Journal of Alloys and Compounds 480 (2009) L25–L28

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Letter

Microstructural evolution behavior of Mg–5Si–1Al alloy modified with Sr–Sb during isothermal heat treatment

Hui-Yuan Wang, Min Zha, Bo Liu, Dong-Ming Wang, Qi-Chuan Jiang*

Key Laboratory of Automobile Materials of Ministry of Education, Department of Materials Science and Engineering, Jilin University, Nanling Campus, No. 5988 Renmin Street, Changchun 130025, PR China

ARTICLE INFO

Article history:
Received 14 January 2009
Accepted 11 February 2009
Available online 24 February 2009

Keywords:
Metals
Casting
X-ray diffraction
Partial remelting

ABSTRACT

The microstructural evolution behavior of Mg–5Si–1Al alloys modified with Sr–Sb during isothermal heat treatment was investigated in the present study. Although the morphology of eutectic Mg_2Si phase varied with isothermal holding temperature increasing from 620 to 670 °C, no spheridization occurred for primary Mg_2Si polyhedrons in Sr–Sb-modified alloy even when the temperature reaches 660 or 670 °C. Such an abnormal phenomenon of primary Mg_2Si, during partial remelting isothermal treatment, might be ascribed to both the spheridization restriction effect caused by incorporation of Sb in Mg_2Si and stability of octahedral primary Mg_2Si crystals faced by {1 1 1} planes.

1. Introduction

Recently, improving the elevated temperature properties has become a critical issue for the further application of magnesium alloys [1–4]. Previous investigations showed that the Mg–Si series alloys were very interesting and had high potential as heat-resistant light alloys, because the Mg_2Si phase exhibited a high-melting temperature, low density, low-thermal expansion coefficient and a reasonably high-elastic modulus, and the Mg_2Si phase was very stable and could impede the grain boundary sliding at elevated temperature [4–7]. However, the undesirable, coarse dendritic primary Mg_2Si and brittle Chinese script eutectic phases tended to be formed in Mg–high Si alloys under conventional solidification process, which would apparently give a detrimental effect on the mechanical properties of the alloys [5,6].

More recently, the refinement in size and modification in morphology of Mg_2Si phases have reportedly been responsible for the improvement of mechanical properties of Mg–Al–Si alloys [8–10], and therefore the application of Mg–Si series alloy will be greatly promoted if the dendritic primary and Chinese script eutectic Mg_2Si phases could be modified by a cheep way [4,6].

Semi-solid metal processing (SSM) explored by Flemings in 1972 [11], has a low processing temperature that can effectively resolve the problem of oxidation and burning of magnesium alloys, and thus becomes an important forming process for the manufacture of magnesium alloys [12,13]. Partial remelting process, also called semi-solid isothermal treatment, which relies on the ripening of a more or less dendritic structure when it is heated and held for a period of time between solidus and liquidus temperatures [14], is a promising method for achieving microstructural control, e.g. transforming dendritic crystals to globular grains.

Qin et al. [15,16] have demonstrated that it was feasible to transform the morphology of primary Mg_2Si from coarse dendrite to globular and/or elliptic in A1–15Mg–10.5Si–4Cu alloys by an isothermal heat treatment process (at 565–575 °C for 140 min, or 580 °C for 60 min). Yang et al. [4] also reported that after semi-solid isothermal treatment at 580 or 585 °C for 120 min, the eutectic Mg_2Si phases in Mg–6Al–1Zn–0.7Si alloy could transform from the initial Chinese script shape to granule and/or polygon shapes. In our previous study [17], we found that it was difficult to acquire the designed microstructures in Mg–5Si–1Al alloys only by a single partial remelting, since either the globular primary Mg_2Si or the granular eutectic Mg_2Si phase could be produced in this process. The desired microstructures consisting of both globular primary and granular eutectic Mg_2Si phases were successfully produced by secondary partial remelting [17].

However, investigation about the effect of partial remelting isothermal treatment on the morphological evolution of modified Mg_2Si crystal in Mg–high Si alloys has seldom been carried out. In a previous study [18], it was found that the combined addition of Sr and Sb caused an evident modification effect on both primary and eutectic Mg_2Si phases in Mg–3.5Si–1Al alloys, and that the complex modification of Sr and Sb on Mg_2Si crystals differs greatly from the single modification of Sr or Sb in mechanisms. Hence, the present study was aim to investigate the influence of isothermal heat treatment on the microstructural evolution behavior of

* Corresponding author. Tel.: +86 431 8509 4699; fax: +86 431 8509 4699.
E-mail address: jiangqc@jlu.edu.cn (Q.-C. Jiang).

