Microstructural change and precipitation hardening in melt-spun Mg–X–Ca alloys

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Abstract

Mg–Al–Si–Ca and Mg–Zn–Ca base alloys were rapidly solidified by melt spinning at the cooling rate of about a million K/s. The melt-spun ribbons were aged in the range 100–400°C for 1 h. The effect of additional elements on microstructural change and precipitation hardening after heat treatment was investigated using TEM, XRD and a Vickers microhardness tester. Age hardening occurred after aging at 200°C in the Mg–Al–Si–Ca alloys mainly due to the formation of Al\textsubscript{2}Ca and Mg\textsubscript{2}Ca phases, whereas in the Mg–Zn–Ca alloys mostly due to the distribution of Mg\textsubscript{2}Ca. TEM results revealed that spherical Al\textsubscript{2}Ca precipitate has the coherent interface with the matrix. Considering the total amount of additional elements, Mg–Zn–Ca alloys showed higher hardness and smaller size of precipitates than Mg–Al–Si–Ca alloys. With the increase of Ca content, the hardness values of the aged ribbons were increased. Among the alloys, Mg–6Zn–5Ca alloy showed the maximum value of age hardening peak ($H\textsubscript{\text{v}}$ 180) after aging at 200°C for 1 h. © 2001 Published by Elsevier Science Ltd.

Keywords: Mg–Al–Si–Ca; Mg–Zn–Ca; Melt spinning; Age hardening; Precipitation

1. Introduction

Among the light-weight alloys, magnesium and its alloys show a good possibility for high performance aerospace and automotive applications [1,2], however the widespread use of magnesium alloys has been limited mainly by its low strength, and poor oxidation and corrosion resistance [3–7]. Thus, rapid solidification [8–10] can play an important role because of its advantages, i.e. homogeneity of refined microstructure, increased solid solubility and precipitation hardening. Applications of the rapid solidification processes to Mg-based alloys have resulted in the design of new stronger alloys at room temperature and elevated temperature. In alloy designing [11,12], Ca element draws a great attention to refine the microstructure and to modify precipitation behavior in the Mg alloys, and Al, Zn and Si are considered as good candidates which gives some increase in tensile properties and hardness.

The objective of this paper is to investigate the effects of Ca additions to Mg–Al–Si and Mg–Zn base alloys on the microstructure and precipitation hardening in the melt-spun and heat treated alloy ribbons.

2. Experimental procedure

The present alloys were prepared using a high purity (99.9%) magnesium, calcium, aluminum, zinc and silicon. These ingots were remelted by induction heating, and rapidly solidified at a cooling rate of about a million K/s. The resultant ribbons were approximately of 35–40 μm thickness and 3–5 mm width. Sound sections of the melt-spun ribbons were annealed in the range 100–400°C for 1 h. The structure of as-quenched and annealed ribbons was examined by X-ray diffractometry using Cu K\textsubscript{\alpha} radiation, and the thin samples for TEM observation were prepared using an ion beam thinning technique. More than 10 measurements for microhardness determination were made for all specimens using a 10 g load and 30 s dwell time with a Vickers indenter. Table 1 shows the chemical composition of the rapidly solidified Mg-based alloys.

3. Results and discussion

The initial criterion to evaluate the mechanical property was microhardness change of the melt-spun ribbon aged at various temperatures for 1 h, as shown in Fig. 1. Mg–Al–Si(–Ca) alloys generally possessed lower hardness values than Mg–Zn(–Ca) alloys, and the both alloy systems
Table 1
Chemical composition of the Mg-based alloys (wt%)  

