

The Mg₂Sn Precipitation Process in the Mg–7Sn Alloys with the Addition of Silicon and Aluminum

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In this paper the influence of alloying elements (Si and Al) on the precipitation process of Mg₂Sn phase in Mg–Sn alloys is presented. X-ray diffraction analysis was used to determine the lattice parameters of α -Mg solid solution, the phases content and size of the Mg₂Sn precipitates. It was found that silicon causes the refinement of the precipitates of Mg₂Sn phase, however it does not result in a significant increase of hardness increment after ageing treatment at 250 °C. The addition of aluminum has a positive effect on the hardness of Mg–7Sn–5Si alloy.

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1. Introduction

Mg–Sn system has shown some promising properties to replace Mg–RE systems since the phase diagram of Mg–Sn system shows similarity in several aspects compared with typical Mg–RE phase diagrams, such as Mg–Nd and Mg–Y systems [1]. The Mg–Sn system is known as a precipitation system, which has a relatively high solubility limit (3.35 at.%) at 561 °C and low solubility at ambient temperature [2]. In addition, since the main precipitate phase, Mg₂Sn, has a high melting temperature of about 770 °C, a creep resistance superior to that of the AZ alloys is anticipated [3]. Generally, the hardening response of Mg–Sn alloys after solution treatment and ageing, despite the relatively large content of plate-like precipitates of Mg₂Sn phase, is very low. Moreover, the peak hardness is obtained after long times of ageing. The low hardness increment of aged Mg–Sn alloys is related to an unfavorable crystallographic orientation of Mg₂Sn precipitates and their large size [4]. Therefore, in recent years the studies have focused on improving the hardening response of Mg–Sn alloys. These studies concentrated on decrease of the size of precipitates, increasing their number density in the matrix and optimizing the crystallographic orientation. The alloying elements improve the hardening response include Zn, Al, Si and microadditions of Na, In, Li [3–6]. In this work the Si and Al additions were introduced to the binary Mg–7Sn alloy in order to check the possibility to refine Mg₂Sn phase.

2. Experimental procedure

Three magnesium alloys with compositions (in wt%): Mg–7Sn–1Si, Mg–7Sn–5Si, and Mg–7Sn–5Si–2Al were prepared. Melting of the alloys was performed by induction melting in an alumina crucible under the protection of an argon atmosphere. The melt was maintained at 730 °C for 3 min then poured into sand moulds.

Heat treatment consists of two stages: solution treatment and ageing treatment. Solution treatment was performed at 500 °C for 24 h in argon atmosphere. Ageing treatment was performed at 250 °C in time range from 4 h to 148 h. Microstructural observations of the alloys were carried out by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Microanalysis of the chemical composition of the intermetallic compounds was performed by energy-dispersive X-ray spectroscopy (EDS). Phase identification was carried out by X-ray diffraction analysis (XRD). The peak profile analysis (pseudo-Voigt function) was used to determine the lattice parameters and integral breadths of diffraction lines. The phase contents were determined by reference intensity ratio (RIR) method. Due to the presence of random texture the intensity of diffraction lines has been corrected.

3. Results and discussion

In the earlier work [7] it was reported that the microstructure of Mg–7Sn–1Si alloy consists of α -Mg solid solution, Chinese script Mg₂Si phase, and irregular Mg₂Sn phase. The microstructure of as-cast Mg–5Si–7Sn alloy is similar, however the primary crystals of Mg₂Si are additionally observed due to the hypereutectic composition (Si content is above 1.2 at.%). In the Mg–5Si–7Sn alloy the dissolution of Al in the α -Mg matrix and in the Mg₂Sn phase was found. The solution heat-treatment of the tested alloys at 500 °C for 24 h causes the dissolution of the Mg₂Sn phase in the α -Mg matrix and spheroidization of the Chinese script Mg₂Si compound. The Mg₂Si primary crystals are stable at solution temperature.

It was found that after ageing at 250 °C, morphology of the Mg₂Si phase remains unchanged when compared to the solution-treated alloy. The most significant changes are visible in the α -Mg matrix. During the artificial ageing, the precipitation process from the supersaturated α -Mg matrix is observed. From the X-ray diffraction results it can be concluded that the precipitates of Mg₂Sn phase are formed during the ageing of the Mg–5Si–7Sn

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alloy aged at 250 °C (Fig. 1). It is well known that in binary Mg–Sn alloys the formation of Mg_2Sn phase is not preceded by the formation of intermediate phases (G-P zones, non-equilibrium compounds) [4]. Also in our case non-equilibrium phases were not observed and the precipitation process begins with the formation of equilibrium Mg_2Sn phase.

