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Phase Change of Precipitates and Age Hardening in Rapidly Solidified Mg-Zn-Ca Base Alloys

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Abstract Various kinds of Mg-Zn-Ca base alloys were rapidly quenched via melt spinning process. The melt-spun ternary and quaternary alloy ribbons were heat-treated, and then the effects of additional elements on age hardening behavior and phase change of precipitates were investigated using Vickers hardness tester, XRD, and TEM equipped with EDS system. In ternary alloys, age hardening was mostly due to the distribution of $Mg_6Ca_2Zn_3$ and Mg_2Ca. The stable phases of precipitates were varied according to the aging temperature and the alloy composition. With the increase of Ca content, Mg_2Ca precipitates were detected more than $Mg_6Ca_2Zn_3$ precipitates. In quaternary alloys, the precipitates taken from Mg-Zn-Ca-Co were identified as new quaternary phase, whereas those taken from Mg-Zn-Ca-Zr as MgZnCa containing Zr. In general, the ternary alloy showed higher peak hardness and thermal stability than the quaternary considering the total amounts of the solutes. It implies that the structure of precipitate should be controlled to have the coherent interface with the Mg matrix.

Keywords : Mg alloy, Melt spinning, Precipitate, Age hardening, Microstructure

1. Introduction

There has been a growing industrial demand to develop the high temperature magnesium alloy via powder metallurgy [1], of which applications include aerospace, automotive, and nuclear parts as well as appliances and sporting goods. Based on the reported works on Mg-Zn alloys [2-6], the addition of Zn to magnesium increased the strength at elevated temperatures, and a considerable amount of Zn up to 8.4 wt% could be retained as a solid solution in magnesium alloys by rapid solidification. In addition, Ca is known [7, 8] to be one of the most potent alloying elements for refining the microstructure as well as increasing the corrosion resistance of magnesium alloys. Thus, rapidly solidified Mg-Zn-Ca base alloys have been studied to improve their characteristics in many research groups [9-12]. However, the microstructural change and age hardening of the alloys were not investigated in detail.

In this paper, the phase identification of precipitates was carried out to understand how the alloy compositions and the heat treatment affected both phase change of precipitates and age hardening in the rapidly solidified Mg-Ca-Zn base alloys. For quaternary alloys, Co and Zr were added to the Mg-6Zn-5Ca ternary alloy because their hardening phases were expected to be precipitated during aging.

2. Experimental Procedure

Table 1 shows the chemical composition of rapidly solidified Mg-based alloys. The alloys were melt-spun at the cooling rate of about 10^6 °C/s. The resultant ribbons were approximately 35~40 μm in thickness, and ~5 mm in width. Sound sections of the melt-spun ribbons were annealed at the temperature range of 100~400°C for 1 hour. Microhardness measurements were performed using a 10 g load and 15 seconds dwell time with a Vickers indentor.

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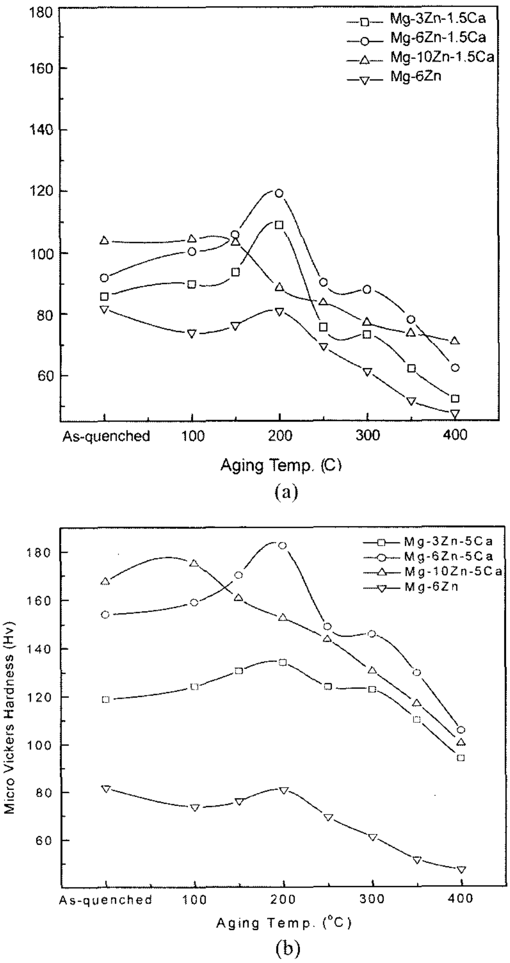
Table 1. Chemical composition of Mg-based alloys (wt%)

