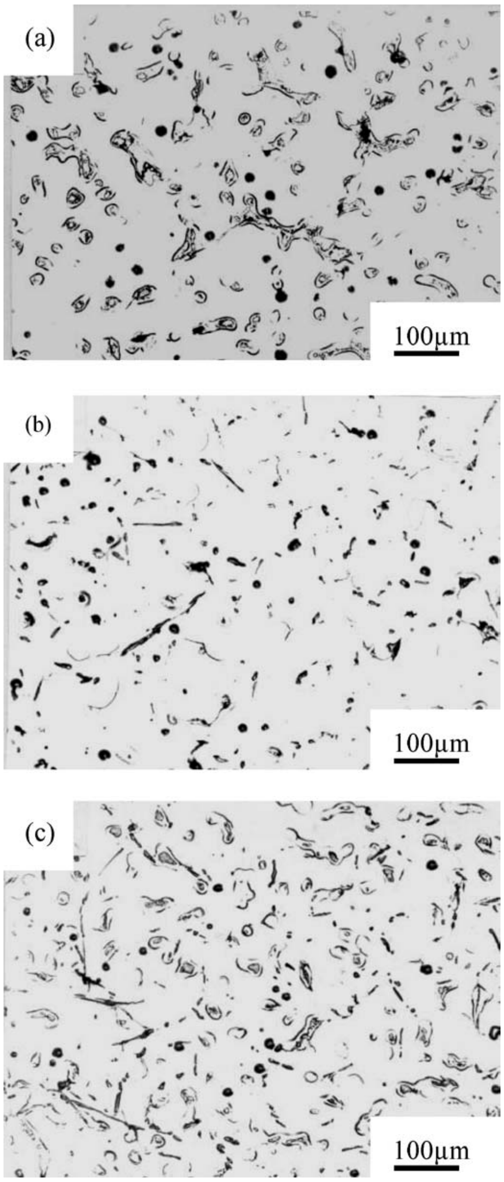

Figure 1 The optical micrographs of as cast alloy: (a) Alloy I, (b) Alloy III, and (c) Alloy IV.

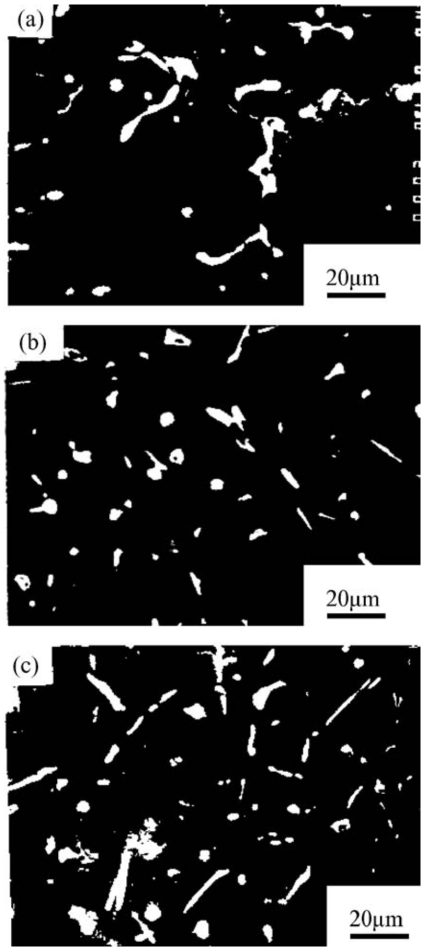

Figure 2 SEM image of as cast alloys: (a) Alloy I, (b) Alloy III, and (c) Alloy IV.

