Hardness and Electrical Resistivity Changes during Ageing of Rapidly Solidified Al-12.5Si-1Mg Alloy

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Ribbons with the composition Al-12.5Si-1Mg were prepared by melt spinning. X-ray diffraction of as melt spun ribbons showed complete solubility of Si in aluminum. The as melt spun resistivity was $36 \mu\Omega \text{ cm}$ for ribbons of $24 \mu\text{m}$ thickness. This value relaxes to $9.0 \mu\Omega \text{ cm}$ on prolonged annealing. The hardness of the as melt spun ribbons was 1500 MN/m^2 , and relaxes to reach a value of 800 MN/m^2 after prolonged annealing. The activation energy estimated from isothermal ageing ranged from 1.05 to 1.26 eV. An equation is given to fit the kinetics of relaxation. Discussion of resistivity and hardness relaxation is given and is related to ordering and silicon precipitation.

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I. Introduction

Cast aluminum alloys of the type Al α and gamma (Al, 10–13Si, 0.6Mg) have widespread applications, especially for gear cases, instrument housings, and engine components. Increasing demands on various material properties and corrosion resistance have pointed to the need for the consideration of the casting method and the subsequent heat treatment.

One of the important parameters in determining the properties of these alloys is the rate of solidification. In general, increasing solidification rate results in large extensions of solid solubility⁽¹⁾, finer microstructure and improved mechanical properties⁽²⁾⁽³⁾. Studies on rapid solidification of some binary Al-Si alloys have been reported^{(4)–(7)}. Rapidly solidified Al-12.4Si-2.8Mg powder was studied by Todeschini *et al.*⁽⁸⁾

In the present work, long uniform ribbons of Al-12.5Si-1Mg which is very close in chemical composition to Al α alloys were prepared by melt spinning. The effect of rapid solidification on the physical and mechanical properties of alloys is studied. The structure of the ribbons was studied by X-ray diffraction. Resistivity relaxation was followed by *in-situ* isothermal resistivity changes in the range of 140–229°C. Microhardness relaxation was also followed at 200°C.

II. Experimental

Long uniform ribbons of nominal composition Al-12.5 mass%Si-1 mass%Mg were prepared by melt spinning⁽⁹⁾. A stream of the molten alloy at 750°C was ejected by argon gas at gauge pressure $1.5 \times 10^5 \text{ Pa}$., from a silica tube having an orifice diameter of 0.35 mm onto a copper

wheel of 15 cm diameter rotating at 2950 r.p.m. The cooling rate estimated was about 10^5 °C/s . This produced uniform ribbons with thickness $24 \mu\text{m}$.

In-situ resistivity measurements were performed using a specially constructed controlled atmosphere annealing system⁽¹⁰⁾ under argon gas. The electrical resistivity was measured using a Kelvin double bridge having an accuracy of ± 0.05 with reproducibility better than 1%. Because the prepared ribbons were very thin, and retain slight curvature after quenching, a special specimen glass holder⁽¹⁰⁾ was constructed, and fixed inside the chamber of the controlled atmosphere annealing system.

X-ray diffraction study was performed with 1390 Philips X-ray diffraction apparatus using $\text{CoK}\alpha$ radiation ($\lambda = 0.17902 \text{ nm}$). The X-ray specimens were formed from a number of ribbons stuck parallel and closed to each other on a glass slide using vaseline.

Hardness was measured at room temperature using the Vicker hardness Leitz Wetzlar Germany Instrument with loads ranging from 25 to 100 g.

III. Results and Discussion

1. Microstructure

Scanning electron micrographs of the polished samples are shown in Fig. 1. The as-melt spun wheel side resists the polishing with only minor cracking of the lift off area (darker part). On annealing the sample becomes homogenized, giving rise to the polished regions ranging from 20 to $40 \mu\text{m}$. These regions are subdivided into smaller structures $2 \mu\text{m}$ in size. The large regions are separated from each other probably by an eutectic mixture.

Fig. 1 Scanning electron micrograph of the wheel side (a) as melt spun (b) annealed for 30 h at 250°C.

2. X-ray diffraction

X-ray diffraction patterns for various parts of the melt spun ribbons were obtained using filtered $\text{CoK}\alpha$ radiation ($\lambda = 0.17902 \text{ nm}$). A sample of the diffraction patterns for the as melt spun, intermediately annealed ($R(t)/R(0)$ equals 0.4), and annealed at 250°C for 30 h are presented in Fig. 2. The line intensities obtained from the X-ray diffraction patterns are presented in Table 1. The intensities were obtained both by the peak intensity times the full width at half maximum and by and planimeter methods. The difference between the two results is 10% at most on the average.

