Behaviour of calcium in Mg-6Li-3Al alloy

R. Wu[1]*, C. Wang[2], M. Zhang[1]

[1] Key Laboratory of Superlight Materials & Surface Technology, Harbin Engineering University, Ministry of Education, Harbin 150001, P. R. China
[2] College of Materials Science & Engineering, Chongqi University, Chongqi 400030, P. R. China

Received 5 January 2009, received in revised form 5 March 2009, accepted 17 March 2009

Abstract

As-cast and extruded alloys of Mg-6Li-3Al-(0-5)Ca were prepared. The microstructure was characterized and the mechanical properties of these alloys were measured. Results show that the addition of Ca can inhibit the formation of AlLi and promote the formation of Al_2Ca. The Al_2Ca phase exists in the lamellar form. The addition of Ca can also refine the microstructure of the alloys. The influence of Ca on the microstructure leads to the variation of mechanical properties. The decrease of AlLi phase and the increase of bone-like Al_2Ca are both unfavourable for the mechanical properties of alloys, while the refinement effect of Ca improves the mechanical properties of alloys. Therefore, the optimal Ca addition is 2 wt.% for Mg-6Li-3Al alloy.

Key words: Mg-Li alloy, calcium, microstructure, mechanical properties

1. Introduction

Magnesium alloys are the most promising metal materials for their light weight [1–5]. In Mg-Li base alloys, the density of them is decreased further because of containing of Li element. The density of Mg-Li base alloys is about 1.35–1.70 g cm^{-3} [6, 7]. Accordingly, Mg-Li base alloys are more attractive for lightweight materials designer than other magnesium alloys.

Mg-Li alloys can be classified into three major categories based on the constitutional phases present in the system. They are: α alloys with lithium less than 5.7 wt.%, β alloys with lithium more than 11.3 wt.% and $(\alpha + \beta)$ alloys with lithium ranging from 5.7 to 11.3 wt.% [8]. The plasticity property of Mg-Li alloys becomes better because the addition of Li can decrease the c/a value of α crystal lattice, and/or body-centered cubic structure of β phase possesses more sliding systems. However, the β phase is a soft phase, which makes the strength of alloys decrease. The alloying elements in Mg-Li alloys can improve the mechanical properties. Al is the most commonly used alloying element for Mg-Li alloys [9, 10]. To obtain a good combination between strength and plasticity, Mg-6Li-3Al is chosen as the base metal in this paper.

Calcium has the potential to further reduce the density of Mg-Li base alloys because of its low density.

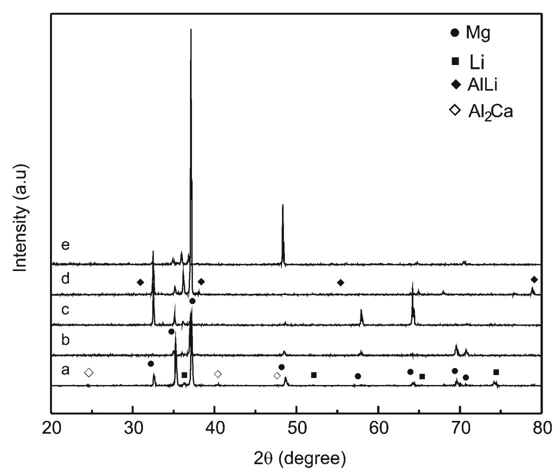

Fig. 1. XRD patterns for Mg-6Li-3Al-xCa: a) $x = 0$, b) $x = 1$, c) $x = 2$, d) $x = 3$, e) $x = 5$.

*Corresponding author: tel.: 86-451-82519696; fax: 86-451-82519696; e-mail address: Ruizhiwu2006@yahoo.com