Fig. 2a is the SEM image of the secondary phase in Alloy I. It is well known that this phase is $Mg_{17}Al_{12}$, which has a *bcc* crystal structure of β (Mn) type and a lattice parameter 1.054 nm [7]. When Ce was added into AZ61 alloy, β particles were refined. From the fact that there were much less β particles in Alloys II and III, it could be concluded that Ce suppressed precipitation of the β phase to a large extent. However, as Fig. 2b and c suggest a new kind of secondary particles that have different morphology and distribution characteristics from β precipitate in the Ce-containing alloys. These particles generally have rod-like shape and do not have an obvious tendency to distribute in grains [8]. Further, when the Ce content is in the range from 0.5 to 1.0%, as that in Alloy III, these particles are very fine. With increasing the content of Ce, both size and amount of these particles increase. When the Ce content is 1.5%, the particles become a little coarse.

Figs 3 and 4 show the results of XRD analysis and EPMA analysis respectively of as-cast Ce-containing alloys. From XRD spectrum, it can be concluded that Ce-containing alloys have three kinds of phases, i.e., magnesium matrix (i.e., α), $Mg_{17}Al_{12}$ (β) and a new phase as Al_4Ce [9, 10]. EPMA study proves that the chemical composition of the new phase is Ce:20.18%, Al:79.12%, Zn:1.70%. That can be defined as Al_4Ce which is in correspondence with XRD analysis.

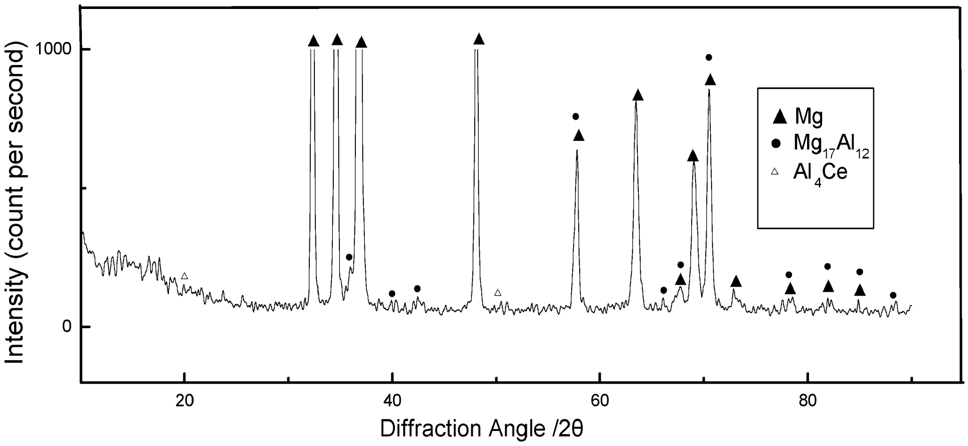

Figure 3 X-ray result of Alloy III.

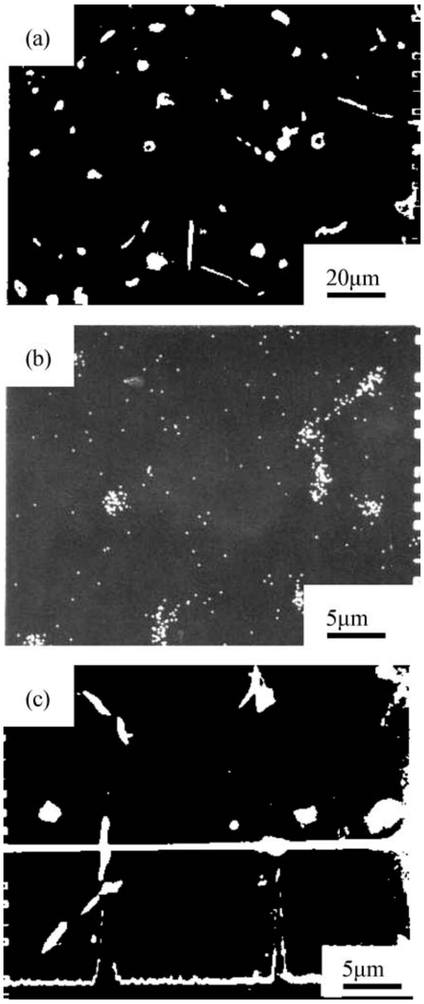

Figure 4 SEM image and distribution of Ce in as cast Alloy III.