Group	Alloys	Composition				
		Zn	Ca	Co	Zr	Mg
I	Mg-6Zn	6.34	-	-	-	bal.
	Mg-3Zn-1.5Ca	3.27	1.46	-	-	bal.
	Mg-6Zn-1.5Ca	5.91	1.34	-	-	bal.
	Mg-10Zn-1.5Ca	10.6	1.54	-	-	bal.
II	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.
III	Mg-6Zn-5Ca-2Co	5.45	4.44	1.71	-	bal.
	Mg-6Zn-5Ca-0.5Zr	5.11	4.31		0.33	bal.

The precipitates in as-quenched and aged ribbons were examined by X-ray diffractometer to identify the phases and to evaluate the volume % of each phases, and the thin samples for TEM equipped with EDS analyzer were prepared by ion beam thinning technique.

3. Results and Discussion

The microhardness changes of the melt-spun ribbon aged at various temperatures for 1 hour were shown in Fig. 1. Mg-xZn-1.5Ca alloys and Mg-xZn-5Ca alloys showed age hardening phenomena after aging at 200°C, which is attributed by the precipitation of hardening phases finely dispersed in the Mg matrix. Fig. 2(a-d) showed XRD traces of the melt-spun ribbons. Depending on the compositions, the alloys were solidified as a single phase of Mg-supersaturated solid solution (Fig. 2(a)); two-phase mixture of Mg solid solution and Mg_2Ca, or a ternary phase (Fig. 2(b, d)); and three-phase mixture of Mg solid solution, Mg_2Ca, and the ternary phase (Fig. 2(c)). The ternary phase was identified on the basis of interplanar distances and relative intensities of $Mg_6Ca_2Zn_3$ phase [13]. The phases of precipitates, identified by XRD, in melt-spun and annealed specimens were listed in Table 2. As-solidified Mg-3Zn-1.5Ca consisted of a single crystalline phase, therefore it could be assumed that the extension of



(a)

(b)

Fig. 1. Hardness change of Mg-Zn-Ca base alloys after heat treatment for 1 hour at various temperatures. (a) Mg-xZn-1.5Ca alloys, (b) Mg-xZn-5Ca alloys

Table 2. Phase identification of the precipitates formed in Mg-Zn-Ca ternary alloy ribbons in as-solidified state and after aging treatment at = 400°C for 1h

Alloy	As-solidified	Annealed at T = 400°C, t = 1h
Mg-3Zn-1.5Ca	-	$Mg_6Ca_2Zn_3$
Mg-6Zn-1.5Ca	$Mg_6Ca_2Zn_3$	$Mg_6Ca_2Zn_3$
Mg-10Zn-1.5Ca	$Mg_6Ca_2Zn_3$,	$Mg_6Ca_2Zn_3$
Mg-3Zn-5Ca	Mg_2Ca	Mg_2Ca, $Mg_6Ca_2Zn_3$
Mg-6Zn-5Ca	Mg_2Ca, $Mg_6Ca_2Zn_3$	Mg_2Ca, $Mg_6Ca_2Zn_3$
Mg-10Zn-5Ca	Mg_2Ca, $Mg_6Ca_2Zn_3$	Mg_2Ca, $Mg_6Ca_2Zn_3$

