Electron microscopic studies on the effect of Sn addition on the ageing characteristics of Al-0.7% Mg₂Si alloy

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Abstract. The effect of trace addition of Sn on the ageing characteristics of Al-0.7% Mg₂Si has been studied by hardness measurements and transmission electron microscopy. The changes observed in the microstructural features have been explained on the basis of the strong interaction existing between Sn atoms and quenched-in vacancies. At ageing temperatures below 200°C Sn addition brings about a retardation in the kinetics of G.P. zone growth whereas at higher ageing temperatures, it aided the precipitate nucleation and growth. The hardness data agree well with the deductions based on observations made on the thin foils.

Keywords. Ageing characteristics; trace addition; hardness; transmission electron microscopy.

1. Introduction

Precipitation process in a quenched and aged alloy may be significantly altered by trace elements. Trace additions can have two distinct effects on precipitation. Firstly, their presence can alter the kinetics of zone formation (Kimura and Hasiguti 1961) and secondly, they can assist the nucleation of an intermediate precipitate (Sen and West 1969). Transmission electron microscopy (TEM) has emerged as a convenient and reliable method to study the structural changes during precipitation from super-saturated solid solution. The ageing characteristics of Al-Mg-Si system, which forms a pseudo-binary at Mg:Si ratio of 1.73 have been studied by many investigators using electron microscope (Thomas 1962, 63; Jacobs 1972; Pashley *et al* 1967; Smith 1973). Although data on the effect of trace addition are available, studies with trace atoms having strong interaction with vacancies are limited (Muromachi 1971; Gouthama and Kishore 1981). For the present investigation Sn having a high binding energy with vacancies has been chosen and its influence on the ageing characteristics of Al-0.7% Mg₂Si studied. The experimental techniques employed for this purpose include hardness measurement and TEM.

2. Experimental procedure

The alloy of the required composition was melted in an inert atmosphere using 99.992% pure Al, 99.98% pure Mg and semi-conductor grade Si. The purity of Sn was quoted to be 99.94%. The Sn-bearing alloy is hereafter referred to as alloy B while that without Sn is called alloy A. The composition of the alloys is given in table 1.

The specimens for microscopic and hardness studies were made by cold-rolling the ingot with intermediate annealing carried out at 400°C. For microscopic study, samples measuring 1.5 x 1.5 cm were cut from the flat-rolled sheet of thickness of 0.01 cm and solution-treated for 1.5 hr at 560°C and then quenched in ice-water bath maintained at 2°C. Different ageing treatments were given by introducing the quenched samples into paraffin oil bath, whose temperature was maintained within $\pm 1^\circ\text{C}$ of the required value.

Thin foils for TEM were electrochemically thinned by the standard window technique using a mixture of ethanol, perchloric acid and glycerol in the ratio 7:2:2 maintained at 0°C. Circular aluminium cathode and an operating voltage of 25V were used. The thinned foils were examined in an electron microscope (Phillips EM301) operated at 100kV. The hardness was tested on specimens measuring 1.5 x 1.5 x 0.2 cm. Solutionising of such samples for 2 hrs. Quenching and ageing procedures were similar to the one adopted for TEM work. Hardness was measured using the Vickers hardness tester with 2.5 kg load. At least six hardness readings were taken at random positions at regular intervals of time. The average of such readings was used in hardness vs time plots.

3. Results and observations

The variation of hardness with time, for ageing at various temperatures, is shown in figures 1 and 2 for alloys A and B, respectively. The relevant data obtained from such curves are presented in table 2.

Table 1. Composition (weight percent) of the alloys

Alloy designation	Magnesium	Silicon	Tin
Alloy A (Base Alloy) Al-0.70 Mg ₂ Si	0.46	0.26	-
Alloy B Al-0.70 Mg ₂ Si- 0.018 Sn	0.45	0.26	0.018

Table 2. Time-to-peak and peak hardness values for the two alloys aged at different temperatures.

Ageing temperature (°C)	Time-to-peak (hr)		Peak hardness (VHN)	
	Alloy A	Alloy B	Alloy A	Alloy B
140	165	180	78	76
180	14	17	71	72
220	4	1.6	56	67
260	0.4	0.25	53.5	59

Figure 1. Hardness variation with time at different temperatures for alloy A quenched from 560°C.

Figure 2. Hardness variation for alloy B at various ageing temperatures ($T_q = 560^\circ\text{C}$).

The following observations emerge from these data :

- As the ageing temperature increases the time-to-peak and the peak-hardness decrease for both alloys.
- The Sn-bearing alloy, when compared to the base alloy, shows the peak occurring at longer times for ageing experiments carried out below 180°C. On the other hand, for the same alloy B, peak value was recorded earlier when aged above 220°C.

- (c) In the case of ageing at 140 and 180°C, the peak hardness is almost the same for both the alloys.
- (d) For ageing above 220°C, alloy B shows higher peak hardness.