3.2. Effects of solution treatment on microstructures of the alloys

Fig. 5 shows the optical microstructure of the alloys that were solutionized at 400°C for 10 h. When there is no Ce addition, as Alloy I (Fig. 5a), almost all secondary particles were dissolved into magnesium matrix. In contrary, there are still secondary particles in the Ce-containing alloys even after solution heat treatment. Thus, it can be concluded that solution at this temperature can only cause dissolution of the β particles, but cannot affect the precipitation morphology of Al_4Ce.

Above conclusions from optical observations were further proved by SEM observations and EPMA analyses on both Alloy I and Alloy III, as shown in Fig. 6. The fact that Al_4Ce could not be dissolved into magnesium matrix suggests that it has high solid solution temperature and it is stable under high temperature [9].

3.3. Effects of Ce on microstructures during hot deformation

Fig. 7 shows typical microstructures with different contents of Ce after hot extrusion at 350°C. Apparently, recrystallization occurred in both alloys because the hot extrusions temperature were above the recrystallization temperature of 250°C [2]. As shown in the figures, recrystallization made the grains become fine and equiaxed. Further, the grain size of the Ce-containing alloy (Fig. 7b) is much smaller than the alloy without Ce addition (Fig. 7a). Thus, it can be concluded that Ce can bring about better grain-refining effect on AZ61 alloy.

As Fig. 8 shows, best grain-refining effect can be obtained when the content of Ce is 1.0%. When the content of Ce is over 1.0%, grain size increases again. This phenomenon may be explained by the following mechanisms. The thermodynamically stable Al_4Ce can act as nuclei for dynamic recrystallization (DRX) when the alloys are hot extruded. When Ce content is lower than 1.0%, the precipitation of the Al_4Ce phase increases along with the increase of Ce content, but growth or coalesce of Al_4Ce particles cannot occur. Therefore, the number of nuclei of DRX grain increases and in turn brings about better DRX refinement.

When the content of Ce exceeds 1.0% (e.g., 1.5%), Al_4Ce particles are likely to grow and coalesce with neighbor particles. This can greatly decrease the number of particles. Since Al_4Ce particles act as nuclei of DRX grains, growth and coalesce of them can cause serious loss of nuclei. Thus, the DRX refining effect of Al_4Ce is greatly weakened and grain size increases. As Fig. 8 shows, optimal DRX grain refining effect can be obtained at 1.0%Ce addition.

When the hot-extruded alloys were annealed at 320°C for 1 h, grain growth occurred, as shown in Fig. 9. For example, the grain sizes for both Alloy

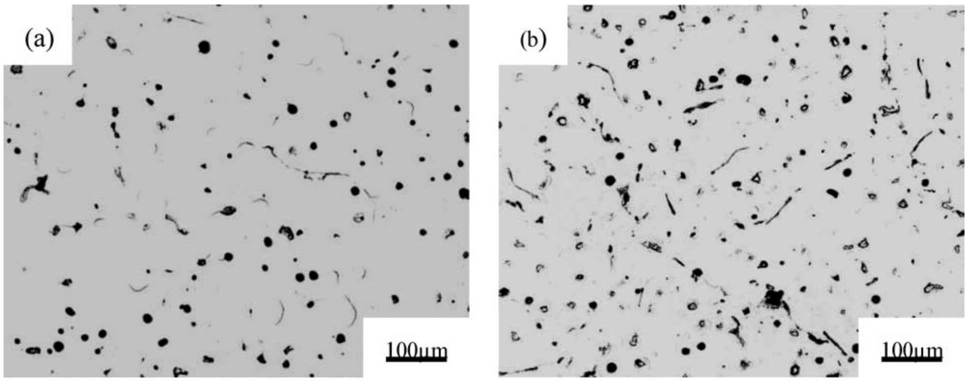

Figure 5 The optical micrographs of solution treatment: of (a) Alloy I and (b) Alloy II.