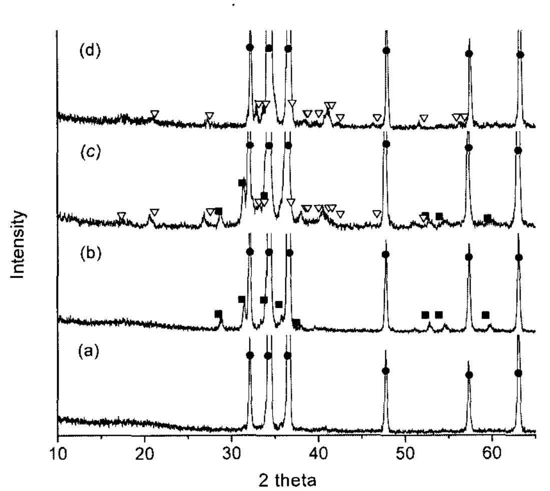
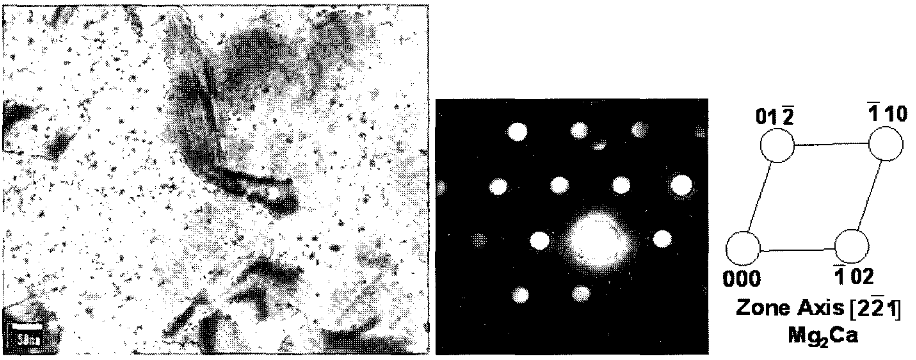


Fig. 2. XRD patterns for as-solidified ribbons (a) Mg-3Zn-1.5Ca, (b) Mg-3Zn-5Ca, (c) Mg-6Zn-5Ca, (d) Mg-6Zn-1.5Ca (● : Mg, ■ : Mg_2Ca, ▽ : Ternary phase, $Mg_6Ca_2Zn_3$)

Zn solid solubility in Mg reached 3.27 wt.%. The precipitation of $Mg_6Ca_2Zn_3$ phase occurred with the increase of solute content, Zn and Ca. However, with a Zn/Ca atomic ratio of less than 1.4, the Mg_2Ca phase was observed instead of $Mg_6Ca_2Zn_3$. The Mg_2Ca [14] is well-known age hardening phase, which has a coherent interface with Mg matrix. The ternary $Mg_6Ca_2Zn_3$ was observed in all ternary alloys heat-treated at 200~400°C. This was independent of whether it was detected in the initial melt-spun condition or not. Considering the hardness change and the phase of precipitate, the ternary phase could play a significant role in age hardening of Mg-Ca-Zn alloys.

On the other hand, it was shown that Ca additions to Mg-Zn base alloys resulted in a notable hardness increase (Fig. 1). With the increase of Ca content from 1.5 to 5wt% in Mg-Zn-Ca alloy, the hardness increased dramatically in all the range of aging temperatures. Among the Mg-Zn-Ca alloys, Mg-6Zn-5Ca showed the highest peak hardness of ~180 Hv when it was aged at 200 °C for 1 hour. Furthermore,



(a) (b)