0925-8388/$ – see front matter
doi:10.1016/j.jallcom.2009.02.044

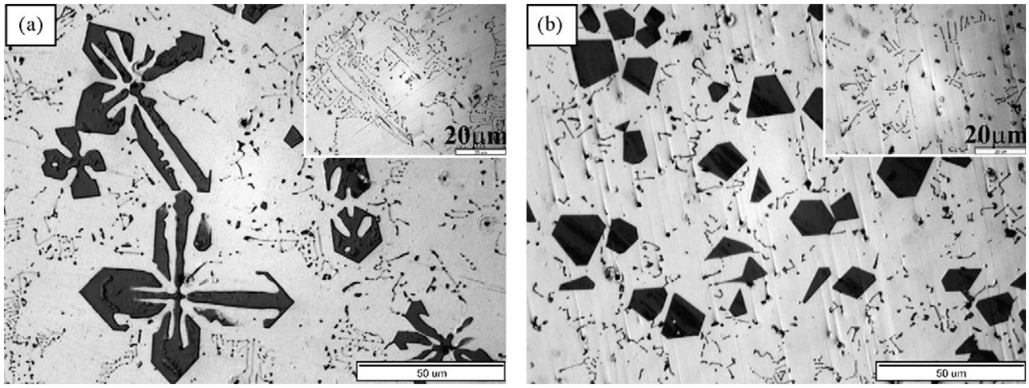

Fig. 1. The as-cast microstructures of (a) unmodified and (b) Sr–Sb-modified Mg–5Si–1Al alloys (the inserts show the high magnification of eutectic Mg_2Si phases).

Mg–5Si–1Al alloys after combined addition of Sr and Sb modifiers. It is expected that the preliminary results could be helpful in the understanding of the morphological evolution of modified primary Mg_2Si crystals.

2. Experimental procedure

Industrial pure Mg ingot (99.85 wt.% purity) and Si (99.02 wt.% purity) were used as starting materials to prepare Mg–high Si casting alloys. The detailed preparation procedure was described in a previous study [7]. About 250 g of Mg–Si alloys were remelted in a graphite crucible in an electric resistance furnace under the protection of a mixed gas atmosphere of SF_6 (1 vol.%) and CO_2 (Bal.). After the melt was held at 750 °C for 5 min, the pure Al (99.98 wt.% purity), Al–10Sr master alloy and pure Sb preheated to ∼150 °C were added to the melts to get the designed Mg–5Si–1Al and Mg–5Si–1Al–0.2(Sr–Sb) alloys, respectively. The Sr and Sb were designed at a molar ratio of 11:10, corresponding to $Sr_{11}Sb_{10}$. The melts were manually stirred for about 2 min using a graphite impeller, held at 780 °C for 20 min, and then poured into a copper mold preheated at 100 °C to produce circular samples of Ø10 mm × 100 mm.

The isothermal heat treatment was performed in an electric resistance furnace under a protective atmosphere of flowing gas of SF_6 (1 vol.%) and CO_2 (Bal.) to prevent oxidation [17]. When the furnace was heated to the predetermined temperature (620, 640, 650 or 660 °C), the semicircular column samples (Ø10 mm × 10 mm) were placed in the furnace and isothermally held at those temperatures for 30 min. The temperature was monitored using a thermocouple placed at the center of the sample with an accuracy of ±1 °C. To preserve the morphology and content of the unmelted fractions which existed at high temperatures, the samples were withdrawn and then quenched in cold water immediately.

Metallographic samples were prepared in accordance with standard procedures used for metallographic preparation of metal samples, and etched with 3 vol.% HF solution for 5–10 s at 25 °C. Microstructure and phase analyses were investigated by using optical microscopy (OM) (OLYMPUS PMG3), and X-ray diffraction (XRD) (D/Max2500PC Rigaku, Japan).