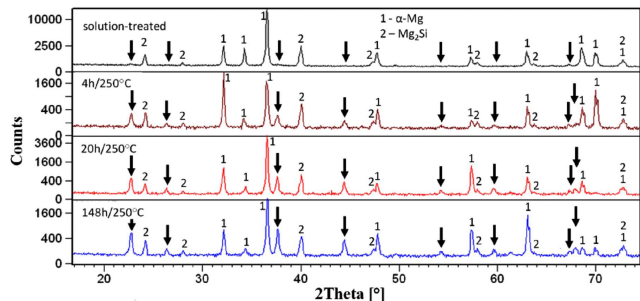


Fig. 1. X-ray diffraction patterns of the Mg–5Si–7Sn alloy aged at 250 °C. Arrows indicate the position of the diffraction lines belonging to the Mg_2Sn phase.

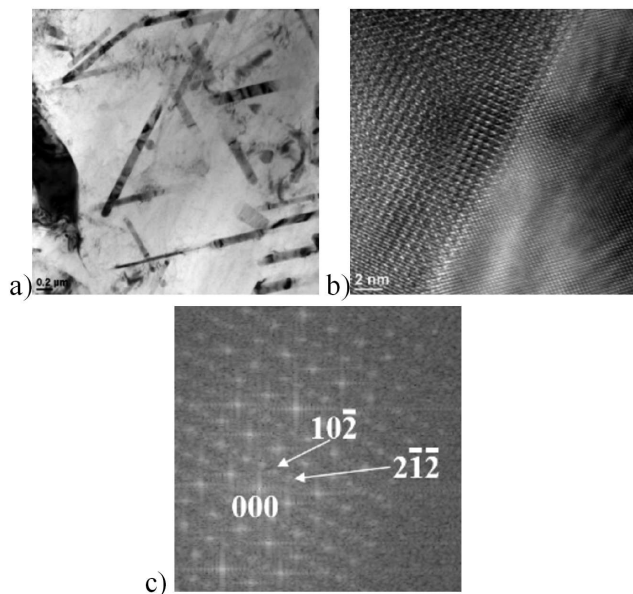


Fig. 2. The rod-shaped morphology of the Mg_2Sn precipitates observed in the Mg–5Si–7Sn alloy aged at 250 °C for 20 h (a), HRTEM image of the interface between the Mg_2Sn precipitates (left side) and the α -Mg phase (right side) (b), FFT pattern from the rod-shaped of Mg_2Sn precipitates, [221] zone axis (c).

Figure 2a shows a bright-field image of a typical microstructure of the Mg–5Si–7Sn alloy aged at 250 °C for 20 h. It can be seen that the Mg_2Sn phase precipitating during ageing treatment has mainly the rod-shaped morphology. The FFT pattern (Fig. 2c) confirms that the rod-shaped precipitates has the Mg_2Sn cubic crystal structure. Besides the rod-shaped precipitates, the polygonal precipitates of Mg_2Sn compound are also visible in the α -Mg matrix of the tested alloys [8].

The microstructure of the tested alloys after ageing at 250 °C for 148 h is shown in Fig. 3. It can be seen that the size and arrangement of Mg_2Sn precipitates in the Mg–7Sn–5Si and Mg–7Sn–5Si–2Al alloys are similar. In the Mg–7Sn–1Si alloy the Mg_2Sn precipitates are clearly larger. Moreover, in hypereutectic (>5 wt% of Si) alloys more of the polygonal particles are observed as compared to hypoeutectic Mg–7Sn–1Si alloy. More detailed analysis is reported in work [8]. In order to characterize the microstructure changes occurring during ageing of the tested alloys, the more detailed X-ray diffraction analyses were performed. This method is more useful than transmission electron microscopy due to the larger volume of the material analyzed and enables the initial analysis of the precipitation process.

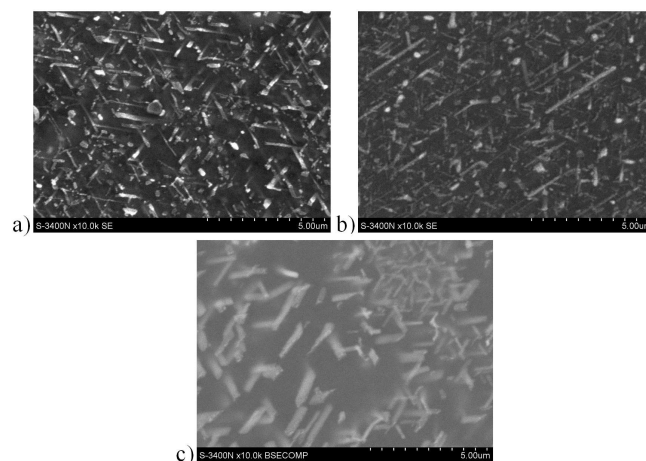


Fig. 3. SEM micrographs of the Mg–7Sn–5Si (a), Mg–7Sn–5Si–2Al (b) and Mg–7Sn–1Si (c) alloys aged at 250 °C for 148 h with the precipitates of Mg_2Sn phase.

