J Mater Sci (2007) 42:8374–8376
DOI 10.1007/s10853-007-1945-7

LETTER

Observation of the suppression of $Mg_{17}Al_{12}$ formation in a La-containing AZ91 alloy

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Received: 7 June 2007 / Accepted: 15 June 2007 / Published online: 11 July 2007
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AZ91 magnesium alloy has been widely used in automobile and aerospace industries owing to its good castability, mechanical and excellent corrosion properties among the other Mg-based alloys. However, the application of this alloy is restricted to temperatures below 120 °C because of the reduction in strength and creep properties due to poor thermal instability of the microstructure [1, 2]. Therefore, improving the elevated temperature properties of AZ91 has become a major issue for possible applications of this alloy in power train components in the automobile industry. Recently, it has been reported that the addition of rare earth elements such as mischmetal, Ce, La, etc., in AZ91 alloy yielded an improvement in high temperature properties. This is due to suppression of the formation of the β-$Mg_{17}Al_{12}$ phase and the introduction of new thermally stable intermetallics along the grain boundaries, which restrict grain boundary sliding [3, 4]. However, there is no systematic study on the quantitative analysis of the β phase suppression in the literature. In this context, a study on the β phase suppression of La added AZ91 alloy using the DTA technique has been undertaken and the results have been validated with the microstructure.

Three alloys having different chemical compositions as listed in Table 1 were prepared by standard melting procedures reported elsewhere [1, 2]. The phases present in these alloys were analyzed using a PHILIPS PW 1710 powder X-ray diffractometer with Cu K_α radiation. For microstructural characterization, samples (15 mm in diameter and 10 mm in length) were machined from these castings, and were polished using standard metallographic techniques. The polished samples were etched in a solution of 6 g picric acid, 5 mL acetic acid, 100 mL ethanol and 10 mL water. Subsequently, they were evaluated using a Leica DMRX optical microscope and a JEOL JSE 35C scanning electron microscope equipped with an energy dispersive spectrometer (EDS). In order to study the effect of the La additions on the β-phase suppression, samples weighing ≈10–12 mg were cut from the respective castings and kept in an alumina crucible, which was placed inside the SETRAM-TG-1600 instrument. These experiments were conducted under argon atmosphere using a scanning rate of 10 K/min. The reproducibility of every measurement was confirmed by conducting three heating cycles.

The X-ray diffraction (XRD) pattern taken from Z1 alloy is shown in Fig. 1a. The peaks are indexed as the α-Mg hcp matrix and the β-$Mg_{17}Al_{12}$ phase, which has a bcc crystal structure. The scanning electron micrograph of Z1 alloy presented in Fig. 1b shows the presence of the α-Mg matrix and two different morphologies of β phase: (i) massive $Mg_{17}Al_{12}$ phase that is mainly distributed at the grain boundaries, and (ii) lamellar discontinuous $Mg_{17}Al_{12}$ phase, which is adjacent to the massive phase. The EDS results listed in Fig. 1c confirm that both phases have compositions consistent with the $Mg_{17}Al_{12}$ phase. The microstructures of Z2 and Z3 alloys are presented in Fig. 2a, b. It can be observed from the figures that the lanthanum addition to the base alloy has resulted in significant changes in both volume fraction as well as the morphology of β phase. The fine β phase in the

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Table 1 Chemical compositions of the alloys investigated