The as-melt spun diffraction pattern is shown in Fig. 2(a). Only the aluminum lines are present. This means that the solidification rate was high enough to retain most of the alloying elements in solid solutions in the aluminum matrix. This 12.5 mass%Si in solution is very high compared with the normal equilibrium solid solubility at room temperature which does not exceed 0.01%⁽¹¹⁾.

The diffraction pattern for a ribbon annealed for 114 min at 194°C, which corresponds to resistivity relaxation $R(t)/R(0) = 0.4$ is shown in Fig. 2(b). The appearance of the Si lines can be observed. Figure 2(c) represents the diffraction pattern for a ribbons annealed for 30 h at 250°C. Almost complete precipitation of Si is effected. No line corresponding to Mg_2Si reflections⁽¹²⁾ was observed. This can be attributed to the small amount of Mg (1 mass%), and the possibility that the Mg_2Si lines will be

Fig. 2 X-ray diffraction patterns for Al-12.5Si-1Mg, 24 μm thick melt spun ribbons. (a) as prepared, (b) aged up to $R(t)/R(0) = 0.4$, 114 min at 194°C. (c) aged up to $R(t)/R(0) = 0.25$, 30 h at 250°C.

Table 1 Intensities of X-ray lines from melt spun Al-12.5Si-1Mg ribbons.

$d(\text{nm})$	Assignment hkl	Relative intensities			
		Reported	Observed		
			As prepared	Annealed* $R(t)/R(0)$ =0.4	Annealed 30 h at 250°C
Al lines					
0.2338	(111)	100	100	100	100
0.2024	(200)	47	63	65	71
0.1431	(220)	22	15	21	23
0.1221	(311)	24	**	23	28
Si lines					
0.3135	(111)	100	0	100	100
0.19201	(220)	55	0	50	62
0.16374	(311)	30	0	***	41
Si(111)/Al(111)		—	0	8	19

Filtered $\text{CoK}\alpha$, radiation.

*114 min at 194°C. **Not recorded in the chart. ***Very weak.

lost in the back ground.

Only 40% of the total Si (as estimated from the ratio of intensities of the Si(111)/Al(111) lines) are precipitated after intermediate annealing corresponding to resistivity relaxation ($R(t)/R(0)$ of 0.4). After the same intermediate annealing no Si precipitation was observed in melt spun Al-12.5Si-1Ni ribbons⁽¹³⁾, while 80% of the total Si precipitated in melt spun Al-16Si ribbons⁽¹⁴⁾. This suggests that Mg has a retardation effect on the Si precipitation from the Al matrix which is less than Ni. Compar-

ing the observed and calculated intensities of the two most intense lines of Al and Si⁽¹⁰⁾, an average amount of Si soluble in Al is estimated to be 16%. This is in fair agreement with the nominal composition value of 12.5 mass%. No shift in 2θ was detected in the X-ray diffraction patterns of the as melt spun ribbons, contrary to that observed in Al-16 mass%Si⁽¹⁴⁾. This may be partly due to the presence of Mg which produces a shift opposite in sign to that of Si.

In the present work, no meta stable phase was detected. Todeschini *et al.*⁽⁸⁾ prepared Al-12.4Si-2.8Mg powder by rapid solidification. They observed the presence of a metastable phase which disappears completely after ageing for 24 h at 250°C. The presence of the metastable phase could not be due to a higher cooling rate in Ref. (8) than in the present work. The contrary is true, since X-ray diffraction patterns of their as melt spun Al-12Si and Al-12.4Si-2.8Mg rapidly solidified powder showed the presence of Si lines, indicating that their cooling rate is lower than in the present work. For binary Al-Si alloys, Shingu *et al.*⁽¹⁵⁾ using splat cooling with cooling rate more than 10^7 °C/s, observed no metastable phase up to 12 mass%Si. On the other hand, Taran *et al.*⁽¹⁶⁾ observed a metastable phase in melt spun Al-14.72 mass%Si ribbons. They stored the ribbons at 77 K until X-ray analysis, which presumably preserved the metastable phase. It could be that Mg atoms act as a bonding atom to both Al and Si as Al-Mg-Si to initiate such a metastable phase. A similar explanation was given in the high concentrated Al-M-Si alloys which existed in the amorphous form⁽¹⁷⁾. The lack of the presence of a metastable phase in the present work may be due to the small amount of Mg (1 mass%) as compared with 2.8 mass% in Ref. (8).