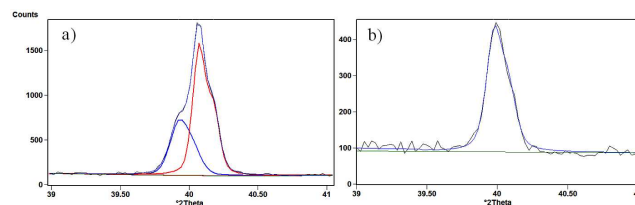


Fig. 4. The strongest (022) diffraction line of Mg_2Si phase in the Mg–7Sn–5Si (a) and Mg–7Sn–1Si (b) alloys.

Before discussing the results obtained for the Mg_2Sn phase it should be noted that in the case of the hypereutectic alloys (Mg–7Sn–5Si and Mg–7Sn–5Si–2Al), the diffraction lines of Mg_2Si phase are split into two peaks (Fig. 4a). This effect was not observed in the hypoeutectic Mg–7Sn–1Si alloy (Fig. 4b). Taking into account the observations of the microstructure [7, 8] and location of the diffraction peaks of Mg_2Si phase in the hypoeutectic alloy, it has been found that the higher peaks belong to primary crystals of Mg_2Si phase and lower peaks are related to the Mg_2Si phase formed in the eutectic reaction (Chinese script). The split of the Mg_2Si diffraction

lines is related to the differences in the lattice parameters between the primary crystals and the eutectic phase with Chinese script morphology. Presumably, these differences are due to the presence of tin in the Mg_2Si phase. The EDS results of primary crystals [8] confirmed that the Mg_2Si phase dissolves up to 2 at.% Sn indicating the formation of the ternary solubility of Mg_2Si phase. Measurements of the Mg_2Si content using the RIR method showed that the weight fraction of the Chinese script phase is approximately up to 2.3 wt%, whereas the content of the primary crystals is in the range of 10–12 wt%. The time of ageing does not influence on the Mg_2Si content due to the lack solubility of Si in the α -Mg matrix and high thermal stability of this compound.

TABLE I

The lattice parameters of α -Mg phase, the Mg_2Sn phase content, the breadth peak of Mg_2Sn , and hardness Hv2 of the tested alloys (t — time of ageing at 250 °C, a_0, c_0 — the lattice parameters of α -Mg solid solution, V_{Mg_2Sn} — the content of Mg_2Sn phase, β — integral breadth of the (111) peak of Mg_2Sn).

Alloy	t [h]	a_0 [Å]	c_0 [Å]	V_{Mg_2Sn} [wt%]	β (111) Mg_2Sn	Hv2
Mg-7Sn-1Si	4	3.2078	5.2068	1.0	0.119	50
	20	3.2082	5.2069	5.4	0.138	55
	48	3.2090	5.2093	6.7	0.115	56
	96	3.2091	5.2093	6.6	0.074	57
	148	3.2093	5.2099	6.8	0.087	56
Mg-7Sn-5Si	4	3.2073	5.1996	2.5	0.236	65
	20	3.2074	5.2002	2.7	0.187	65
	48	3.2078	5.2021	4	0.182	67
	96	3.2082	5.2035	6.4	0.155	67
	148	3.2088	5.2097	6	0.165	67
Mg-7Sn-5Si-2Al	4	3.2011	5.1979	1.8	0.247	81
	20	3.2013	5.2007	2.4	0.201	82
	48	3.2018	5.2009	3.6	0.191	82
	96	3.2024	5.2042	5.9	0.162	83
	148	3.2029	5.209	6.8	0.168	84

Table I shows the lattice parameters of α -Mg phase, the Mg_2Sn content, the integral breadth of the strongest peak of Mg_2Sn (111) and hardness Hv2 of the tested alloys after ageing at 250 °C. In case of the Mg-7Sn-1Si alloy it can be seen that the lattice parameters of α -Mg solid solution increase with the increasing ageing time. Obviously, it is related to the high solubility of Sn in α -Mg and precipitation process of Mg_2Sn phase during the ageing treatment (the Mg_2Si phase has not been dissolved in the α -Mg solid solution due to the very low solubility of silicon in magnesium (0.005 at.%). Because the atomic radius of Sn (140.5 pm) is smaller than that of Mg (159.9), the decreasing Sn content will cause an increase in the α -Mg lattice parameters. It should be noted that in the case of Mg-7Sn-1Si and Mg-7Sn-5Si alloys, the a_0 and c_0 parameters are similar, whereas in the case of Mg-7Sn-5Si-2Al alloy these parameters are smaller. It is related to the presence of Al in the α -Mg solid solution.