3. Results and discussion

The XRD analysis reveal that both unmodified and Sr–Sb-modified Mg–5Si–1Al alloys consist of Mg_2Si and Mg phases, indicating that the addition of Sr–Sb has no influence on phase compositions of the alloys. Since Al has a relatively high solubil-

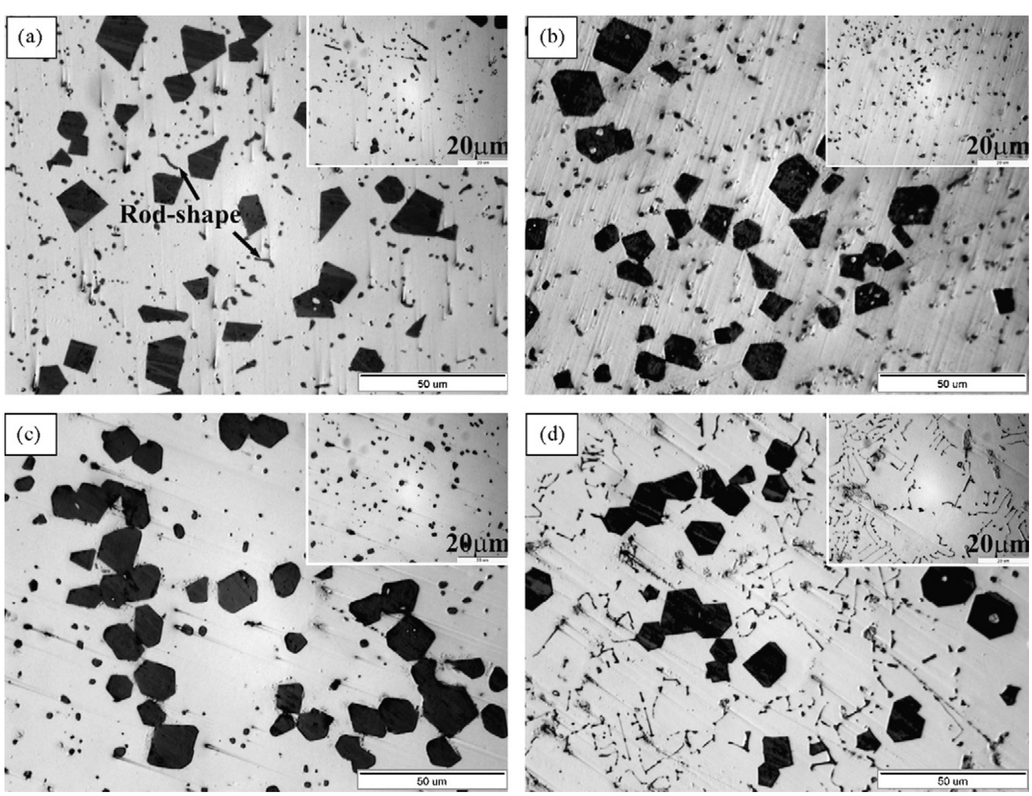

Fig. 2. The microstructures of Sr–Sb-modified Mg–5Si–1Al alloy isothermally treated at the temperature of (a) 620 °C, (b) 640 °C, (c) 650 °C and (d) 660 °C, respectively (the inserts show the high magnification of eutectic Mg_2Si phases).

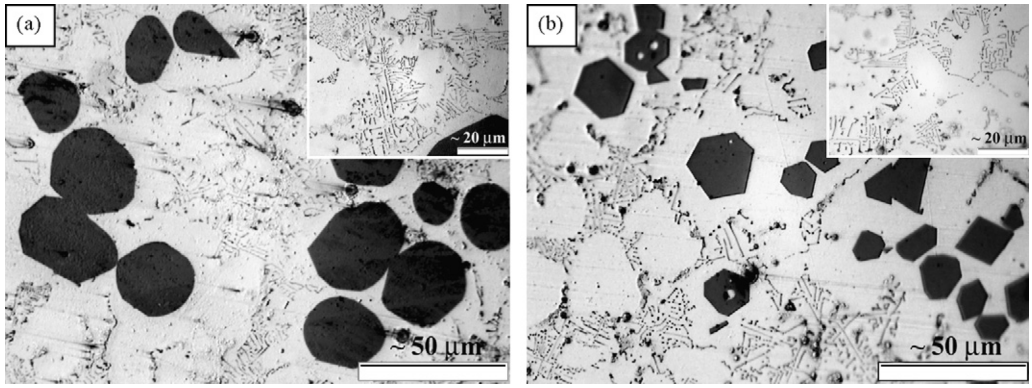

Fig. 3. The microstructures of (a) unmodified and (b) Sr–Sb-modified Mg–5Si–1Al alloys isothermally treated at 670 °C for 30 min (the inserts show the high magnification of eutectic Mg_2Si phases).

ity in magnesium matrix, no $Mg_{17}Al_{12}$ phase was detected by XRD, which is consistent with the previous study [17].

