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Precipitation hardenable Mg-Ca-Al alloys

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Abstract

The age-hardening responses and the corresponding microstructures of Mg–0.5Ca–xAl (x = 0, 0.1, 0.3, 0.5, 1 wt. %) alloys were investigated by hardness tests and transmission electron microscopy. For the optimum Al addition of 0.3 wt. % an enhanced age-hardening response with the highest peak hardness of HV=72 was achieved. TEM analyses confirmed that the improvement in the peak hardness is associated with the dense precipitation of ordered monolayer G.P. zones. Whereas, lower content of Al resulted in the formation of G.P. zones and Mg_2Ca and the excess addition of Al causes the formation of the G.P. zones and the grain boundary Al_2Ca phase.

Introduction

The precipitation hardening of Mg–Ca binary alloys is very low due to the coarse precipitation of the equilibrium Mg_2Ca phase [1]. However, the age-hardening response of the Mg–Ca alloys can be enhanced due to the precipitation of plate type G.P zones by microalloying of Zn, or both Zn and Nd [1,2]. At elevated temperatures, the alloy strengthened by such plate type G.P zones in a Mg–1Ca–1Zn–1Nd–0.6Zr alloy exhibits better properties in strength, ductility and creep resistance compared to AZ91 (Mg–9Al–1Zn) [2]. The formation of the plate like precipitates on the basal plane is related with the microalloying elements. The combinations of oversized element like Ca and RE and undersized element like Zn in Mg causes the formation of plate like internally ordered G.P zones on the basal plane. The age hardening response and good creep properties in both Mg–Ca–Zn and Mg–RE–Zn alloys are attributed to the formation of the plate like G.P zones [2-7].

In order to understand the mechanism of the formation of the internally ordered GP zones, it will be useful to see whether or not other undersized elements like Al exhibit the similar effect in the formation of G.P zones in Mg–Ca system. Like Zn in Mg–Ca–Zn system, Al and Zn have similar atomic sizes and the heat of mixing of Al in Mg is similar to that of Ca in Mg. Based on this concept, we selected Al as a microalloying element to the Mg–0.5Ca binary alloy and found that the similar G.P. zones are formed in the Mg–0.5Ca–xAl alloys [8]. This paper updates the results reported in reference [8] for this symposium.

Experimental procedures

Mg–0.5Ca–xAl (x = 0.1, 0.3, 0.5, 1, wt. %) alloys were prepared by induction melting high purity Mg, Al and Mg–13.3Ca (wt. %) master alloy in an Ar atmosphere. The compositions of the alloys are shown in Table 1 with both wt. % and at. %. Hereafter, all alloy compositions are indicated in wt. %. Samples sectioned from the ingots were solution-heat treated at 500 °C for 2 h and then quenched into water. Aging treatments were performed at 200 °C in an oil bath for different time intervals. The hardness values were measured by a Vickers hardness tester with a 500g load. Scanning electron microscopy (SEM) observation was performed using a Carl Zeiss Cross beam 1540 microscope. TEM specimens were prepared by twin jet electro-polishing as explained elsewhere [8]. Microstructure observations were carried out using a TECNAI G^2 20 TEM. High-angle annular dark field (HAADF) observations were carried out using a TECNAI G^2 F30 TEM.

Designations	at. %			wt. %		
	Mg	Ca	Al	Mg	Ca	Al
Mg–0.5Ca	Bal.	0.3	-	Bal.	0.5	-
Mg–0.5Ca–0.1Al	Bal.	0.3	0.1	Bal.	0.5	0.1
Mg–0.5Ca–0.3Al	Bal.	0.3	0.3	Bal.	0.5	0.3
Mg–0.5Ca–0.5Al	Bal.	0.3	0.5	Bal.	0.5	0.5
Mg–0.5Ca–1Al	Bal.	0.3	1.0	Bal.	0.5	1.0

Table 1 Alloy compositions in wt.% and at.%.

Result and discussion

Figure 1 shows the age hardening response of Mg–0.5Ca–xAl (x = 0.1, 0.3, 0.5, 1, wt. %) alloys at 200 °C. The hardness value of all these alloys at as-quenched condition was approximately 40 HV. The peak hardness of Mg–0.5Ca binary alloy was low at about 50 HV. However, the addition of Al to Mg–0.5Ca significantly improved the age-hardening responses. In particular, the peak hardness of the Mg–0.5Ca–0.3Al alloy reached to 72 HV in 2 h and the increment in hardness (ΔHV=32) was the highest among all the alloys. For the other alloys, the peak hardness reached about 60 HV. As aging progress the hardness decreased to a lower value due to the coarsening of the microstructure. However, the Mg–0.5Ca–0.3Al alloy shows better resistance against coarsening with the over-aged hardness value remained high at about 60 HV until 1000 h of aging times. The developed ternary Mg–0.5Ca–0.3Al alloy shows similar peak hardness compared to that of the reported quinary Mg–1Ca–1Zn–1Nd–0.6Zr alloy. This indicates that the micro-alloying of Al to Mg–Ca system is highly advantageous considering the lower cost of Al compared to Nd.

