Effect of Sn Addition on the Precipitation Behavior in AZ91 Magnesium Alloy

Jeong Kyun Kim¹, Seung Hyun Oh¹, Kang Cheol Kim¹, Won Tae Kim² and Do Hyang Kim¹,*

¹Department of Materials Science and Engineering, Center for Noncrystalline Materials, Yonsei University, Seoul 120–749, South Korea
²Department of Optical Engineering, Cheongju University, Cheongju 363–764, South Korea

The effect of Sn (1, 3 and 5 mass%) addition on the precipitation behavior of AZ91 alloy has been investigated in the present study. The addition of Sn is effective in suppression of discontinuous precipitation as well as acceleration of continuous precipitation. The MgSn particles at the grain boundary effectively reduce the nucleation sites for discontinuous γ precipitates, and slow down the movement of the grain boundary. The addition of Sn remarkably enhances the aging response of AZ91. The hardness increases steeply with the start of the aging treatment, resulting in significantly higher peak hardness within shorter aging time. The addition of Sn enhances the aging response by solid solution hardening effect as well as by co-precipitation of Mg17Al12 and Mg2Sn in the α-Mg matrix. [doi:10.2320/matertrans.M2017011]

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1. Introduction

Recently, Mg alloys receive an attention as one of the potential light weight alloys. In particular, AZ91 Mg alloy (Mg-9 mass%Al-1 mass%Zn-0.2 mass%Mn) has been widely used for producing cast parts for automobiles due to its good combination of castability, resistance to corrosion and room-temperature mechanical property.¹,² Since there is a large difference in the maximum solid solubility of Al between at room temperature and at eutectic temperature in Mg-Al binary system,³ AZ91 alloy can exhibit better mechanical property by forming Mg17Al12 (β) precipitates in the α-Mg matrix.⁴ The precipitation of β occurs in two different ways, i.e. discontinuous and continuous precipitation. In general, discontinuous precipitation occurs by cellular growth of alternating plates of β and α-Mg at high-angle grain boundaries,⁵ while continuous precipitation occurs by cellular growth of alternating plates in the α-Mg matrix.⁶ The continuous precipitates exhibiting an orientation relationship with the α-Mg matrix primarily contribute to the age hardening in AZ91 alloy, whereas the discontinuous precipitates are known to be detrimental to the mechanical properties.⁷ Thus, it has been recognized that suppression of discontinuous precipitation is essential in improvement of the mechanical property of AZ91 alloy. There have been several works on the suppression of discontinuous precipitation by adding minor elements such as Au, Pb, Si, Sb and Sn in AZ91 alloy.⁸–¹⁰ However, the suppression of discontinuous precipitates has not been always associated with the enhanced association of the age hardening response. Li et al. have shown that the hardness decreases with increasing Sn content in (AZ91)100-xSnx (x = 0, 0.5, 1, 1.5 and 2 mass%) alloys after aging at 443 K for 24 h, although discontinuous precipitation is suppressed.¹¹ However, Jung et al. have shown that the addition of 5 mass% Sn in AZ91 alloy leads to suppression of the discontinuous precipitation as well as significant improvement of peak hardness and strength when aged at 441 K up to 28 h.¹² Therefore, the aim of the present study is to investigate the effect of Sn addition (1, 3 and 5 mass%) on the precipitation behavior of AZ91 alloy. The emphasis was placed on the role of Sn in continuous and discontinuous precipitation behavior in AZ91 alloy.

2. Experimental

The alloy ingots of AZ91 (Al: 8.7 mass%, Mn: 0.13 mass%, Zn: 0.7 mass%) and 1, 3 and 5 mass% Sn containing AZ91 alloys (will be referred to as AZT911, AZT913 and AZT915, respectively, hereafter) were prepared in an electrical resistance furnace under a mixture of SF6 and CO2 protective gas atmosphere using high purity metals. Molten metal was poured into a preheated (~373 K) rectangular steel mold with a dimension of 10 mm in thickness, 60 mm in width, and 100 mm in height. The resulting alloys were solution treated at 683 K up to 24 h, and then were immediately water-quenched. After solid solution treatment, the cast ingot was cut into disks with a dimension of 10 mm in diameter and 4 mm in thickness for the isothermal aging treatment. Artificial aging treatments were conducted at 441 K up to 28 h in an oil bath. The conditions for solution treatment and aging followed the ASTM Handbook.¹³ Age-hardening response was investigated by using Vickers hardness measurements (LEICA DMRM optical microscope) and scanning electron microscopy (JEOL™, JSM7001F) were prepared by etching with a solution of 4 vol% nitric acid and ethanol. Specimens for transmission electron microscopy (JEOL™, JEM2000EX) were prepared using an ion milling equipment (Gatan™, model 600). During ion milling, the sample was cooled by circulating liquid N2.