Due to the non-equilibrium solidification [7], the as-cast microstructures of Mg–5Si–1Al alloys consist of primary Mg_2Si, sub-primary α-Mg halos and eutectic Mg + Mg_2Si phases (Fig. 1). However, the primary Mg_2Si turns from dendritic morphology (Fig. 1(a)) to polyhedral shape (Fig. 1(b)) with Sr–Sb modification, and its size decreases significantly from more than 50 to ~15 μm or less; furthermore, also the Chinese script eutectic Mg_2Si (the insert in Fig. 1(a)) is considerably refined as fibers or rod-shapes (the insert in Fig. 1(b). Apparently, the combined addition of Sr and Sb causes an evident modification effect on both primary and eutectic Mg_2Si phases in Mg–5Si–1Al alloys.When the Sr–Sb-modified Mg–5Si–1Al alloy is isothermally treated at 620 °C, the primary Mg_2Si keeps an invariable polyhedron (Fig. 2(a)); however, most of the eutectic Mg_2Si phases transform from fibrous type (Fig. 1(b)) to individual granular shape except for some short rod-shaped ones (Fig. 2(a)). When the isothermal holding temperature increases to 640 °C, the primary Mg_2Si still exhibits a polyhedral shape, and the eutectic Mg_2Si almost completely turns into granular shape (Fig. 2(b)). With the temperature further increasing to 650 °C, the edge of primary Mg_2Si polyhedron has a slight blunt tendency, while the eutectic Mg_2Si granular becomes relatively coarser (Fig. 2(c)). When the temperature reaches 660 °C, the primary Mg_2Si exhibits a polyhedral shape (Fig. 2(d)), instead of transforming into globular morphology as expected. Interestingly, the eutectic Mg_2Si turns from granular shape (Fig. 2(c)) into fibers or short rod-shapes again (Fig. 2(d)). It should be mentioned that when the temperature increased from 650 to 660 °C, however, the primary Mg_2Si in unmodified Mg–5Si–1Al alloy had already transformed from coarse dendritic into globular morphology, through a touching, dissolving and fragmentation, as well as Ostwald ripening and coalescence processes [17].

The isothermal holding temperature of 620 °C is lower than the eutectic temperature of Mg–Mg_2Si (637.6 °C), while the 660 °C exceeds the melting point of Mg (650 °C). Consequently, when the predetermined temperature of 620 changes to 640 or 650 °C, and then to 660 °C, the evolutional mechanism of eutectic Mg_2Si phase in Sr–Sb-modified alloys changes from solid diffusion (Fig. 2(a)) to solid–liquid diffusion (Fig. 2(b) and (c)), and then to liquid diffusion-controlled mechanisms (Fig. 2(d)). These transformation processes are similar to the ones in unmodified Mg–5Si–1Al alloy [17]. Since the mechanisms of morphological evolution of eutectic Mg_2Si phases in unmodified alloys have been discussed in detail in our previous study [17], we will not repeat it here.

Compared Fig. 2(a) (620 °C) with Fig. 2(b) (640 °C), the disappearance of rod-shaped eutectic Mg_2Si in the latter should be attributed to the formation of liquid phase (the melting of eutectic structures), while the coarsening of granular eutectic Mg_2Si in Fig. 2(c) (650 °C) is mainly resulted from an increase in liquid fraction (both the melting of eutectic structures and partial melting of α-Mg halos). As the temperature increased to 660 °C, the sub-primary α-Mg halos have completely melted during the isothermal treatment process [17]. The liquid fraction increased dramatically, which led to the primary solid Mg_2Si polyhedrons suspended in the liquid. During the water-quenching process, the α-Mg nucleated on the Mg_2Si crystal and grew as halos surrounding the Mg_2Si polyhedrons, and the eutectic Mg_2Si subsequently precipitated along the α-Mg grain boundaries and developed to fibrous or short rod-shaped morphology (Fig. 2(d)). This process is similar