Figure 2a and 2b shows the backscattered electron SEM image of the solution treated Mg–0.5Ca–0.3Al and Mg–0.5Ca–1Al alloy respectively. No secondary phase can be seen in the solution treated Mg–0.5Ca–0.3Al alloy, indicating the formation of super saturated solid solution of Mg–(Ca–Al). In contrast, insoluble white bright phases were observed along the grain boundaries of the grey dark phase for the solution treated Mg–0.5Ca–1Al alloy. Since heavy elements (high atomic number; Ca = 20, Al =13) backscatter electrons stronger than the light elements (low atomic number; Mg = 12), the appeared brighter phase in Fig. 2b could be Ca–Al bearing phase. Microstructure investigations on the solution treated Mg–0.5Ca–0.1Al and Mg–0.5Ca–0.5Al alloys showed similar features to that of the Mg–0.5Ca–0.3Al and Mg–

0.5Ca–1Al alloys respectively (figures not shown).The insoluble phase formed could be identified as Al_2Ca was reported for the alloys containing Al higher than 0.3 wt.% [9].This result indicate that the highest concentration of solute atoms would exists for the solution treated Mg–0.5Ca–0.3Al alloy and suggests that the optimum Al content for the age hardening Mg–0.5Ca alloy is 0.3 wt.%.

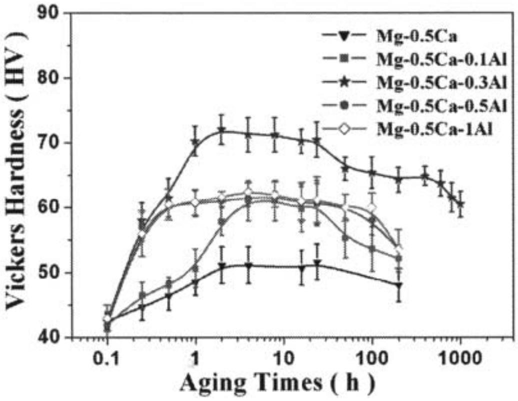

Figure 1 Age hardening response of Mg–0.5Ca–*x*Al (*x* = 0.1, 0.3, 0.5, 1, wt. %) alloys during isothermal aging at 200 °C. Reproduced from reference [8].

The microstructure causing the peak aging and over aging of the alloys with different Al content was characterized by TEM. Figure 3a and 3b show the TEM bright field images of the peak aged and over aged Mg–0.5Ca–0.1Al samples respectively. The images are taken with the incident beam along the [10$\bar{1}$0] zone axis of the Mg matrix. The peak aged and over aged samples showing the precipitates with the strain contrast are expected to be Mg_2Ca phase as shown for the Mg–0.5Ca binary alloy [4]. The Mg_2Ca phase in the over aged is coarser than the peak aged sample. In addition to the Mg_2Ca precipitates, a speckled contrast implying the presence of extremely fine plate-like precipitates lying on the (0001) basal plane of this peak aged and over aged conditions of Mg–0.5Ca–0.1Al samples. Selected area electron diffraction (SAED) patterns of the peak aged and over aged Mg–0.5Ca–0.1Al in the [10$\bar{1}$0] zone axis shows continuous streaks at the 1/3{11$\bar{2}$0}, 2/3{11$\bar{2}$0} positions and parallel to [0001]. The SAED pattern in the [11$\bar{2}$0] zone axis shows the streaks parallel to [0001]. Precipitates exhibiting such diffraction features have been reported in Mg–Ca–Zn (–Nd) [2-4], Mg–RE–Zn–Zr [5] and Mg–Gd–Zn [6] based alloys, which were denominated as ordered Guiner-Preston (G.P.) zones [4-6]. Figure 4a and 4b show the TEM bright field images of the peak aged and over aged Mg–0.5Ca–1Al samples respectively. The images are taken with the incident beam along the [10$\bar{1}$0] zone axis of the Mg matrix. The speckled contrasts in the bright field images and the positions of streaks in the SAED pattern as explained above indicates the presence of G.P zones for the peak aged and over aged Mg–0.5Ca–1Al samples. Apart from the G.P zones, plate type precipitates with the length of 50 nm are present in the over aged condition. Those plate precipitates causing over aging formed on the basal planes have not been identified in this work. Figure 5a and 5b show the TEM bright field images of the peak aged and over aged Mg–0.5Ca–0.3Al samples respectively. The images are taken with the incident beam along the [10$\bar{1}$0] zone axis of the Mg matrix. The speckled contrasts in the bright field images and the positions of streaks in the SAED pattern as explained for Fig.3 indicates the presence of G.P zones for the peak aged and over aged Mg–0.5Ca–0.3Al samples. The additional weak spots appeared in the SAED pattern are considered to be the reflections from the oxide layer that were formed during the TEM sample preparation. For the over aged sample, several disc shaped fine precipitates with different length scales of about 5-10 nm and 60 nm were observed. From our previous work, the micro-diffraction pattern analysis revealed that the coarse precipitate is the Al_2Ca phase with the C15 structure [8]. The crystallographic orientation relationship between the Al_2Ca phase and the Mg-matrix is consistent with that was reported by Suzuki et al. [10].