3. Electrical resistivity

Resistance measurements indicate that resistivity of the as prepared ribbons depends on the ribbon thickness. It is higher for thinner ribbons. Ribbons used for resistivity measurements have thickness as low as 24 μm .

The measured resistivity of the as melt spun samples was $36.0 \times 10^{-8} \Omega \cdot \text{m}$. The variation of resistivity along the length of the ribbons does not exceed 2%. After prolonged annealing, the resistivity value decreases to $9 \times 10^{-8} \Omega \cdot \text{m}$.

As for the bulk resistivity, it was measured for the as-cast rods of 25 mm length and 4 mm diameter, from which the ribbons were prepared. The measured resistivity was $5.3 \times 10^{-8} \Omega \cdot \text{m}$. Ageing the rod at 250°C for 30 h, resulted in a resistivity decrease of at most 8%.

Isothermal resistivity changes were studied in the temperature range from 140 to 229°C. Figure 3 shows the variation of the resistance with time at different temperatures. From these curves, it is clear that aging the as-melt spun ribbons at 229°C which is the highest annealing temperature, reduces the resistance ratio $R(t)/R(0)$ to 0.8 of its initial value after 2 min. It was not possible to follow the resistance relaxation above 229°C. At the lower annealing temperatures, there exists an incubation time (t_{inc}) before which no resistance change could be

Fig. 3 The variation of relative resistance $R(t)/R(0)$ versus ageing time at different temperatures for melt spun Al-12.5Si-1Mg ribbon.

detected.

At the lowest annealing temperature of 140°C, t_{inc} is equal to 22 min, after which the resistance decreases very slowly to reach $R(t)/R(0)$ of 0.8 of its as melt spun value after 190 min.

To determine the activation energy for the relaxation process, Arrhenius plots showing the logarithm of the time needed to reach different values of $R(t)/R(0)$ versus the reciprocal of the absolute ageing temperature are made. The results are shown in Fig. 4. From the slopes of these lines, activation energies 1.05, 1.09, 1.15 and 1.26 eV[†] corresponding to $R(t)/R(0)$ of 0.9, 0.8, 0.7 and 0.6 respectively are obtained.

As for the kinetics, under isothermal conditions, the following equation has been proposed to best fit the data

$$X(t') = 1 - 1/(1 + (t'/\tau)^n) \quad (1)$$

where $X(t')$ is the fraction transformed at time $t' = (t - t_{\text{inc}})$, since the start of the transformation is given by:

$$X(t') = [R(t') - R(0)]/[R(\infty) - R(0)] \quad (2)$$

where $R(t')$ is the resistance at ageing time (t') and $R(\infty)$ is the equilibrium resistance after prolonged ageing, (n) is the order of the reaction, (τ) is a constant to be independent of time, but depends on the temperature. Equation

[†] 1 eV = 1.602×10^{-19} J.

Fig. 4 Determination of activation energy from isothermal measurements for Al-12.5Si-1Mg ribbons.

(1) gave better fit than an equation of the Johnson-Mehl-Avrami (JMA)⁽¹⁸⁾ form used in such previous publication as by Bastawros *et al.*⁽¹⁹⁾ This is because the evolution of eq. (1) with time is slower than the exponential (JMA) form. This allows better matching of fast and slow stages. To obtain the values of both (n) and (τ) using eq. (1), $\ln [X/(1-X)]$ is plotted versus $\ln (t-t_{\text{inc}})$. Straight line best fits are shown in Fig. 5. The general characteristics of the curves is that the relaxation proceeds in two stages, a fast stage followed by a slower one. The extracted values of (n) and (τ) for the two stages are given in Table 2. From this table, it is clear that the incubation time is almost zero at the higher annealing temperature, while its value is measurable at the low annealing temperatures. Incubation time is 1 min at ageing temperature of 210°C and increases to 22 min by decreasing the ageing temperature to 140°C. As regards the value of n , it decreases from $n_1=0.86\pm0.1$ in the first stage to $n_2=0.41\pm0.07$ in the second stage if the average is taken over the range of temperature from 140 to 229°C. The ratio (n_2/n_1) decreases from 0.6 at 140°C to 0.3 at 229°C. The value (n_2/n_1) describes the ratio of the rate of relaxation between the two stages.

With respect to the value of τ , which stands for the relaxation time for each stage, it gives in conjunction with n a measure of the rate of relaxation. The value of τ decreases as the temperature increases from 140 to 229°C by about two and three orders of magnitude for the first and the second stages respectively.