In electron microscopy, the influence of Sn addition on the size and distribution of the different precipitates occurring at various stages of decomposition of the super-saturated solid solution is investigated qualitatively.

Figure 3. Electron micrograph of specimens aged at 160°C for 24 hrs after quenching from 560°C. (a) alloy A, (b) alloy B.

Figure 4. Microstructure obtained after ageing for 5 hr at 200°C (a) alloy without Sn (b) alloy with Sn.

Figures 3a and 3b show the microstructure obtained with alloys A and B respectively, after ageing the quenched samples at 160°C. For alloy A, needles can be seen (figure 3a) while very few such features are apparent in alloy B (figure 3b). Ageing for a few hrs at 200°C produces copious amount of needle-shaped zones in both the alloys (figures 4a, b). The needles which are steeply inclined exhibit excellent dotted contrast. The

Figure 5. Transmission electron micrograph of specimens aged for 3 hr at 220°C. (a) Sn-free alloy (b) Sn-containing alloy.

needles are found to increase in length for ageing at 220°C while the diameter seems to be slightly larger (figures 5a, b).

On further increasing the ageing temperature, the needles transform into rods (intermediate precipitates) by an increase in both length and diameter. This is clearly evident from micrographs obtained with specimens aged at 250°C for 7 hr (figures 6a, b). Comparing figure 6a with 6b shows that the precipitates in the Sn-bearing alloy are thicker and longer.

The equilibrium precipitate appears when ageing was carried out around 300°C. The Mg_2Si platelets were larger in size and smaller in number in the base alloy

Figure 6. Photomicrograph obtained after ageing at 250°C for 7 hr (a) base alloy (b) Sn-containing alloy.

(figure 7a) as compared to the Sn containing alloy (figure 7c). The selected area diffraction pattern of precipitate seen on figure 7a is shown in figure 7b.

4. Discussion

The microstructural changes introduced due to Sn can be explained on the basis of the high binding energy between the quenched-in vacancies and Sn atoms.

Figure 7. Micrograph showing the Mg₂Si equilibrium precipitates obtained when ageing was carried out for 5.5 hr at 320°C (a) base alloy (b) SAD with precipitate spot of 7a. (c) Sn bearing alloy.

The zones in Al-Mg-Si system are coherent with the matrix along their length (Thomas 1962, 63; Jacobs 1972). The failure to observe the needles clearly on the micrograph for alloy B aged at 160°C (figure 3b) can be attributed to the retarded growth of the zones. This retardation in zone growth results from the Sn-vacancy pair formation which reduces the concentration of free vacancies available for solute atom transport from the matrix to the clusters. Thomas (1962, 63) considers the elastic strain involved in the formation of GP zones in this system to be very small and hence the zones could be resolved only when they are somewhat well grown. Figures 4a and 4b show well-grown needles along the three cube axes.

The needle-shaped zones gradually transform to semicoherent rod-shaped intermediate precipitates. Specimens aged at 250°C showed thicker and longer rods for alloy B (figure 6b) than those obtained for alloy A (figure 6a). This could imply that Sn atoms, when present, favour the intermediate precipitate growth. The equilibrium Mg₂Si precipitates appear for ageing around 300°C. At high ageing temperatures the growth of precipitate that have reached critical size would be rapid as the thermal vacancies can help in solute atom transport. The micrograph for a specimen of alloy A aged for 5½ hrs at 320°C reveals a few large plate-shaped precipitates (figure 7a). On the other hand, for a similar treatment in Sn-bearing alloy a large number of such precipitates which are smaller in size resulted (figure 7b). This clearly highlights the role of Sn in aiding the nucleation of precipitates at high temperatures.

The image of a small defect critically depends upon its position and distance from the foil surface as measured in extinction distances of the operating reflection (Ashby and Brown 1963). The dotted appearance of precipitates on a few micrographs is due to the contrast reversals (Bell *et al* 1966) which occur when the needle-shaped precipitate is inclined to the foil surface (figures 4a, b, 5a).

The delay in the occurrence of the peak hardness below 180°C can be attributed to the effect of Sn in slowing down the kinetics of precipitation. The early peak observed when ageing was done at temperatures above 220°C for alloy B could be ascribed to the enhancement of the kinetics due to vacancies released by tin atoms as stated earlier. Observation (d) could be interpreted as an indication of Sn helping the nucleation and growth of precipitates at higher temperatures.

5. Conclusions

The following conclusions can be arrived at from the foregoing investigations :
(i) The strong interaction existing between tin atoms and vacancies results in the retardation of GP zone growth. (ii) The intermediate precipitate formation and growth is more in Sn-bearing alloy. The release of vacancies by Sn atoms helps in the growth of precipitates. (iii) Sn atoms present in trace amounts aid the nucleation of precipitates at high temperatures. (iv) Sn-bearing alloy exhibits a dual nature as far as time to peak hardness is concerned, viz, ageing $\leq 180^\circ\text{C}$ peak occurs earlier in Alloy A and later in B, while the trend gets reversed for higher ageing temperatures.

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