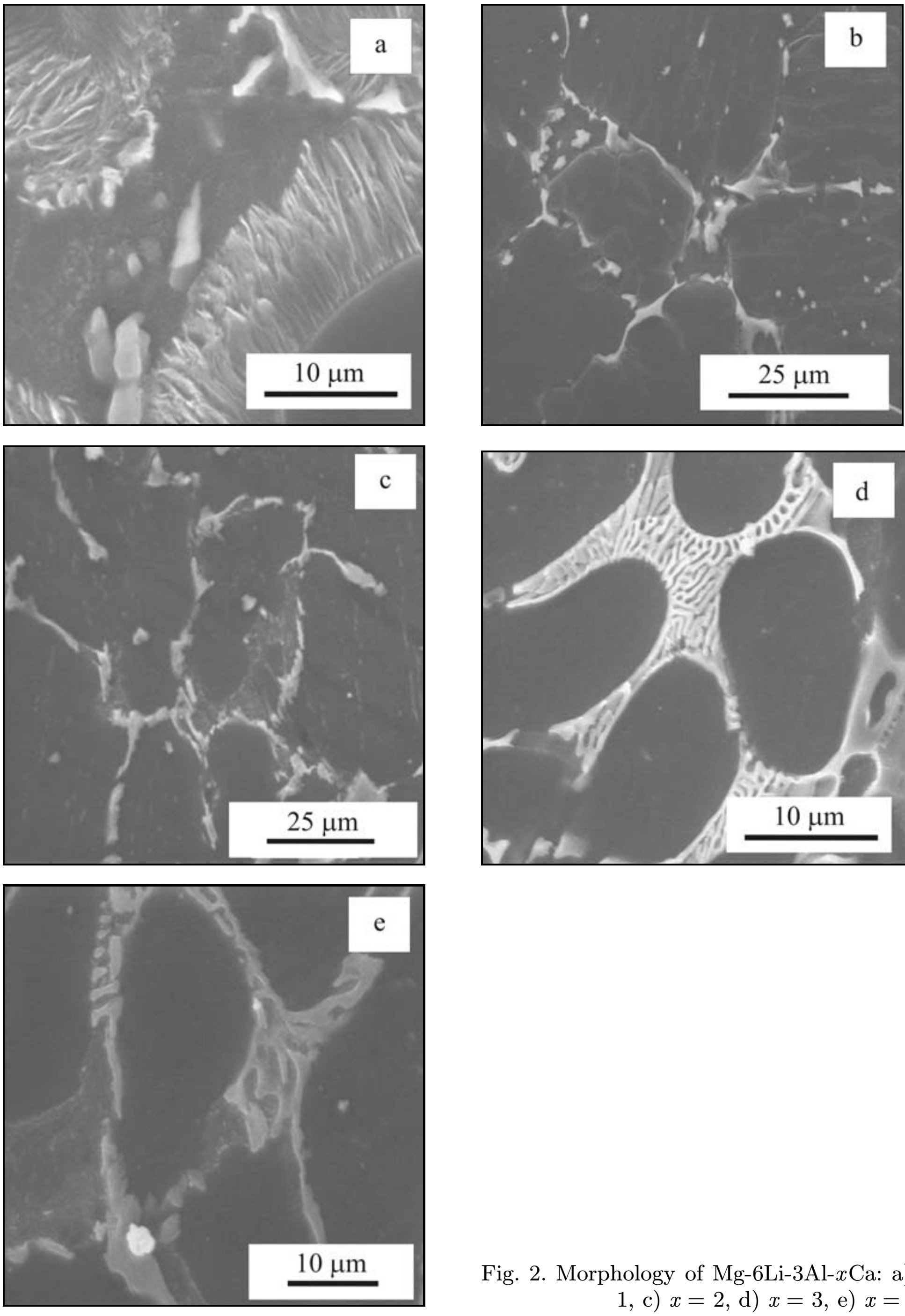

Fig. 2. Morphology of Mg-6Li-3Al-xCa: a) $x = 0$, b) $x = 1$, c) $x = 2$, d) $x = 3$, e) $x = 5$.

Ca also has obvious refining effect on the microstructure of Mg base alloys [11]. Additionally, Ca is known to inhibit the ignition of molten magnesium [12]. Improving oxidation resistance is an important issue to be addressed for the application of Mg alloys as structural materials and Ca has been reported to reduce solid oxidation of Mg-Li alloys [13].

Presently, little information is available in the literature with regard to influence of Ca on the microstructure and mechanical properties of Mg-Li-Al alloys [11, 14, 15]. In this paper, the emphasis is placed on the behaviour of Ca on Mg-6Li-3Al alloy. The microstructure and mechanical properties of Mg-6Li-3Al-xCa with x ranging from 0 to 5 wt.% are studied.