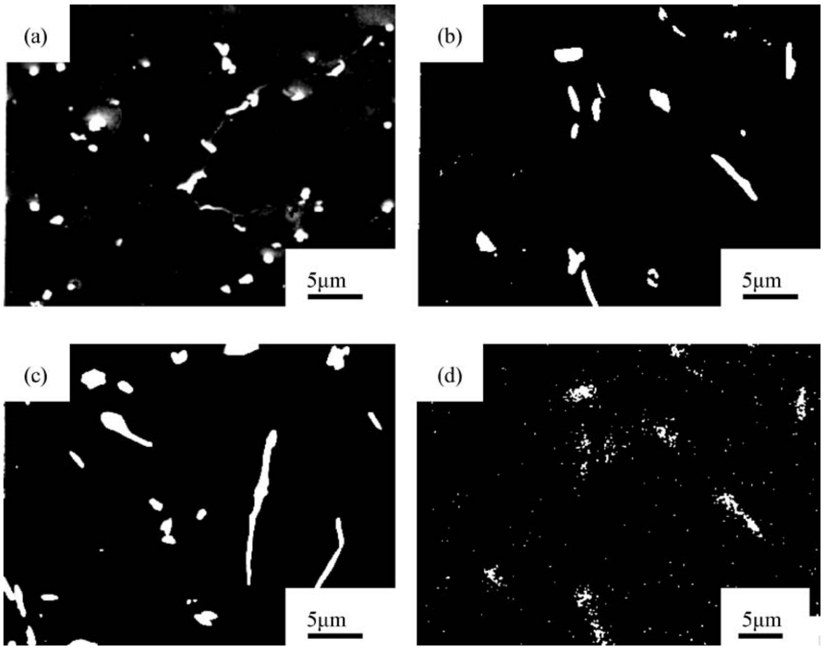

Figure 6 SEM image of the solution treatement: (a) Alloy I, (b) Alloy III, (c) Alloy IV, and (d) Ce distribution in Alloy III.

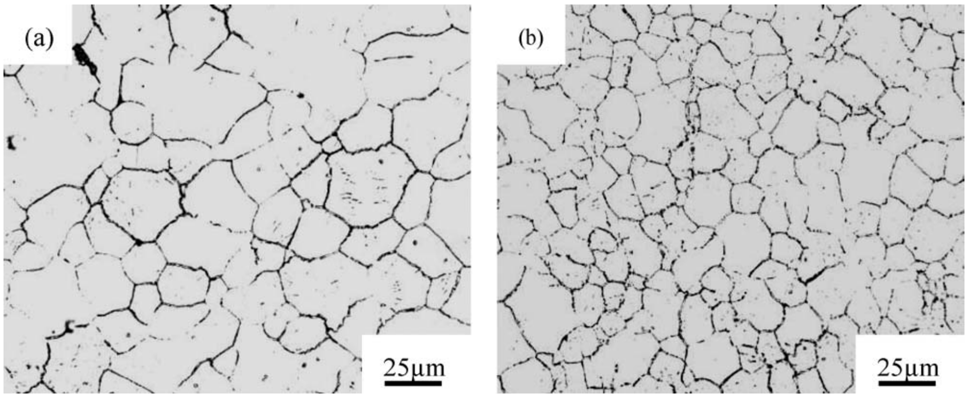

Figure 7 The optical micrographs of hot extrusion: (a) Alloy I and (b) Alloy III.

I and Alloy III after hot extrusion are 19.7 and 13.2 μm respectively. After annealing, the grain sizes for Alloy I and Alloy III are 23.3 and 16.3 μm. The grain growth rates of the alloys seem to be same as shown in Fig. 8. Thus, it can be concluded that the grain growth in Ce-containing alloys seem to be that in AZ61 alloy, and Ce takes a little function during annealing.