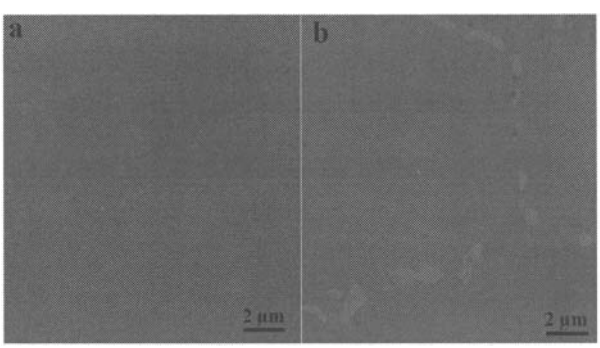

Figure 2 Backscattered electron SEM images of the alloys after solution treatment (a) Mg–0.5Ca–0.3Al (b) Mg–0.5Ca–1Al

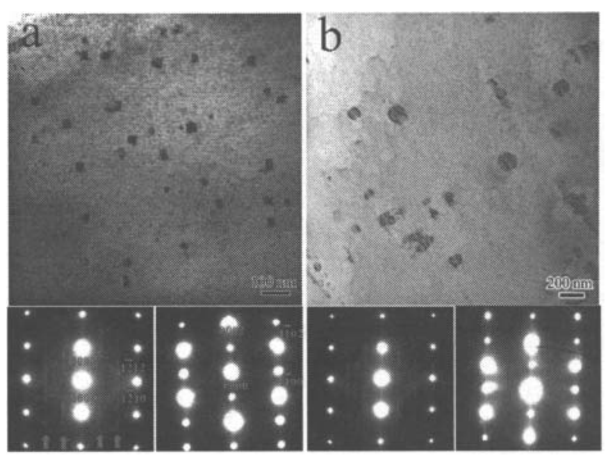

Figure 3 TEM bright field images of the Mg–0.5Ca–0.1Al aged alloy taken from the [10$\bar{1}$0] and corresponding SAED pattern of the [10$\bar{1}$0] and [11$\bar{2}$0] directions. (a) Peak aged at 200 °C for 4h (b) Over aged at 200 °C for 200h.

Figure 6a and 6b show the HAADF image of the peak aged and over aged Mg–0.5Ca–0.3Al samples respectively. The image is taken with the incident beam along the [10$\bar{1}$0] zone axis of the Mg matrix. For the peak aged condition, no precipitates were observed in the HAADF image. In the over aged condition the precipitates appear as bright lines along the basal plane for a fine (short) and coarse (long) precipitate. Since, the contrast of the HAADF image is related to the square of the atomic number [11], indicating that the precipitates are enriched with Ca and Al. It is clear from the image that the fine precipitate is a (0002) monolayer precipitates enriched with solute atoms, whereas the coarse precipitate is composed of several (0002) layers. Considering the speckled contrast in Fig. 5 and the streaks in the inset SAED pattern, we conclude the fine precipitates are ordered monolayer G.P. zones as reported in the Mg–Ca–Zn and Mg–RE–Zn–Zr systems [4, 5].