Fig. 3. TEM micrographs and selected area diffraction patterns taken from Mg alloy ribbons aged at 200°C for 1 hour. (a) microstructure of Mg-6Zn-5Ca, (b) SADP of finely dispersed precipitates in the matrix of (a)

it seemed that Mg-6Zn-5Ca alloy was desirable for high temperture application in that the hardness could be maintained to ~100 Hv even after aging at 400°C. In case of Mg-xZn-1.5Ca alloys, most of diffraction peaks taken from precipitates were identified as $Mg_6Ca_2Zn_3$ by X-ray diffractometry It seemed that $Mg_6Ca_2Zn_3$ phase contributed to the age hardening due to a coherent interface with the Mg matrix as reported before [7]. From the previous study [8], the fact that Ca additions in rapidly solidified Mg alloys generally induce the age hardening has already been proved. Transmission electron microscopy and selected area diffraction pattern (SADP) of alloy ribbons can help to explain the role of precipitates finely dispersed in the grain interior. Fig. 3 showed TEM micrographs and SADPs taken from melt-spun Mg-6Zn-5Ca alloy ribbons after aging at 200 °C for 1 hour. Very fine precipitates of ~10 nm in diameter dispersed within fine grain structure was analyzed as Mg_2Ca. It seems that this fine microstructure and precipitates can lead the enhanced hardening peaks more effectively than $Mg_6Ca_2Zn_3$ in as-quenched and aged Mg-Zn-Ca alloys. Fig. 4 showed the dependencies of the matrix and precipitate volume fractions according to the annealing temperature in Mg-3Zn-5Ca and Mg-10Zn-5Ca alloys. As seen in each case, the solid solution decomposed at the temperature range of 100-300 °C, accompanied by the $Mg_6Ca_2Zn_3$. It is noteworthy that the amount of Mg_2Ca remained almost the same in any case of aging temperature, and the volume fraction of $Mg_6Ca_2Zn_3$ increased with the increase of aging temperature.

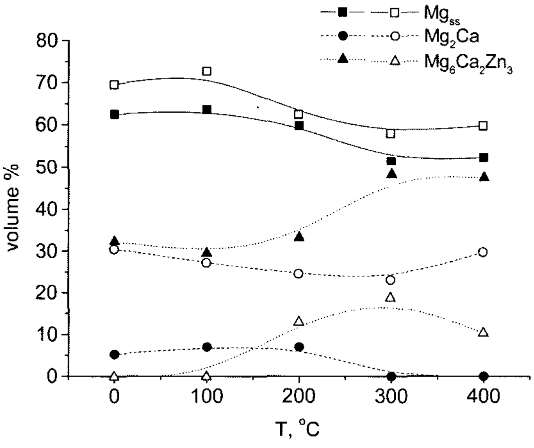


Fig. 4. Change of the volume fraction of the Mg matrix (■, □) and precipitates-Mg_2Ca(▲, △) and $Mg_6Ca_2Zn_3$ (p, r) with annealing temperature. (Open points : Mg-3Zn-1.5Ca alloy, Closed points : Mg-3Zn-5Ca alloy)

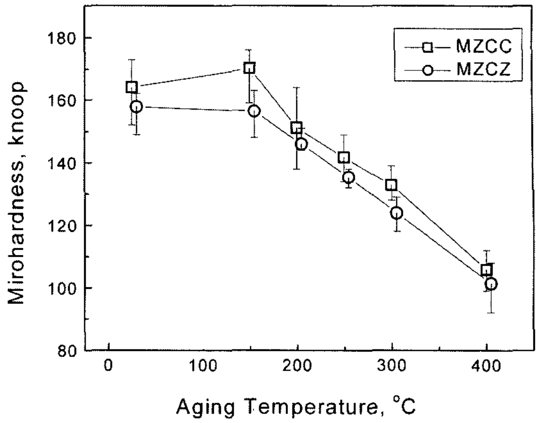


Fig. 5. Hardness change of Mg-6Zn-5Ca-2Co(MZCC) and Mg-6Zn-5Ca-0.5Zr(MZCZ) alloy ribbons after heat treatment for 1 h at various temperatures.