| Group | Alloys                | Composition               |
|-------|-----------------------|--------------------------|
|       |                       |                          |
| 1     | Mg–10Al–1Si           | 9.91 0.87 –< 0.005       | Bal.                     |
|       | Mg–10Al–2Si–1Ca       | 10.0 2.16 –1.21          | Bal.                     |
|       | Mg–10Al–2Si–3Ca       | 10.3 2.21 –2.47          | Bal.                     |
|       | Mg–10Al–2Si–6Ca       | 9.98 1.82 –5.85          | Bal.                     |
|       | Mg–10Al–2Si–10Ca      | 9.96 1.93 –10.07         | Bal.                     |
| 2     | Mg–6Zn                | – – 6.34 –              | Bal.                     |
|       | Mg–3Zn–5Ca            | – – 3.24 4.79          | Bal.                     |
|       | Mg–6Zn–5Ca            | – – 5.88 4.74          | Bal.                     |
|       | Mg–10Zn–5Ca           | – – 10.4 4.90          | Bal.                     |

showed age hardening phenomena after heat treatment. Compared to Mg–Al–Si–(Ca) ribbons, Mg–Zn–Ca ribbons were a little more brittle so that the ribbons could be easily pulverized. In Mg–Al–Si–(Ca) alloys (Fig.1(a)), Mg–10Al–2Si–10Ca showed the highest hardness value and age hardened peak, but was very brittle. Mg–10Al–2Si–6Ca possessed a peak hardness of ~120HV, when aged at 200°C, and was relatively ductile to enable bending without fracture. Mg–10Al–1Si alloy without Ca did not show any big change in hardness after aging. On the other hand, among Mg–Zn–(Ca) alloys (Fig.1(b)), Mg–6Zn–5Ca showed the highest hardness of about ~180HV, peak when aged at 200°C for 1 h. With the increase of aging temperature above 250°C, the hardness gradually decreased. However, Mg–6Zn–5Al alloy was desirable in that the hardness could be maintained as the high value of ~100HV after aging at 400°C.

As seen in the X-ray diffraction patterns of Mg–10Al–2Si–6Ca alloy (Fig. 2), most of the peaks were analyzed as magnesium and Mg12Al12 in the as-quenched state and after aging at 200°C, and X-ray peaks taken from Al2Ca, Al4Ca and Mg2Ca were found after aging at 400°C. It is suggested that the fine precipitate of Al2Ca, Al4Ca and Mg2Ca contribute the age hardening when aged at 200°C, but X-ray diffraction patterns could not establish the existence of small volume of the precipitates in the matrix. In case of Mg–6Zn–5Ca (Fig. 3), the main peaks were obtained from Mg2Zn3 and Mg2Ca, whereas Mg2Zn3 and Mg2Zn2 were rarely detected.

According to previous studies [3,4], the fact that Ca additions in rapidly solidified Mg alloys generally induce the age hardening was already confirmed. Transmission electron microscopy and selected area diffraction pattern (SADP) of the alloy ribbons can help explain the role of precipitates finely dispersed in the grain interior. Fig. 4 shows TEM micrographs and selected area diffraction patterns taken from melt-spun Mg–10Al–2Si–6Ca ribbon. As-quenched alloy consisted of small grain of 1–2 μm in size (Fig. 4(a)), and primarily precipitated fine particles was identified as Mg12Al12 (Fig. 4(b)). After annealing at 200°C for 1 h, fine precipitates of 10–20 nm in diameter could be seen in the grain interior (Fig. 4(c)), which were regarded as metastable coherent precipitates. SADP (Fig. 4(d)) revealed that Al2Ca phase has a coherent interface with the Mg matrix. The relationship of crystal orientation was as follows: (111)Mg//[111]Al2Ca and [101]Mg//[110]Al2Ca.