3.4. Effects of Ce addition on mechanical properties

Fig. 10 shows the effect of Ce addition on the room temperature mechanical properties of the AZ61 alloy. Compared to the AZ61 alloy, the tensile strength and yield strength show a little increase with a suitable Ce addition. At Ce content of 1.0%, the tensile strength and yield strength have a maximum value of 302.0

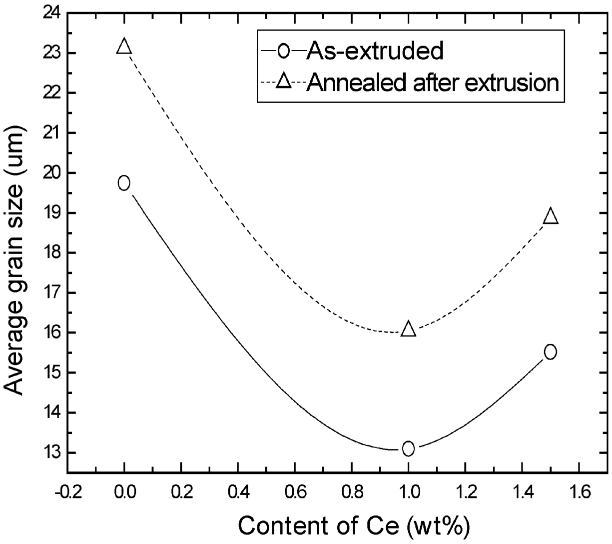

Figure 8 The relationship between grain size and Ce content.

and 180.0 MPa respectively. As Ce content is 1.5%, the tensile strength and yield strength decrease obviously. Similarly, the elongation has a maximum when Ce content is 1.0%. Extra Ce content leads to a decrease in strength and elongation. After annealing, the tensile strength and yield strength somewhat decreases, but elongation increases. At Ce content of 1.0%, the elongation reaches a maximum value of 16.5%, whereas the elongation has a minimum value at Ce content of 1.5%. It is concluded that the effect of Ce on the tensile strength is not very obvious after hot extrusion or annealing, but the yield strength is increased by Ce addition less than or equal to 1.0% after hot extrusion.

4. Discussion

4.1. Effect of Ce on microstructures

The AZ61 alloy is composed of primary α(Mg) solid solution of aluminum in magnesium and the intermetallic compound β($Mg_{17}Al_{12}$), of which the eutectic isothermal temperature is 433°C [11]. When Ce is added to AZ61, it is possible to form Al-Ce and Mg-Ce compound. This is dependent on its chemical activity and the capability of reaction with other elements like Al or Mg. Because it has positive electronic characteristics with both Al and Mg, Ce is likely to react with Al in priority. Based on the Al-Ce binary phase diagram [12], Al_4Ce can be formed when Ce content is less than 60%. XRD and EPMA analyses of the Ce-containing alloys proved the precipitation of the needle-like A_4Ce particles in these alloys (Figs 1 and 2). As a result, much Al is bounded by Al_4Ce, and the amount of Al for formation of the β phase ($Mg_{17}Al_{12}$) is decreased. Therefore, the precipitation of β particles is suppressed by the formation of Al_4Ce. When the alloys are solutionized, thermodynamically unstable phases will dissolve into α matrix, like β ($Mg_{17}Al_{12}$). However, A_4lCe cannot be dissolved because it is stable at the process temperature. Therefore, the morphology of Al_4Ce can hardly be changed by general annealing treatment.

4.2. Effect of Ce on dynamic recrystallization

As is well known, dynamic recrystallization occurs in common magnesium alloys during hot deformation [13]. Under the hot extrusion conditions in this work, DRX completed in the AZ61 alloy because the process temperature is above the recrystallization temperature [2]. Microstructure observations indicate that fine DRX grains exist in the extruded AZ61 alloy and the grain size is about 20 μm.