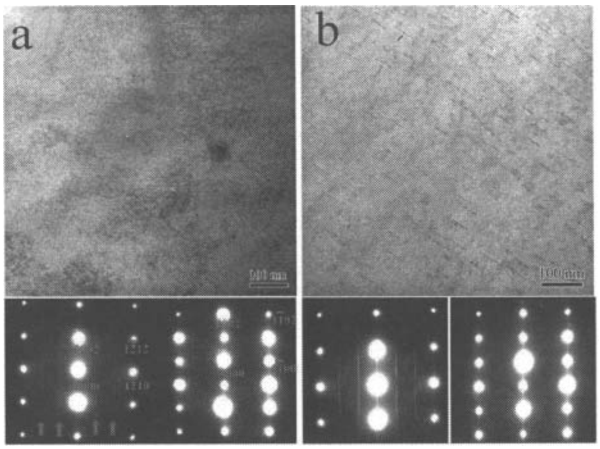

Figure 4 TEM bright field images of the Mg–0.5Ca–1Al aged alloy taken from the [10$\bar{1}$0] and corresponding SAED pattern of the [10$\bar{1}$0] and [11$\bar{2}$0] directions. (a) Peak aged at 200 °C for 4h (b) Over aged at 200 °C for 200h.

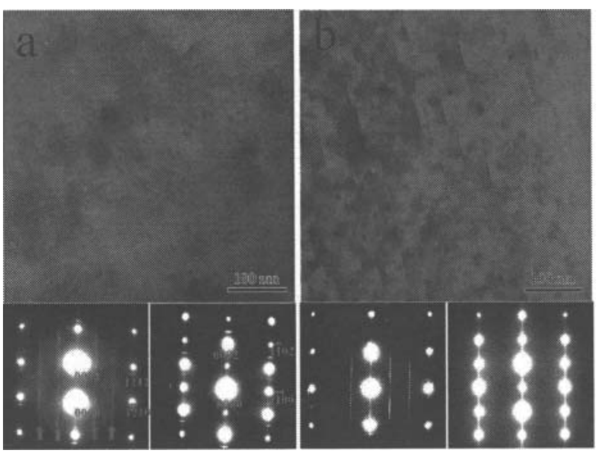

Figure 5 TEM bright field images of the Mg–0.5Ca–0.3Al aged alloy taken from the [10$\bar{1}$0] and corresponding SAED pattern of the [10$\bar{1}$0] and [11$\bar{2}$0] directions. (a) Peak aged at 200 °C for 2h (b) Over aged at 200 °C for 1000h. The figure is reproduced from [8].

Our earlier 3DAP investigations on the Mg–0.5Ca–0.3Al peak aged alloy shows that the solute atoms, Ca and Al are distributed essentially within a few atomic planes of $(0002)_{Mg}$ which revealed the presence of disc shaped G.P. zones [8]. The thickness of the G.P zone is within two atomic layers (~ 1 nm) and the disc diameter is approximately 3 nm. The average composition of the G.P. zone in the peak aged sample was estimated to be Mg–6Ca–7Al (at. %). The total solute concentration in the ordered monolayer G.P. zones of this peak aged Mg–Ca–Al alloy is about 13 at. %. It should be noted that these value are lower than the ~ 33 at. % of the solute concentration from the model proposed by Ping et.al for the fully ordered G.P. zone formed on a single (0001) Mg plane [5].

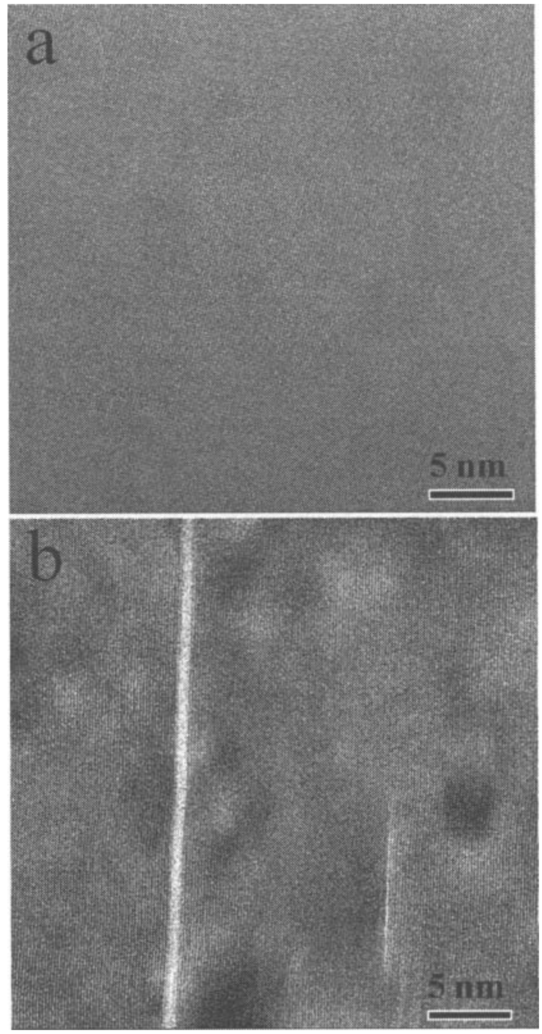

Figure 6 HAADF images of the Mg–0.5Ca–0.3Al aged alloy taken from the [10$\bar{1}$0] (a) Peak aged at 200 °C for 2h (b) Over aged at 200 °C for 1000h.