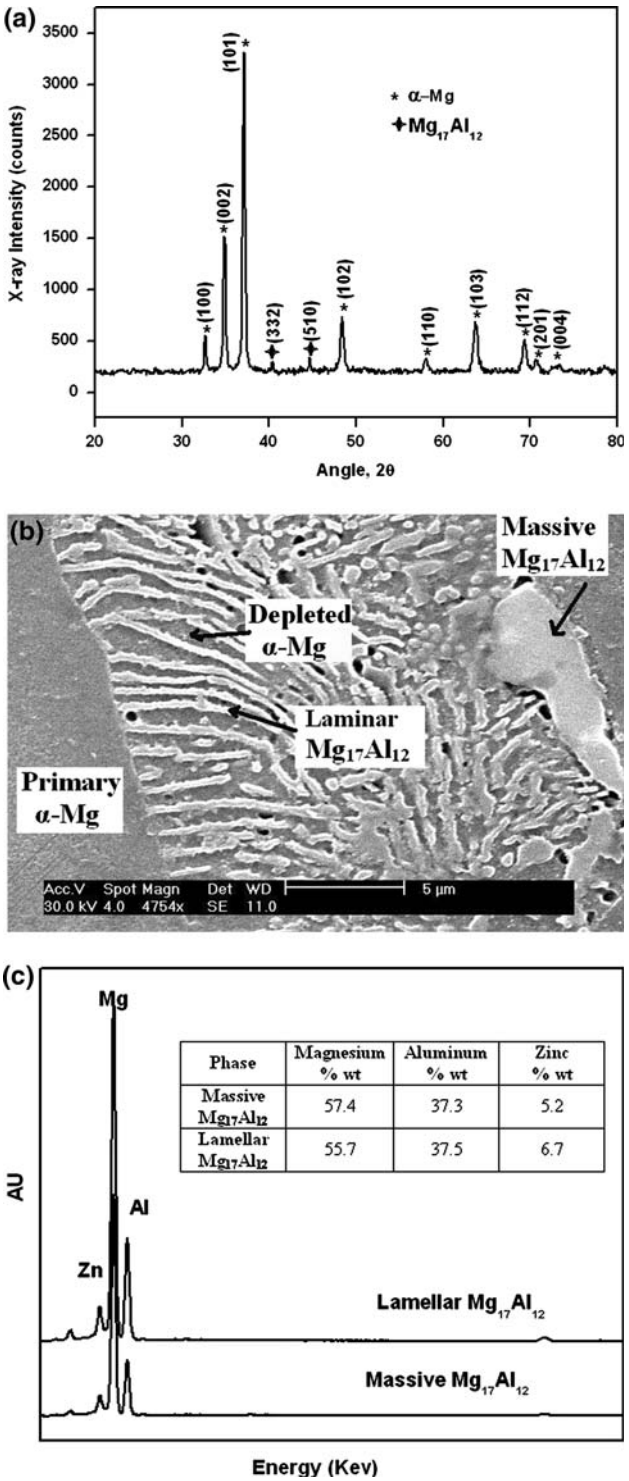
Alloy code	Elemental composition, in wt%			
	Al	Zn	Mn	La
Z1	8.87	0.81	0.22	0
Z2	9.11	1.05	0.18	0.92
Z3	8.74	0.94	0.28	1.91

microstructure is distributed more uniformly compared to base alloy microstructure. Furthermore, new black needle-shaped precipitates distributed mainly at the grain boundaries are observed in the microstructure. It can be further seen in the microstructures (Fig. 2) that the β phases in the Z2 and Z3 alloys are finer with lesser volume. The X-ray diffraction pattern obtained from the Z3 alloy, shown in Fig. 3, contain peaks that confirm the presence of $Al_{11}La_3$ precipitates with Mg matrix and β phase.

Figure 4 shows the DTA heating thermograms of the three alloys. The characteristic values of enthalpies for phase transformations, peak and onset temperatures are summarized in Table 2. It can be inferred from the thermogram of Z1 alloy that there are two peaks: one corresponds to dissolution of the second phase according to reaction $\alpha\text{-Mg} + \beta \rightarrow \alpha\text{-Mg} + L_1$; and the second peak is associated with melting of the Mg matrix, which corresponds to the reaction $\alpha\text{-Mg} + L_1 \rightarrow L$. The enthalpy required for β phase dissolution is 3.9901 mW/mg. The La additions to base alloy have resulted in significant changes in the energy required for β phase dissolution. The enthalpy of alloy with the 1% La addition decreased from 3.9901 to 2.8712 mW/mg, and it decreased further to 0.6348 mW/mg for the Z3 alloy. Furthermore, new endothermic peaks are observed in La-containing alloys, which correspond to dissolution of the $Al_{11}La_3$ phase near the liquidus temperature. Under equilibrium conditions, the La-containing alloys follow the reactions: $\alpha\text{-Mg} + \beta + \gamma \rightarrow \alpha\text{-Mg} + \gamma + L_1 \rightarrow \alpha\text{-Mg} + L_2 \rightarrow L$ (where γ represents the $Al_{11}La_3$ intermetallic).

These results of this study indicate that the addition of La to the AZ91 alloy suppresses the formation of the $Mg_{17}Al_{12}$ phase. This behavior can be explained by the following factors:

1. La has low solid solubility in Mg, hence it will form a La-containing intermetallic.
2. The high chemical affinity of La for Al leads to the formation of the $Al_{11}La_3$ intermetallic.
3. One unit (in mass) of La consumes 3.5 units (in mass) of Al at the initial stage of solidification to form $Al_{11}La_3$, and, as a result, the amount of Al for the eutectic reaction is reduced.