When Ce of suitable content is added to AZ61, it brings about precipitation of an extra phase, i.e., Al_4Ce. The Al_4Ce particles can be broken and dispersed in magnesium matrix. These dispersed Al_4Ce particles play an important role in recrystallization. Firstly, thermally stable Al_4Ce_3 intermetallics with a relatively high melting point can pin grain boundaries and impede grain growth during hot deformation. Secondly, concentrated strain in the vicinity of Al_4Ce particles can introduce sites of high dislocation density and large orientation gradient (particle deformation zone). Such sites are ideal for nucleation of recrystallized grains. It is known that a particle deformation zone may extend to a distance of even one diameter from the surface of the particles and may be disoriented by tens of degrees from the adjacent matrix. In these deformation zones, second phase particles can stimulate nucleation of DRX grains [14]. Thus, nucleation of recrystallization can be promoted by Ce addition in AZ61 alloy. As a result, the grains of the alloys with 1.0%Ce addition are finer than that of the AZ61 alloy, and the size is

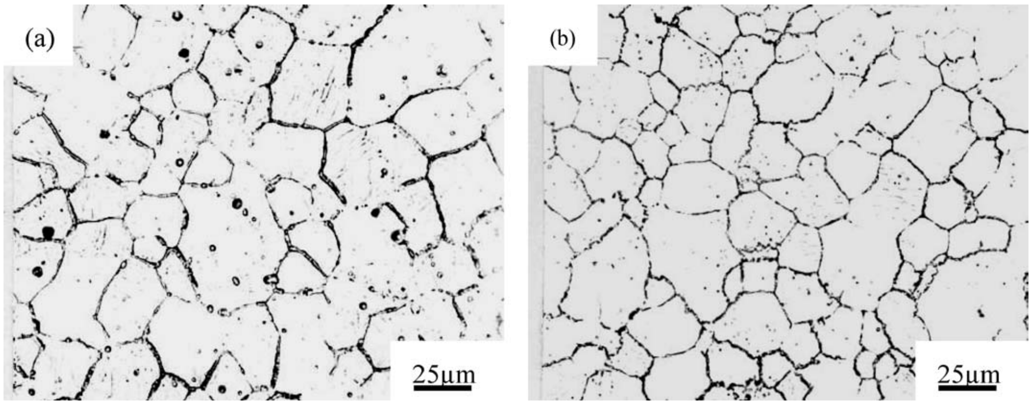

Figure 9 The optical micrographs of hot extrusion after annealing at 320°C: (a) Alloy I and (b) Alloy III.

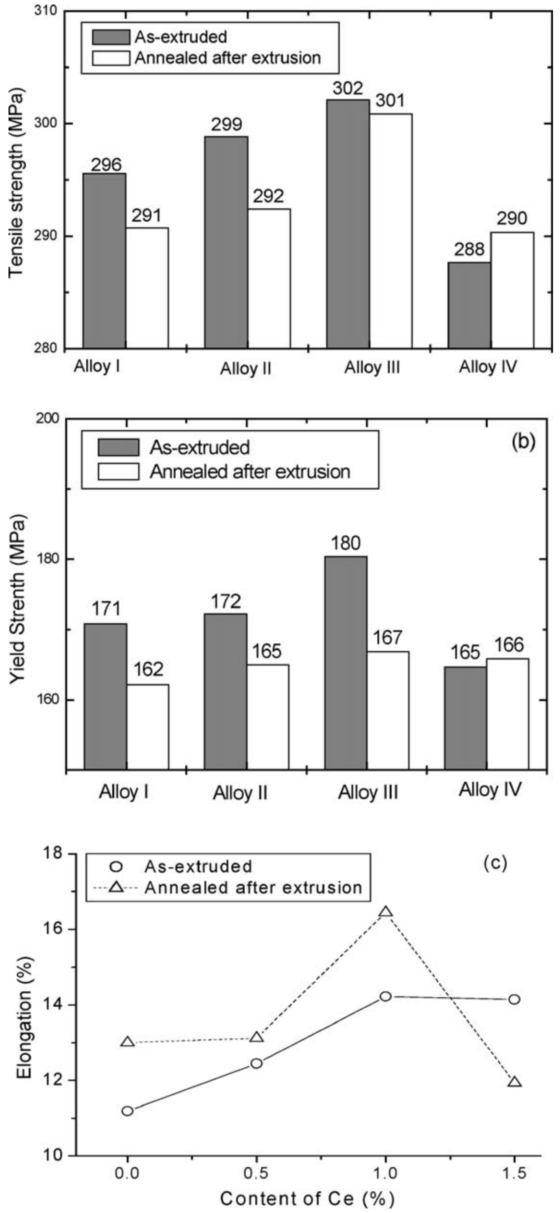

Figure 10 The mechanical properties of Alloy I–IV: (a) the tensile strength, (b) the yield strength, and (c) the elongation.