In the studied Mg–Ca–Al system, for the optimum Al content, TEM analyses confirmed that the improvement in the peak hardness is associated with the dense precipitation of ordered monolayer G.P. zones. Whereas, lower content of Al resulted in the formation of G.P. zones and Mg_2Ca and the excess addition of Al causes the formation of G.P. zones and the grain boundary

Al_2Ca phase. It is interesting to compare the Mg–Ca–Al system with the other G.P zone forming system such as Mg–Ca–Zn [4] and Mg–Gd–Zn [6]. As that of Mg–Ca–Al, Mg–Ca–Zn system was strengthened by monolayer G.P. zones whereas the Mg–Gd–Zn forms tri-layered G.P. zones. The common features in these systems are that the solute atoms are oversized and undersized to Mg atoms. The atomic radius of Ca (1.97 Å) and Gd (1.78 Å) are larger than that of Mg (1.60 Å), while the atomic radius of Zn (1.48Å) and Al (1.43Å) are smaller than that of Mg atom. Another feature is that the mixing enthalpy between two solute elements is negatively large, i.e., there is a strong attractive interaction between the two solute elements. The mixing enthalpy values of Ca–Zn, Gd–Zn and Ca–Al are −22, −31 and −20 kJ/mol, respectively. These values are one order of magnitude larger than the other combinations, like Mg–Ca, Mg–Al, Mg–Zn and Mg–Gd. The difference in atomic size and large negative heat of mixing favors the formation of the G. P. zones enriched with Ca and Al atoms rather than Mg–Ca. Without microalloying or lower content of Al, the Mg_2Ca phase precipitates [1, 4]. For higher content of Al, the insoluble grain boundary Al_2Ca phase forms. Thus it could be speculated that high number density of G.P zones enriched with Ca and Al atoms is present in the alloy containing optimum Al content of 0.3 wt. %. Also, by comparing the atomic sizes, a large lattice misfit is expected for the Mg_2Ca precipitate, whereas the lattice misfit is lower for the G.P. zones composed of Ca–Al, resulting in coherency with the matrix. Thus due to the combinations of coherency, extremely fine size and high numerical density of the G.P. zones in the peak aged Mg–0.5Ca–0.3Al alloy the highest hardness value is achieved.

Conclusion

In summary, it was confirmed that the effect of addition of Al as an undersized element to Mg–Ca system promotes the formation of ordered monolayer G.P zones as similar to Mg–Ca–Zn. The composition for the highest age hardening response has been optimized to Mg–0.5Ca–0.3Al. The major strengthening precipitate is ordered monolayer G.P. zones and shows high resistance to coarsening. Since only a trace addition of inexpensive alloying elements contribute to the age hardening, this alloy may be suitable for wrought applications.

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References

[1] J. F. Nie, B. C. Muddle, Scripta Mater. 37 (1997) 1475-1481

[2] X. Gao, S. M. Zhu, B. C. Muddle, J. F. Nie, Scripta Mater. 53 (2005) 1321-1326

[3] J. C. Oh, T. Ohkubo, T. Mukai, K. Hono, Scripta Mater. 53 (2005) 675-679

[4] K. Oh-ishi, R. Watanabe, C. L. Mendis, K. Hono, Mater. Sci. Eng. A 526 (2009) 177-184

[5] D. H. Ping, K. Hono, J. F. Nie, Scripta Mater. 48 (2003) 1017-1022

[6] J. F. Nie, K. Oh-ishi, X. Gao, K. Hono, Acta Mater. 56 (2008) 6061-6076

[7] J. F. Nie, X. Gao, S.M. Zhu, Scripta Mater. 53 (2005) 1049-1053

[8] J. Jayaraj, C. L. Mendis, T. Ohkubo, K. Oh-ishi, K. Hono, Scripta Mater. 63 (2010) 831-834

[9] E. F. Emley, Principles of Magnesium technology, Pergamon Press, (Oxford, New York) 1966, p.248,

[10] A. Suzuki, N. D. Saddock, J. R. Terbush, B. R. Powell, J. W. Jones, T. M. Pollock, Metall. Mater. Trans. A 39A (2008) 696-702

[11] D. E. Jesson, S. J. Pennycook, Proc. R. Soc. A 449 (1995) 273-293