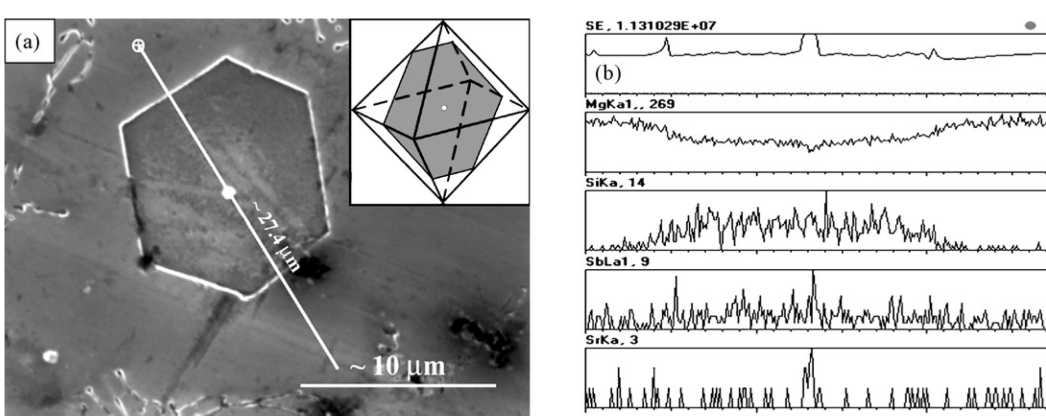

Fig. 4. The (a) SEM micrograph and (b) elemental line scanning spectra of Sr–Sb-modified Mg_2Si in Mg–5Si–1Al alloy after isothermal heat treatment at 660 °C (the insert shows a schematic illustration of the hexagonal outlines of octahedron).

to the formation of Chinese script eutectic Mg_2Si in unmodified Mg–5Si–1Al alloy during partial remelting at 660 °C [17].

To further investigate the influence of isothermal holding temperature on morphological evolution of primary Mg_2Si, the samples of unmodified and Sr–Sb-modified Mg–5Si–1Al alloys were isothermally treated at 670 °C for 30 min, respectively (Fig. 3). One can see that the primary Mg_2Si dendrites have turned into globular crystals in unmodified alloy when the temperature increased to 670 °C (Fig. 3(a)). Though the liquid fraction increases with holding temperature increasing, the primary Mg_2Si polyhedrons in Sr–Sb-modified alloy still remains the polyhedral shape (Fig. 3(b)). Surprisingly, the eutectic Mg_2Si phase transforms to Chinese script morphology (Fig. 3(b)), though which is much refiner compared with the coarse one in unmodified alloy (Fig. 3(a)). Note that even holding for 55 min at 670 °C, no spheridization occurs for primary Mg_2Si polyhedrons in the modified alloy (not shown). Seemingly, the non-spheridization can be ascribed to neither the holding temperature nor the time.

Consequently, it is rational to deduce that the complex modification of Sr and Sb should be responsible for the non-spheroidization of polyhedral primary Mg_2Si during partial remelting. According to our previous study [18], the mechanism of complex modification of Sr and Sb on primary Mg_2Si was that the formation of Sr–Sb (might be $Sr_{11}Sb_{10}$) compound could act as a heterogeneous nucleation site for the Mg_2Si crystal, together with the growth restriction effect caused by incorporation of Sb in Mg_2Si. The SEM micrograph and elemental line scanning spectra of Sr–Sb-modified Mg_2Si in Mg–5Si–1Al alloy after isothermal heat treatment at 660 °C are shown in Fig. 4(a) and (b), respectively. One can see that besides enriched in nucleus (the peak of Sb overlaps that of Sr at the nucleus), also some Sb atoms are incorporated in Mg_2Si crystal (Fig. 4(b)). Hence, it is believed that the Sb atoms, being in solid solution in Mg_2Si crystal, may restrict the spheroidization of polyhedral primary Mg_2Si during partial remelting process. Moreover, most primary Mg_2Si crystals in Sr–Sb-modified alloys are, in fact, the octahedrons, including both perfect and defective ones [18]. The various outlines (Figs. 1(b), 2(a)–(d), and 3(b)), such as quadrilateral, square and hexagon (Fig. 4(a)), correspond to the different sections of the octahedron [18]. Melting off of dendritic arms at their roots as a result of normal ripening and/or combining of two dendritic arms into a large structure on condition of short arm spacing are general phenomena for unmodified dendrites during isothermal heat treatment [16,17,19]. Conversely, octahedral primary Mg_2Si crystals faced by {1 1 1} planes, which are the close-packed planes in the face-centered cubic crystal structure, are relatively stable during heat treatment, and therefore, it may also be cited as a reason for the non-spheroidization of primary Mg_2Si in Sr–Sb-modified Mg–5Si–1Al alloy during partial remelting.