2. Experimental procedure

Alloys of nominal composition Mg-6Li-3Al-xCa (x = 0–5 wt.%) were prepared by melting commercial pure Mg, Li, Al, and Ca in an induction furnace under an argon atmosphere. The materials of Mg, Al

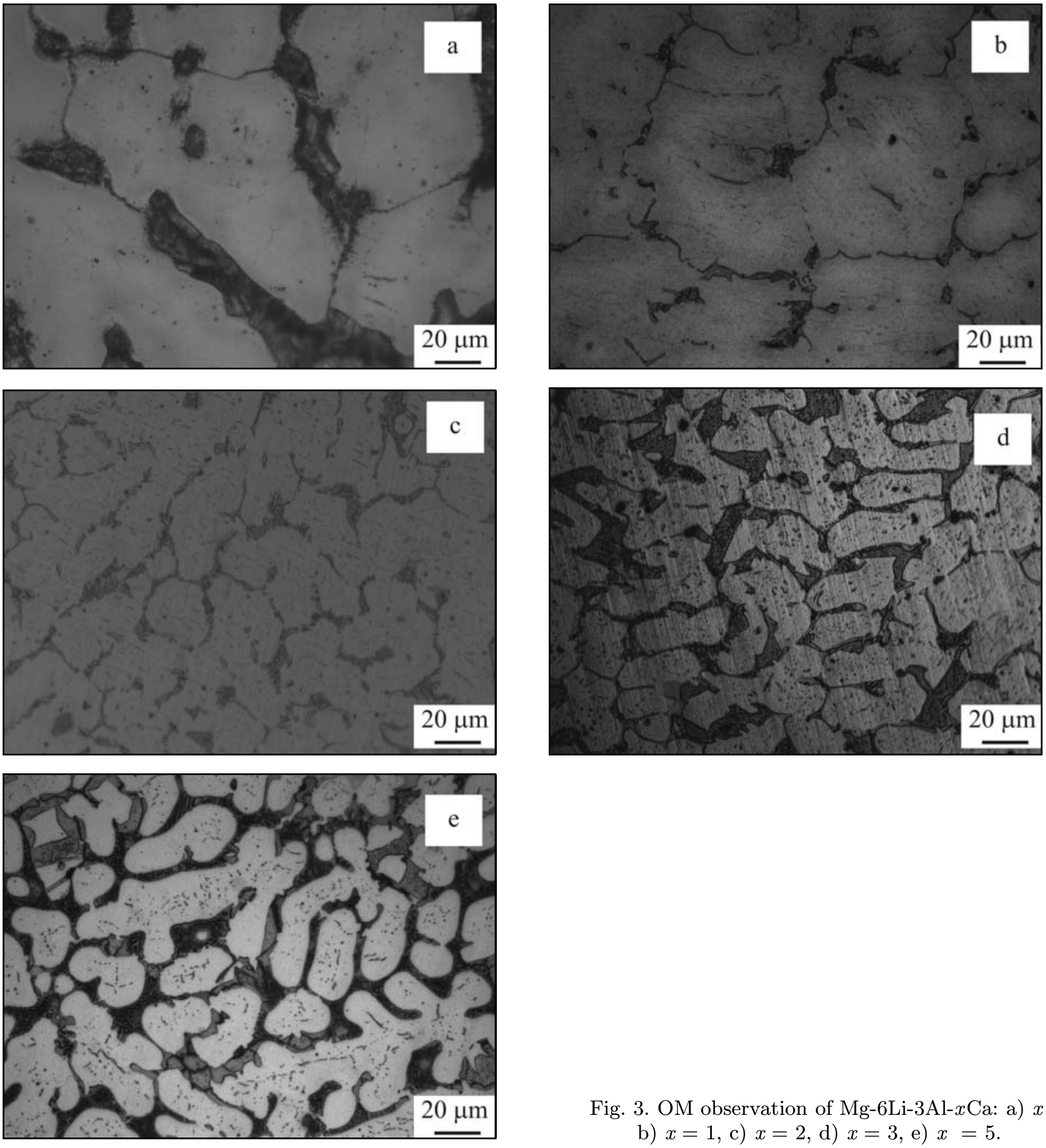

Fig. 3. OM observation of Mg-6Li-3Al-xCa: a) $x = 0$, b) $x = 1$, c) $x = 2$, d) $x = 3$, e) $x = 5$.

and Ca were loaded in a graphite crucible and then were inductively heated. The melt was then cast into steel moulds to obtain as-cast ingots. An annealing heat treatment was conducted at 250 ℃ for 12 h for the ingots. Then the ingots were extruded (from ø 50 mm to ø 10 mm) at the extruding speed of 50 m min^{-1}.