Phase	Magnesium % wt	Aluminum % wt	Zinc % wt
Massive $Mg_{17}Al_{12}$	57.4	37.3	5.2
Lamellar $Mg_{17}Al_{12}$	55.7	37.5	6.7

Fig. 1 (**a**) X-ray diffraction pattern (**b**) SEM-micrograph and (**c**) EDS-spectrum of Z1 alloy

In conclusion, the addition of La suppresses the $Mg_{17}Al_{12}$ phase formation by forming a highly stable $Al_{11}La_3$ phase. The β phase suppression has been charac-

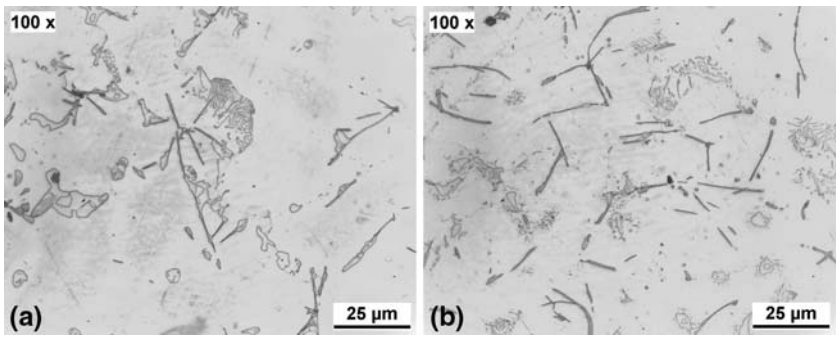


Fig. 2 Microstructures of (**a**) Z2 and (**b**) Z3 alloys

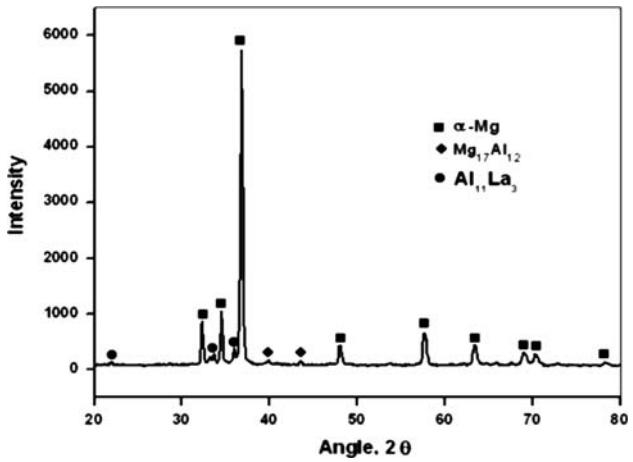


Fig. 3 X-ray diffraction pattern for Z3 alloy

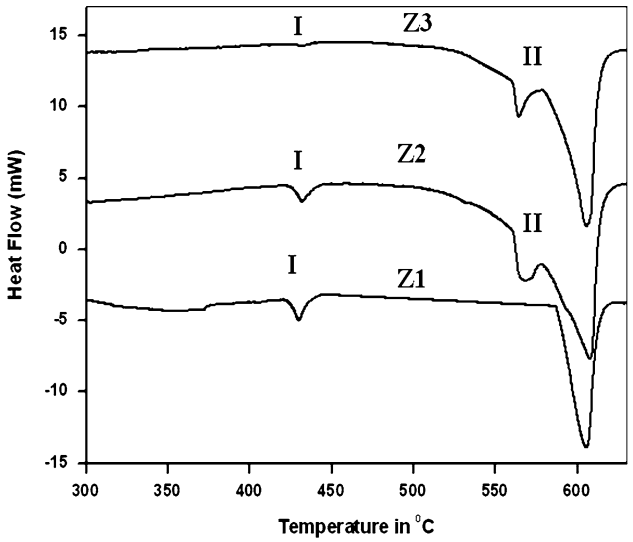


Fig. 4 DTA thermograms of Z1, Z2 and Z3 alloys

terized by variation in the enthalpies of $Mg_{17}Al_{12}$ phase dissolution in DTA, and the results are in agreement with the microstructural observations.

Table 2 Characteristics values emerging from the DTA curves

Alloy	I—$Mg_{17}Al_{12}$ dissolution			II—$Al_{11}La_3$ dissolution		
	Peak temp. in °C	Onset temp. in °C	Enthalpy mW/mg	Peak temp. in °C	Onset temp. in °C	Enthalpy mW/mg
Z1	429.19	421.5	3.9901	–	–	–
Z2	432.11	425.78	2.8712	564.89	560.84	9.6384
Z3	432.08	426.02	0.6348	565.87	561.07	12.2694

Acknowledgements The authors thank the CSIR and DST—New Delhi, Govt. of India for their financial support. The authors wish to acknowledge the help received from Dr. P. Prabakar Rao for SEM and Mr. P. Guruswamy for XRD analyses.

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