4. Conclusions

Comparing with as-cast microstructure, the morphological evolutions of eutectic Mg_2Si phase in Sr–Sb-modified Mg–5Si–1Al alloy during the isothermal heat treatment at 620, 640, 650, 660 and 670 °C are as follows: fiber or rod-shape $\xrightarrow{620\,^\circ\mathrm{C}}$ granule + short rod-shape (minor) $\xrightarrow{640\,^\circ\mathrm{C}}$ granule $\xrightarrow{650\,^\circ\mathrm{C}}$ granule (relatively coarser) $\xrightarrow{660\,^\circ\mathrm{C}}$ fibers or short rod-shapes $\xrightarrow{670\,^\circ\mathrm{C}}$ Chinese script. But even when the temperature reaches 660 or 670 °C, no spheridization occurs for primary Mg_2Si polyhedrons in Sr–Sb-modified alloy, which might be ascribed to both the spheridization restriction effect caused by incorporation of Sb in Mg_2Si and stability of octahedral primary Mg_2Si crystals faced by {1 1 1} planes.

Acknowledgements

This work is supported by The National Natural Science Foundation of China (No. 50501010), and The Special Fund for the Author of Excellent PhD Thesis of Colleges and Universities in China (2007B38). Partial financial support comes from The Innovation Foundation for Graduate Student (No. 20080101) and the Project 985-Automotive Engineering of Jilin University.

References

[1] B.L. Mordike, T. Ebert, Mater. Sci. Eng. A302 (2001) 37–45.
[2] F. Czerwinski, Acta Mater. 52 (2004) 5057–5069.
[3] H.Z. Ye, X.Y. Liu, J. Mater. Sci. 39 (2004) 6153–6171.
[4] M.B. Yang, F.S. Pan, R.J. Cheng, L. Bai, J. Mater. Process. Technol. 206 (2008) 374–381.
[5] H.Y. Wang, Q.C. Jiang, B.X. Ma, Y. Wang, J.G. Wang, J.B. Li, Mater. Sci. Eng. A368 (2004) 159–167.
[6] Y.Z. Lu, Q.D. Wang, X.Q. Zeng, Y.P. Zhu, W.J. Ding, Mater. Sci. Eng. A301 (2001) 255–258.
[7] H.Y. Wang, W. Wang, M. Zha, N. Zheng, Z.H. Gu, D. Li, Q.C. Jiang, Mater. Chem. Phys. 108 (2008) 353–358.
[8] A. Srinivasan, J. Swaminathan, U.T.S. Pillai, B.C. Krishna Guguloth, Pai, Mater. Sci. Eng. A 485 (2008) 86–91.
[9] A. Srinivasan, U.T.S. Pillai, B.C. Pai, Metal. Mater. Trans. 36A (2005) 2235–2243.
[10] L. Liao, X. Zhang, H. Wang, X. Li, N. Ma, J. Alloys Compd. 430 (2007) 292–296.
[11] J.B. Patel, Y.Q. Liu, G. Shao, Z. Fan, Mater. Sci. Eng. A476 (2008) 341–349.
[12] F. Czerwinski, Acta Mater. 50 (2002) 3265–3281.
[13] F. Czerwinski, Scr. Mater. 48 (2003) 327–331.
[14] H. Wang, C.J. Davidson, D.H. StJohn, Mater. Sci. Eng. A368 (2004) 159–167.
[15] Q.D. Qin, Y.G. Zhao, C. Liu, P.J. Cong, W. Zhou, Y.H. Liang, Mater. Sci. Eng. A407 (2005) 196–200.
[16] Q.D. Qin, Y.G. Zhao, C. Liu, P.J. Cong, W. Zhou, Y.H. Liang, J. Alloys Compd. 416 (2006) 143–147.
[17] M. Zha, H.Y. Wang, P.F. Xue, L.L. Li, B. Liu, Q.C. Jiang, J. Alloys. Compd. (2009), doi:10.1016/j.jallcom. 2008.05.016.
[18] H.Y. Wang, M. Zha, B. Liu, D.M. Wang, Q.C. Jiang, J. Cryst. Growth., Submitted for publication.
[19] J.G. Wang, P. Lu, H.Y. Wang, Q.C. Jiang, Mater. Lett. 58 (2004) 3852–3856.