The microstructure and phase information were obtained by a combination of optical microscope (OM), X-ray diffraction (XRD), scanning electron microscope (SEM). Samples for OM and SEM observations were etched using a reagent of 3 vol.% nital for ∼ 30 s.

The strength and elongation percentage were used to characterize the mechanical properties of alloys. They were measured by a tensile tester at the tensile speed of 2 mm min^{-1} at room temperature.

3. Results

3.1. Microstructure of alloys investigated

The results of phases analysis for the alloys investigated are shown in Fig. 1. In Mg-6Li-3Al alloy, there exist α phase, β phase and AlLi phase. With the addition of Ca, the AlLi disappears (as shown in Fig. 1b,c). When the Ca content reaches 3 wt.%, the Al_2Ca phase

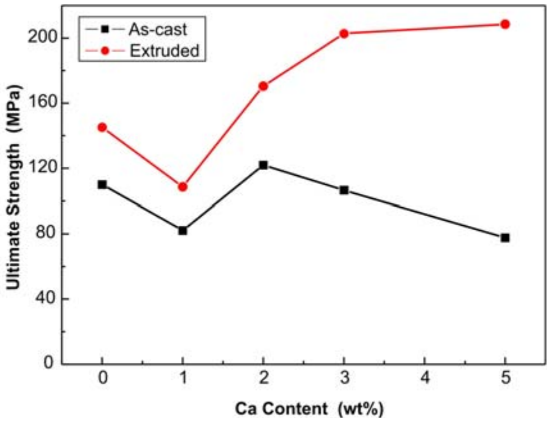

Fig. 4. Ultimate strength of Mg-6Li-3Al-xCa.

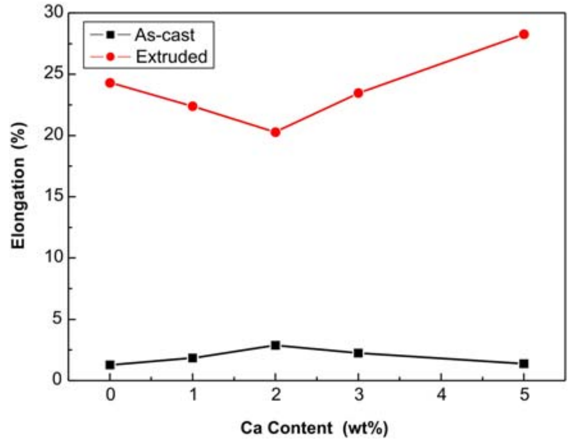

Fig. 5. Elongation of Mg-6Li-3Al-xCa.

begins to exist in the alloys (as shown in Fig. 1d,e).

In Fig. 2a, the feathery AlLi phase exists at the grain boundary of primary α phase. β phase also exists at the grain boundary of primary α phase mainly and a little amount of β phase exists in the grains. With the addition of Ca, the morphology of alloys is composed of primary α phase and β phase, without feathery AlLi phase (as shown in Fig. 2b,c). Further increasing the Ca content brings about the bone-like Al_2Ca, which exists in the β phase (as shown in Fig. 2d,e).

From the OM observation of Fig. 3, it is known that the addition of Ca has refining effect on Mg-6Li-3Al alloy, and the microstructure is the finest when the Ca content is 3 wt.%. Additionally, in the alloys of Mg-6Li-3Al-3Ca and Mg-6Li-3Al-5Ca, the amount of β phase is larger than that of Mg-6Li-3Al-(0,1,2)Ca.

The microstructure of as-extruded alloys is composed of equiaxed grains. This demonstrates that the dynamic re-crystallization happens during the process of extrusion. The grain size of alloys is refined after extrusion. The average grain size of as-extruded Mg-6Li-3Al-(0-5)Ca is 5–10 μm.