In the as-cast alloy, the aluminum does not react with other alloying elements (Si, Sn) and completely dissolves in the α -Mg matrix and Mg_2Sn phase. The content of Al in this alloy is below the maximum solubility of Al in the Mg at 250 °C, therefore during the ageing Al does not form any intermetallic compounds (minor amount of Al can be dissolved in the Mg_2Sn phase). The presence of Al in α -Mg solid solution exerts a strong effect on the hardness of the tested alloys due to the great contribution to the solid-solution strengthening.

The content of Mg_2Sn phase increases with the increasing ageing time, however the kinetics of the precipitation process is not the same for the tested alloys. In the case of Mg-7Sn-1Si alloy, the rate of Mg_2Sn formation is higher than in other alloys. The content of this compound in Mg-7Sn-1Si alloy aged at 250 °C for 48 h is close to 7 wt%, while in the hypereutectic alloys is close to 4 wt%. The maximum weight fraction (approximately 7 wt%) of the Mg_2Sn phase in the hypereutectic alloys is achieved after 96 h.

The peak profile analysis of the strongest (111) diffraction line of Mg_2Sn phase located at $2\theta = 22^\circ$ showed that its integral breadth decreases with the increasing ageing time. The calculation of the crystallite size have been omitted due to plate-like and polygonal morphology of Mg_2Sn precipitates (the classical methods for determining the crystallite size based on the assumption that the particles have a spherical shape). However, the integral breadth of (111) peak decreased with increasing ageing time indicating the increasing size of the precipitates. In case of Mg-7Sn-1Si alloy the integral breadth is clearly smaller than in the hypereutectic alloys and it corresponds well with the results shown in Fig. 3, where it is evident that the Mg_2Sn precipitates are larger in comparison to those of in Si-rich alloys.

It was found that after solution treatment at 500 °C the hardness of Mg-7Sn-1Si alloy is 46 Hv2, Mg-7Sn-5Si alloy is 59 Hv2 and Mg-7Sn-5Si-2Al alloy is 67 Hv2. Obviously, the higher hardness of hypereutectic alloys is related to the presence of hard Mg_2Si primary crystals, which are stable after solution heat treatment. The presence of Al causes further increase of the hardness due to the solid solution strengthening. The hardening response after ageing treatment of the tested alloys is not significant. For the Mg-7Sn-1Si alloy the hardness increment is 11 Hv2, for the Mg-7Sn-5Si alloy is 8 Hv2, for the Mg-7Sn-5Si-2Al alloy is 17 Hv. It is well known that the finer size of precipitates and their higher number effectively strengthen the metallic alloys due to smaller average interparticle spacing and increased number of obstacles to movement of dislocations, thus the smaller size and higher content of Mg_2Sn particles should cause the hardness increment. However, taking into account the results obtained for the Mg-7Sn-1Si and Mg-7Sn-5Si alloys it can be concluded that the size of Mg_2Sn precipitates has negligible effect on the hardening response. If the Mg_2Sn content is higher than about 2 wt%, the changes in the weight fraction of plate-like precipitates

do not significantly increase the hardness. Generally, the age-hardening response in alloys without aluminum is only modest, despite the large content of Mg_2Sn precipitates. The reason for the poor precipitate strengthening response is that the precipitates form a rod-shaped morphology parallel to the basal planes of the Mg matrix. This configuration is relatively inefficient at impeding dislocation motion in the α -Mg matrix [8]. Microscopic observations performed in our work [9] also suggests that the Mg_2Sn precipitates are parallel to the basal planes of the matrix, thus the hardness increment after ageing is relatively poor. Addition of aluminum causes a significant increase in the hardness of Mg–5Si–7Sn alloy. Al atoms may cause a solute-drag like effect for the Mg/Mg₂Sn interfaces, therefore the growth of the Mg_2Sn particles is hindered. However, as mentioned above the size of precipitates does not have a strong effect on the hardness in the tested alloys. Probably, Al promotes the formation of Mg_2Sn precipitates on the non-basal planes (pyramidal and prismatic). The precipitates lying in the non-basal planes are more effective barrier to gliding dislocations in Mg–Sn alloys than those on the slip plane. Thus, the higher hardness increment is observed in the Mg–7Sn–5Si–2Al alloy.

4. Summary

The ageing of Mg–7Sn–1Si alloy at 250 °C causes the formation of coarse precipitates of Mg_2Sn phase, thus the hardness increment is relatively low (≈ 11 Hv). Increasing the Si content to 5 wt% promotes the refinement of Mg_2Sn phase, however it does not affect significantly on hardness increment (≈ 8 Hv). Addition of Al to Mg–7Sn–5Si alloy has a positive effect on the hardness increment (≈ 17 Hv) due to the solid solution strengthening and probably the formation of precipitates lying in the non-basal planes of magnesium.

Acknowledgments

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