3. Results

The microstructure of the as-cast AZ91 consisted of α-Mg dendrite and interdendritic α-Mg/β eutectic.¹⁴,¹⁵ With the increase of Sn content, α-Mg dendritic structure became gradually refined and Mg2Sn particles were additionally present in the interdendritic region, as reported previously.¹⁶ Figures 1 (a)–(d) show the optical micrographs obtained from AZ91, AZT911, AZT913 and AZT915 after solution treatment at 683 K for 24 h followed by water quenching. In the case of AZ91 (Fig. 1 (a)), β was completely dissolved into the ma-
matrix. In the case of AZT911 (Fig. 1 (b)), $\beta$ was completely dissolved into the matrix, and no other phase was present in the matrix. On the other hand, Mg$_2$Sn particles were present in AZT913 and AZT915 (Figs. 1 (c), (d)). Mg$_2$Sn remained after solution treatment due to its high melting temperature of $\sim1043$ K.\(^{17}\)

Figures 2 (a)–(d) show the SEM micrographs obtained from AZ91, AZT911, AZT913 and AZT915 after aging at 441 K for 12 h. The micrographs in Fig. 2 indicate two major effects of Sn addition: 1) suppression of discontinuous precipitation; and 2) acceleration of continuous precipitation with the increase of Sn amount. The average width of the cellular region of discontinuous precipitates in AZ91, AZT911 and AZT913 was $d = 8.4$, $d = 6.3$ and $d = 3.5 \mu$m, respectively (Figs. 2(a)–(c)). The discontinuous precipitation was almost completely suppressed in AZT915. Only Mg$_2$Sn particles were present at the grain boundaries (Fig. 2 (d)) as can be confirmed from the EDS result. The continuous precipitation occurred in the $\alpha$-Mg matrix, and the density of the precipitates increased remarkably with increasing Sn content.

Figure 3 shows the variation of hardness during aging treatment of AZ91, AZT911, AZT913 and AZT915 at 441 K up to 24 h. The result clearly shows that significant increase of hardness occurs with the increase of Sn content. AZT911 showed a slightly higher level of hardness than AZ91, while AZT913 and AZT915 showed much more enhanced hardness values when compared to AZ91. When the aging behavior of AZ91 and AZT915 is compared, it can be noticed that: 1) the hardness after the solution treatment in AZT915 (64.3 HV) is higher than that in AZ91 (57.1 HV); and 2) the hardness in
AZT915 increases steeply with the start of the aging treatment, reaching the peak hardness value of 92.1 HV after aging for 12 h, while AZ91 shows less steep increase of hardness, exhibiting the peak hardness value of 77.2 HV after aging for 16 h.

4. Discussion

Mg-Sn alloy system is known as a precipitation hardening alloy system due to high solubility of Sn in Mg (14.5 mass%) at eutectic temperature. Sasaki et al. and Mendis et al. have reported that the addition of Zn in Mg-Sn alloy enhances the precipitation hardening response due to refinement of the Mg2Sn precipitates. Further work by Elsaye et al. have demonstrated that the addition of Al in Mg-Sn alloy leads to enhancement of the hardening response due to increased driving force for precipitation by the reduced solubility of Sn. Shanghai Wei et al. have reported that Sn containing Mg-Zn alloy shows much finer and denser precipitates due to reduced interfacial misfit energy between the precipitate and the matrix by the combination of Sn and Zn elements in MgZn2 and Mg2Sn precipitates. More recently, the effect of Sn addition on the age hardening behavior of Mg-6Al-4Zn alloy has been investigated. It has been shown that Sn containing Mg-6Al-4Zn alloy exhibits higher density of precipitates, when compared with Mg-6Al-4Zn alloy. All of these previous studies show that the addition of Sn in Mg based alloy is effective in increasing the density of precipitates and enhancing the age-hardening response.