3.2. Mechanical properties

Figures 4 and 5 show the mechanical properties of alloys investigated in this paper. After the extrusion, both strength and elongation are improved obviously. With the increase of Ca content, the strength of as-cast alloys decreases first and then increases. When the Ca content is larger than 2 wt.%, the strength will decrease with the increase of Ca content. However, in the extruded alloys even the addition of Ca is larger than 2 wt.%, the strength of alloys can still be improved further. As for the elongation of alloys, with the increase of Ca content, elongation increases first and then decreases, while the variation trend of elongation of extruded alloys is opposite to

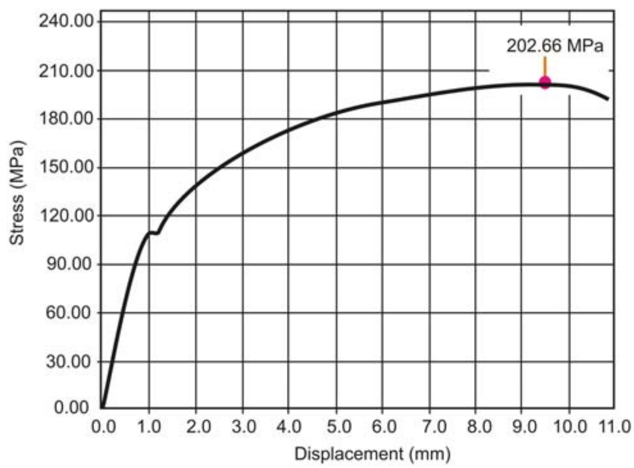

Fig. 6. Stress-displacement curve of Mg-6Li-3Al-3Ca.

that of as-cast alloys. The stress-displacement curve of Mg-6Li-3Al-3Ca is shown in Fig. 6. Because the stress-displacement curves of other alloys investigated in this paper have the same variation trend, they are not displayed in this paper. In these curves, it can be known that yield ratios of the extruded alloys are 1.53–2.01.

4. Discussion

4.1. Influence of Ca on the microstructure of alloys

Because the atomic diameters of Al, Mg, Li, and Ca are close to each other, the Al and Ca are both solid dissolved in α and β phases in the form of substitution solid solutions. The atomic diameter of Ca is larger than that of Li, while the atomic diameter of Al is less than that of Li [16]. Therefore, the solid solution of Ca in β phase can bring about the increase of the solid solubility of Al in β phase. Accordingly, the addition of Ca makes the AlLi phase disappear (as shown in Fig. 1b,c and Fig. 2b,c). When the Ca content reaches 3 wt.%, it cannot be dissolved in α and β phases any longer. It will react with other elements to form compounds. Among the elements of Ca, Al, Mg, and Li, the electronegative difference between Ca and Al is larger than that between Ca and other elements [17]. The Ca that cannot be dissolved in α phase and β phase reacts with Al to form Al_2Ca phase (as shown in Fig. 1d,e). The Al_2Ca exists in the bone-like form at the place of β phase (as shown in Fig. 2d,e). During the solidification of melt, the α phase and β phase form as primary phases in the alloys, then the Al_2Ca phase forms in the primary β phase in the form of eutectic.

The equilibrium distribution coefficients of Ca in Li and Mg are both less than 1 [18]. The addition of Ca in Mg-Li base alloys brings about the increase of constitutional supercooling of melt, refining the microstructure of alloys. When the Ca content is large, because of the formation of Al_2Ca, which consumes some Al and Ca, the constitutional supercooling effect becomes less obvious. Accordingly, the refining effect becomes less obvious when Ca content is large (as shown in Fig. 3).

4.2. Influence of Ca on mechanical properties of alloys

Because the addition of Ca changes the microstructure of alloys, it also makes the mechanical properties of alloys change. There are three factors that affect the mechanical properties of the alloys investigated in this paper. Firstly, with the addition of Ca, because of the disappearance of AlLi phase, which has strengthening effect on alloy, the strength will decrease and elongation will increase. Secondly, the refining effect of Ca on the alloys is favourable for both strength and elongation of alloys. Thirdly, the bone-like Al_2Ca phase in alloys is unfavourable for both strength and elongation of alloys, while the Al_2Ca phase, which crashes from bone-like shape after extrusion deformation is favourable for strength and elongation of alloys.