Based on the results, it is obvious that Al2Ca phase contributed the coherency hardening of Mg–10Al–2Si–6Ca
alloy aged at 200°C. Contrarily, TEM micrographs of Mg–10Al–2Si–10Ca alloy in Fig. 5 consisted of quite a few Mg₃Ca, having the almost same crystal structure as Mg except for about twice the value of the lattice constant (Mg/hcp, \( a = 0.321 \) nm, \( c = 0.521 \) nm; Mg₃Ca/hcp, \( a = 0.624 \) nm, \( c = 1.012 \) nm). Most probably, Mg₃Ca could also have a coherent interface with the matrix, and naturally induce pronounced age hardening. Further, it is analyzed that the excess Ca, after forming Al₂Ca, was precipitated as Mg₃Ca when a large amount of Ca of about 10 w/o was added to Mg–Al based alloys. Thus, the pronounced age hardening peak of Mg–10Al–2Si–10Ca alloy seemed to be caused by the high v/o of coherent Mg₃Ca as well as Al₂Ca precipitates.
Fig. 4. TEM micrographs and selected area diffraction patterns taken from Mg–10Al–2Si–6Ca alloy ribbon: (a) as-quenched microstructure; (b) SADP of the primarily precipitated particles in (a); (c) microstructure aged at 200°C for 1 h; and (d) SADP of the small particle in (c).

Fig. 5. TEM micrographs of Mg–10Al–2Si–10Ca alloy ribbon: (a) as-quenched from the melt; (b) aged at 200°C for 1 h.
Fig. 6. TEM micrographs and selected area diffraction patterns taken from Mg–6Zn and Mg–6Zn–5Ca alloy ribbons aged at 200°C for 1 h: (a) microstructure of Mg–6Zn; (b) SADP of precipitates in (a); (c) microstructure of Mg–6Zn–5Ca; and (d) SADP of small precipitates in (c).

Fig. 6 shows TEM micrographs and SADPs taken from melt-spun Mg–6Zn and Mg–6Zn–5Ca alloy ribbon after aging at 200°C for 1 h. The microstructure of Mg–6Zn (Fig. 6(a)) mainly consisted of rod-shaped precipitates of 30–50 nm in size, which were identified as Mg_{51}Zn_{20} (Fig. 6(b)) [5,6]. Contrarily, very fine precipitate of ~10 nm in diameter could be observed in melt-spun Mg–6Zn–5Ca alloy together with Mg–Zn base compounds such as Mg_{51}Zn_{20} and Mg_{2}Zn_{3} precipitates (Fig. 6(c)), and the SADP of fine precipitate was analyzed as Mg_{2}Ca (Fig. 6(d)). The size of Mg_{2}Ca dispersed in Mg–Zn–Ca alloys was much smaller than that of Al_{2}Ca and Mg_{2}Ca in Mg–Al–Si–Ca alloys, indicating that Mg–Zn–Ca alloys were easily solid-solutionized through rapid solidification because of a small amount of solute content compared to Mg–Al–Si–Ca alloys. It seems that this fine microstructure and precipitates can lead the enhanced hardening peaks in as-quenched and aged Mg–Zn–Ca alloys. Accordingly, it can be concluded that the peak hardness in melt-spun Mg–6Zn–5Ca alloy was caused by the formation of Mg_{2}Ca precipitates finely dispersed in the grain interior, and the refined microstructure was very effective on the coherent hardening in rapidly solidified Mg-based alloys.

4. Conclusions

1. Ca additions to Mg–Al and Mg–Zn base alloys induce age hardening, which is attributed to the formation of fine spherical precipitates such as Al_{2}Ca and Mg_{2}Ca.
2. The precipitate of Al_{2}Ca phase has a coherent interface with the magnesium matrix. The relationship of crystal orientation between the two phases is (111)_{Mg}//(111)_{Al_{2}Ca} and [101]_{Mg}//[110]_{Al_{2}Ca}.
3. Among the Mg–Al–Si–Ca and Mg–Zn–Ca alloys, Mg–6Zn–5Ca alloy showed the highest peak hardness of ~180H, when aged at 200°C for 1 h, and Mg–Zn–Ca base possessed relatively higher hardness values than Mg–Al–Si–Ca base alloys because of the refined microstructure and precipitates.
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