The present study shows that Sn addition in AZ91 alloy is very effective in enhancing the age hardening response. The discontinuous precipitation is effectively suppressed by increasing Sn content up to 5 mass% in AZ91. The Mg2Sn particles at the grain boundary effectively reduces the nucleation sites for discontinuous β precipitates, and slow down the movement of the grain boundary, resulting in suppression of discontinuous precipitation. The effect of various minor alloying elements on the aging response in AZ91 has been reported, for example, it has been shown that the addition of Pb, Ca, Au and RE elements delays the hardening kinetics or decreases the peak hardness value, in spite of suppression of discontinuous precipitation. However, in the present study, with increasing Sn content, the hardness after solid solution treatment becomes higher, and increases steeply during the aging treatment, as shown in Fig. 3. The hardness after solution treatment in AZT913 (59.2 HV) is slightly higher than that in AZ91 (57.1 HV) due to solid solution effect by Sn addition, while AZT915 shows significant increase of hardness (64.3 HV) after solution treatment due to strengthening effect by Mg2Sn particles. This result shows that the significantly higher hardness after solid solution treatment in AZT915 is mainly due to strengthening effect by Mg2Sn particles rather than solid solution effect.

The hardness increases steeply at early stage of annealing, particularly after aging for 2 h, in AZT915 than that in AZ91, as shown in Fig. 3. To reveal the reason why the hardness increases steeply with the start of the aging treatment, TEM investigation was performed, as shown in Fig. 4. All the bright field (BF) TEM images were obtained under the same [1010] zone axis of hcp α-Mg. Figures 4 (a) and (b) compares the precipitation behavior after aging at 441 K for 2 h in AZ91 and AZT915, respectively. It can be noticed that the density of continuous β precipitates much higher in AZT915 than in AZ91, indicating that the continuous precipitation is accelerated by the addition of Sn in AZ91 at the early stage of aging treatment. The acceleration of the nucleation rate in AZT915 is considered to be due to increase of local lattice distortion by the presence of Sn in the α-Mg solid solution matrix.

Figure 4 (c) and (d) show BF TEM images obtained from AZ91 and AZT915 after aging at 441 K for 12 h. It can be noticed that the density of the precipitates is still much higher in AZT915, and a new precipitate is present in AZT915, as marked by circles in Fig. 4 (d). The selected electron diffraction pattern in Fig. 4 (e) obtained from the region marked by an arrow in Fig. 4 (d) was indexed as superimposed [1010] zone of hcp α-Mg, [111] zone of bcc Mg17Al12 (β) and [111] zone of fcc Mg2Sn (schematic diffraction in Fig. 4 (f)), indicating that the three phases, α-Mg, β and Mg2Sn have an orientation relationship which can be expressed as (0001)h//α-Mg// (101)β//(101)β//[111]β//[111]β//[111]Mg2Sn. The result shows that Mg2Sn precipitate forms on the β precipitate during aging in AZT915.

Therefore, the results in the present study indicate that addition of Sn in AZ91 has two major effect on the precipitation behavior: 1) the acceleration of the nucleation rate of the precipitates in the matrix possibly due to the presence of Sn in the α-Mg solid solution matrix at the early stage of aging treatment; and 2) the formation of Mg2Sn precipitate on the β precipitate at the later stage of aging treatment. The less prominent aging response in the previous studies in spite of the effective suppression of the discontinuous precipitation may be due to the less activated continuous precipitation process in the matrix.

5. Conclusions

(1) The addition of Sn effectively suppresses the discontinuous precipitation as well as accelerates the continuous precipitation in the α-Mg matrix. With addition of 5 mass% Sn, the discontinuous precipitation is almost completely suppressed.

(2) With addition of Sn, significantly higher peak hardness...
is obtained within shorter aging time. The values of peak hardness in AZ91 and AZT915 are 77.2 Hv (after aging for 12 h) and 92.1 Hv (after aging for 16 h), respectively.

(3) The addition of Sn facilitates the age hardening behavior by solid solution hardening effect as well as by co-precipitation of Mg17Al12 and Mg2Sn in the α-Mg matrix. Mg2Sn precipitates on Mg17Al12 with the orientation relationship of (0001)α-Mg//(101)β// (101)Mg2Sn and [10¯10]α-Mg//[111]β// [111]Mg2Sn.

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REFERENCES