The microhardness changes of the melt-spun quaternary alloys, aged at various temperatures for 1 hour, were shown in Fig. 5. Mg-6Zn-5Ca-2Co alloy possessed higher hardness values than Mg-6Zn-5Ca-0.5Zr alloy at all aging temperatures, and presented a peak value at 150°C followed by a hardness decrease. However, these alloys did not exhibit the improved age hardening and thermal stability compared to the ternary Mg-Zn-Ca alloys. The X-ray mapping of the MZCC alloy (Fig. 6) revealed that Co, Ca, and Zn segregated in the same region with precipitates along the cell boundary in the as-solidified state of Mg-6Zn-5Ca-2Co alloy. This implies that the stable precipitate is a quaternary compound containing Mg, Zn, Ca, and Co, which is different from Mg_2Ca and $Mg_6Ca_2Zn_3$ structure. Fig. 7 (a), (b) shows the micrographs of Mg-6Zn-5Ca-0.5Zr alloy aged at 300°C for 1 hour. The microstructure appeared to become coarse with the

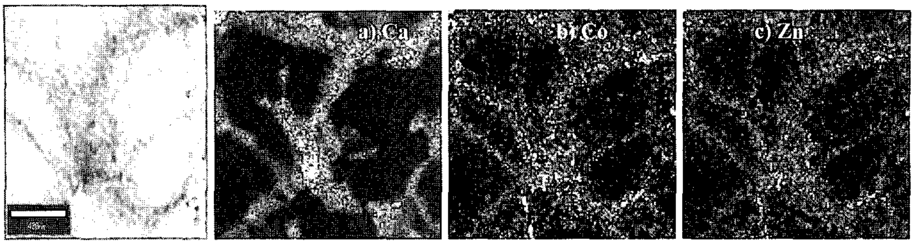


Fig. 6. TEM micrographs and EDS mapping images of Ca(a), Co(b) and Zn(c) in as-solidified Mg-6Zn-5Ca-2Co alloy.

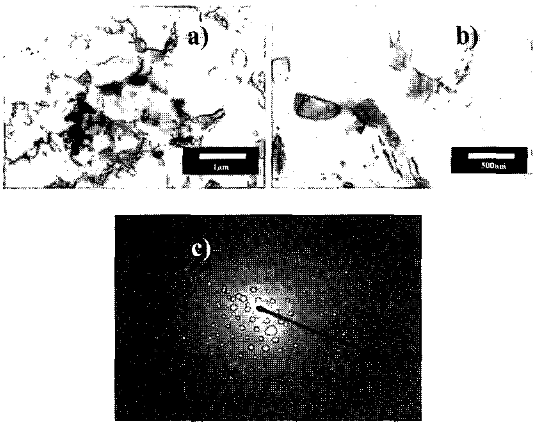


Fig. 7. TEM micrographs (a,b) and SADP (c) of precipitates in Mg-6Zn-5Ca-0.5Zr alloy aged at 300°C.

increase of aging temperature. The grain was relatively coarse (approximately 1 μm), and most of the precipitates coarsened above 0.3 μm in size. SADP taken from the precipitate (Fig. 7c:Z.A.=[101]) indicated that this precipitate was MgZnCa having incoherent intetrface with Mg matrix.

From these results, it is obvious that the addition of minor element to the ternary should be decided carefully according to the stablility of precipitate structure, because it can be affected by both the chemical composition and the atomic fraction of the quaternary alloys.

4. Conclusions

In Mg-Zn-Ca ternary alloys, age hardening was mostly due to the precipitation of $Mg_6Ca_2Zn_3$ and Mg_2Ca. The volume fraction of precipitates was changed according to the aging temperature and the alloy composition. With the increase of Ca content, Mg_2Ca became more stable than $Mg_6Ca_2Zn_3$ to increase the hardness value. The volume fraction of $Mg_6Ca_2Zn_3$ increased at elevated temperature. The ternary alloy showed higher peak hardness and thermal stability than the quaternary considering the total amounts of the solutes, which implied that the structure of precipitate should be controlled to have the coherent interface with the Mg matrix.

Acknowledgements

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