The extra resistivity of the as melt spun ribbons can be attributed partly to the high state of disorder caused by the supersaturation of free and bound vacancies resulting from rapid solidification. Additional contribution comes from the presence of Si and Mg in solid solution (12 mass%Si and 1 mass%Mg) as deduced from the X-ray diffraction analysis. The resistivity increment per 1 at%Si

Fig. 5 Ageing kinetics of melt spun Al-12.5Si-1Mg.

Table 2 Relaxation parameters extracted from isothermal ageing data.

$T/^{\circ}\text{C}$	Stage 1		Stage 2		t_{inc}
	n_1	τ_1	n_2	τ_2	
140	0.836	551.0	0.521	942.6	22.0
155	0.808	155.5	0.464	192.0	8.5
174	0.751	53.30	0.424	31.00	7.0
194	0.823	9.400	0.309	1.260	3.0
210	0.881	4.820	0.364	0.947	1.0
229	1.070	2.086	0.365	0.209	0.5

in solid solution has not been determined, but if it is assumed to be at least equal to that of vacancies, then an appreciable fraction of the observed as quenched resistivity can be accounted for.

Resistivity relaxation is characterised by the existence of an incubation time. This incubation time is temperature dependent, it decreases from 22 to 1 min as the ageing temperature increases from 140 to 210°C.

The incubation time may be related to the period preceding Si precipitation in which vacancy clusters are found, as observed by Ozawa and Kimura⁽²⁰⁾. They studied Si precipitation from dilute Al-Si alloy using electron microscopy. They explained the precipitation as starting with the formation of vacancy clusters which act as centers for nucleation of Si precipitates on thermal ageing.

From Fig. 5, it is clear that resistivity relaxes in two stages after the incubation time. A fast stage followed by

Fig. 6 Variation of hardness with time at 200°C.

a slower one. Si precipitation is accelerated in the early stage of annealing by moving vacancies which undergo a large number of jumps before annihilation to sinks, whose number is small at the beginning. On prolonged ageing, the number of sinks increases, so the number of vacancy jumps before annihilation decreases, thus slowing down the rate of the reaction.

The average activation energy estimated ranged from 1.05 to 1.26 eV which is close to the reported value for the energy of diffusion of Si in aluminium⁽¹¹⁾. An activation energy of 1.14 eV was obtained by isothermal annealing of Al-12.5Si melt spun ribbons⁽⁷⁾ with a thickness of 20 μm . Bendijk *et al.*⁽⁵⁾ obtained a value of 0.93 eV from Al-10.5Si ribbons of irregular thicknesses. Chevrier *et al.*⁽²¹⁾ determined an activation energy of 1 eV for 30 μm thickness Al-20Si melt spun. If we note that the vacancy formation energy in pure Al is 0.76 eV⁽²²⁾ then these activation energy values suggest that only equilibrium vacancies are acting, and both precipitation of Si and ordering take place by means of these vacancies.

4. Hardness

The as melt spun hardness is 1500 MN/m², this value decreases by thermal ageing to reach 800 MN/m². The hardness relaxation was followed at 200°C as shown in Fig. 6. The hardness decreases with ageing time in two stages. An initial fast stage which lasts for about 120 min, results in a decrease in hardness $H(t)/H(0)$ to about 0.8. The second stage which involved ageing time of more than 30 h resulted in a slight decrease over that of the first stage attaining a value of $H(t)/H(0)$ equals 0.5. It was observed that the hardness relaxation during isothermal ageing is much slower than that of the resistivity relaxation. The explanation is that hardness is closely related to size of precipitates. Also, the electrical resistivity is sensitive to point defects which are usually the first properties to recover. On the other hand, the hardness depends more on line imperfections which may require higher temperatures for recovery.

The as-cast rods with the same composition as the ribbons give the hardness value of 670 MN/m². Aging the rod for 30 h at 250°C results in a decrease in hardness by

10% at most. The as melt spun ribbons have hardness value which is much higher than the as-cast rods by a factor of 2.2. So, rapid solidification has a significant effect on increasing the hardness. The high hardness of the as melt spun state can be attributed to the effect of the solute atoms upon the solvent lattice, and the nature of the lattice forces operative, owing to the interaction of different atomic species. Also, the bonding of Mg with Al and Si is stronger than Al-Si bonding⁽¹⁷⁾.

The decrease in hardness on thermal ageing is due to the precipitation of solutes. The hardness attains its limiting low value when the precipitates grow until the solute concentration attains its equilibrium final value on prolonged annealing. Further more, internal stress may arise due to the difference in thermal expansion between the Si precipitates and the Al solvent. These internal stresses when added to the compressive stress of the hardness indenter will assist plastic flow and hence contribute to the decrease in hardness.

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