Under the combining effects that are mentioned above, the mechanical properties of alloys are shown in Figs. 4 and 5. When the Ca content is 1 wt.%, the AlLi phase disappears from the alloys, making the strengthening effect of it disappear as well. Because the Ca content is relatively low, the refining effect of Ca is not obvious. These two aspects lead to the decrease of strength and the increase of elongation. When the Ca content is 2 wt.%, the refining effect of Ca becomes obvious, which causes the increase of strength and elongation. With the increase of Ca content further, because of the formation of bone-like Al_2Ca phase, the strength and elongation of the alloys decrease. After the extrusion, both strength and elongation are higher than those of as-cast alloys. During the extrusion, because the bone-like Al_2Ca phase is crashed to dispersive particles, even when the Ca content is larger than 2 wt.%, the strength and elongation can still further increase.

5. Conclusions

The addition of Ca makes the AlLi phase disappear, and it has refining effect on the microstructure. The disappearance of AlLi phase is unfavourable for strength, and the refining effect is favourable for strength. Both the disappearance of AlLi and the refining effect are favourable for elongation improvement. When the Ca content is larger than 2 wt.%, the bone-like Al_2Ca forms in β phase. The bone-like Al_2Ca is unfavourable for strength and elongation. After extrusion, the bone-like Al_2Ca can be crashed as fine particles, improving the strength and elongation of alloys.

Acknowledgements

Project (2006AA03Z511) supported by the National Hi-Tech Research Development Program of China; Project (2007RFQXG032) supported by the project of Harbin Science and Technology innovative talents.

References

[1] MILIČKA, K.: Kovove Mater., *46*, 2008, p. 323.
[2] TROJANOVÁ, Z.—LUKÁČ, P.—WEIDENFELLER B.—RIEHEMANN, W.: Kovove Mater., *46*, 2008, p. 243.
[3] TROJANOVÁ, Z.—SZÁRAZ, Z.—RYSPAEV, T.—WESLING, V.: Kovove Mater., *46*, 2008, p. 285.
[4] DOBROŇ, P.—BOHLEN, J.—CHMELÍK, F.—LUKÁČ, P.—LETZIG, D.—KAINER, K. U.: Kovove Mater., *45*, 2007, p. 129.
[5] LUKÁČ, P.—KOCICH, R.—GREGER, M.—PADALKA, O.—SZÁRAZ, Z.: Kovove Mater., *45*, 2007, p. 115.
[6] WU, R. Z.—ZHANG, M. L.: J. Rare Earths, *25*, 2007, p. 547.
[7] WU, R. Z.—ZHANG, M. L.: Trans. Nonferrous Met. Soc. China, *17*, 2007, p. 448.
[8] ZHONG, H.—FENG, L. P.—LIU, P. Y. et al.: J. Comput. Aid. Mater. Des., *10*, 2005, p. 191.
[9] WANG, T.—ZHANG, M. L.—WU, R. Z.: Mater. Lett., *62*, 2008, p. 1846.
[10] ZHONG, H.—LIU, P. Y.—ZHOU, T. T. et al.: J. Univ. Sci. Technol. Beijing Eng. Ed., *12*, 2005, p. 182.
[11] SONG, G. S.—KRAL, M. V.: Mater. Charact., *54*, 2005, p. 279.
[12] SAKAMOTO, M.—AKIYAMA, S.—OGI, K.: J. Mater. Sci. Lett., *16*, 1997, p. 1048.

[13] SONG, G. S.—STAIGER, M. S.—KRAL, M. V.: In: TMS Annual Meeting, Magnesium Technology 2003. Ed.: Kaplan, H. I. Warrendale, PA, TSM 2003, p. 77.
[14] RAMESH, C.—SAKAI, T.—KAMADO, S. et al.: J. Jpn. Inst. Light Met., *48*, 1998, p. 13.
[15] LI, H. B.—YAO, G. C.—LIU, Y. H. et al.: Acta Metall. Sin., *19*, 2005, p. 355.
[16] AVEDESIAN, M. M.—BAKER, H.: ASM Specialty Handbook – Magnesium and Magnesium Alloys. Ohio, ASM International 1999.
[17] CALLISTER, W. D.: Materials Science and Engineering: An Introduction. 7^{th} Ed. New York, John Wiley & Sons Inc. 2006.
[18] OKAMOTO, H.: Desk Handbook: Phase Diagrams for Binary Alloys. Ohio, ASM International 2000.