about 13.5 μm. Certainly, better grain-refining effect brings about improvement of both strength and ductility. However, when there is too much Ce, e.g., 1.5%, coarsening of Al_4Ce particles can decrease number of nucleation sites which cause cleavages on surrounding matrix. Therefore, mechanical properties will be affected.

5. Conclusion

(1) When Ce is added to AZ61, rod-like Al_4Ce particles precipitate both inside grains and at grain boundaries. Ce seriously suppresses the precipitation of $Mg_{17}Al_{12}$ particles. Ce refines $Mg_{17}Al_{12}$ particles in as-cast alloys. High Ce content (>1.0 wt pct) can lead to formation of coarse Al_4Ce particles.

(2) Hot extrusion brings about grain refinement in all kinds of alloys. Ce has a refining effect on DRX grains. When the content of Ce is lower than 1.0%, the Ce-containing alloys have smaller grains than AZ61. When the content of Ce is higher than 1.0%, the size of DRX grains increases again.

(3) Ce addition brings about improvement in both strength and ductility of the hot-extruded alloys when its content is lower than 1.0%. When there is 1.5% Ce, the strength and ductility decrease largely. The alloy with 1.0%Ce has optimal mechanical properties. The improvement of mechanical properties by Ce addition is ascribed to the grain-refining effect during DRX.

References

1. J. DAVIS, SAE Technical Paper #910551, International Congress and Exposition, SAE International 1999.
2. "ASM Specialty Handbook, Magnesium and Magnesium Alloys" (ASM International, Materials Park, Ohio, 2000).
3. F. V. BUCH, S. SCHUMANN, E. AGHION, B. BRONFIN and B. L. MORDIKE, in edited by, K. U. Kainer "Magnesium Alloys and their Application" (WILEY-VCH Verlag Gmbh, D-69469 Weiheim, 2000) p. 23.
4. T. G. BASNER, M. EVANS and D. J. SAKKINEN, SAE Tech. Paper No. 930419 (1993).
5. WANG QU-DONG and LU YI-ZHEN, *Mater. Sci. Eng.* A **278** (2000) 66.
6. T. MUKAI, T. MOHRI, M. MABUCHI, M. NAKAMURA, K. ISHIKAWA and K. HIGASHI, *Scripta Mater.* **39** (1998) 1249.
7. P. VILLARS and L. D. CALVERT, PEARSONS, "Handbook of Crystallographic Data Intermetallic Phases," 2nd ed. (ASM International Materials Park, Oh, 1996) Vol. 1, p. 1016.
8. G. PETTERSEN, R. HØIER, O. LOHNE, and H. WESTENGEN, *Mater. Sci. Eng.* A **207** (1996) 115.
9. Y. LI and H. JONES, *Mater. Sci. Tech.* **12**(8) (1996) 651.
10. L. Y. WEI, G. L. DUNLOP and H. J. WESTENGEN, *Mater. Sci.* **31**(2) (1996) 387.
11. K. Y. SOHN, J. W. JONES and J. E. ALLISON, edited by H. I. Kaplan, J. Hryn and B. Clow "Magnesium Technology 2000," (TMS, 2000) p. 271.
12. "American Society for Metals, Metals Handbook" (Metals Park, Ohio, 1973).
13. S. I. ION, F. J. HUMPHRYS and S. H. WHITE, *Act. Metal.* **30** (1982) 1909.
14. R. D. DOHERTY, D. A. HUGHES, F. J. HUMPHRYS ET AL., *Mater. Sci. Eng.* A **238** (1997) 217.

Received 26 December 2002
and accepted 23 June 2004