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Al–12.5 wt % Si ribbons prepared by melt spinning

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Aluminium–silicon alloy with composition 12.5 wt % Si was rapidly quenched from the melt at a cooling rate of about 10^6 K s^{-1} using the melt-spinning technique. The resulting ribbons were investigated by resistivity measurements and X-ray diffraction. The resistivity of the 20 μm thick ribbons was 26.6 μΩ cm. This is 4.4 times its bulk resistivity value. The activation energy calculated from isothermal ageing was 1.14 ± 0.1 eV. The limit of primary solid solubility is extended almost to the eutectic composition and the large supersaturation is relieved by thermal annealing.

1. Introduction

Since the splat-quenching experiments of Duwez *et al.* [1] there has been considerable interest in the formation of metastable phases through rapid solidification. From studies on rapid solidification of some Al–metal alloys, supersaturated solid solutions, metastable crystalline phases and even amorphous phases have been reported [2–6]. Rapidly solidified Al–Si alloys of various compositions and thickness have been prepared by splat cooling [7–9] and by melt spinning [9–12].

These studies centred mainly on the variation of lattice parameter with the amount of silicon assumed to be present in solid solution. Some microstructure studies were also made.

In the present work, long uniform ribbons of Al–Si eutectic alloy were prepared by melt spinning. The structure of the as-quenched and annealed ribbons was studied by X-ray diffraction. Also, isothermal resistivity measurements at ageing temperatures from 100 to 187 °C have been made.

2. Experimental procedure

Aluminium–silicon alloys with composition 12.5 wt % Si were prepared from 99.999 wt % pure Al and 99.99 wt % Si, and the alloy was cast into a copper mould to obtain rods 2.5 cm long and 0.4 cm in diameter. Specimens in the form of ribbons were prepared by a melt-spinning apparatus [13]. In this technique a stream of the molten alloy with a temperature of 750 °C was ejected by pressurized argon from a 0.35 mm diameter orifice on to a copper wheel rotating at 2950 r.p.m. Continuous uniform ribbons of thickness 20 μm were obtained. A cooling rate of about 10^6 K s^{-1} was estimated from the time of stay of the ribbon on the wheel.

Resistance changes at room temperature were followed by using a double Thomson bridge. The accuracy was 0.05% with reproducibility better than 1%. Annealing was done by placing the foils in a low heat-capacity Al container in the furnace for the specified time and then quenching in alcohol before the measurement. Each data point corresponds to an average of measurements on five specimens. X-ray examination of the ribbons was conducted using filtered CoK_α radiation. Short lengths of the ribbon to be X-rayed were stuck on a glass slide parallel and close to each other using Vaseline.

3. Results

3.1. Electrical resistivity

The resistivity depended on the thickness of the ribbons produced. Ribbons having smaller thickness had higher resistivity values. Ageing of melt-spun ribbons at any temperature resulted in a decrease in the electrical resistivity. The decrease occurred for all thicknesses. The rate of decrease of the electrical resistance ratio $R(t)/R(O)$ with ageing time for Al–12.5 wt % Si varied with ribbon thickness, being smaller for thicker ribbons.

Detailed ageing studies were done on ribbons with the least thickness obtained which possess the highest cooling rate. The state of these ribbons is expected to differ appreciably from the equilibrium state. So, ageing was done on the 20 μm thick ribbons.

The variation of electrical resistance ratio $R(t)/R(O)$ with ageing time at ageing temperatures of 95, 128, 142, 154, 162, 173 and 187 °C for melt-spun Al–12.5 wt % Si, 20 μm thick ribbons is shown in Fig. 1. A rapid decrease in $R(t)/R(O)$ is followed by a slower one for ageing temperature above 128 °C. At a lower temperature such as 128 °C, the decrease is slow all

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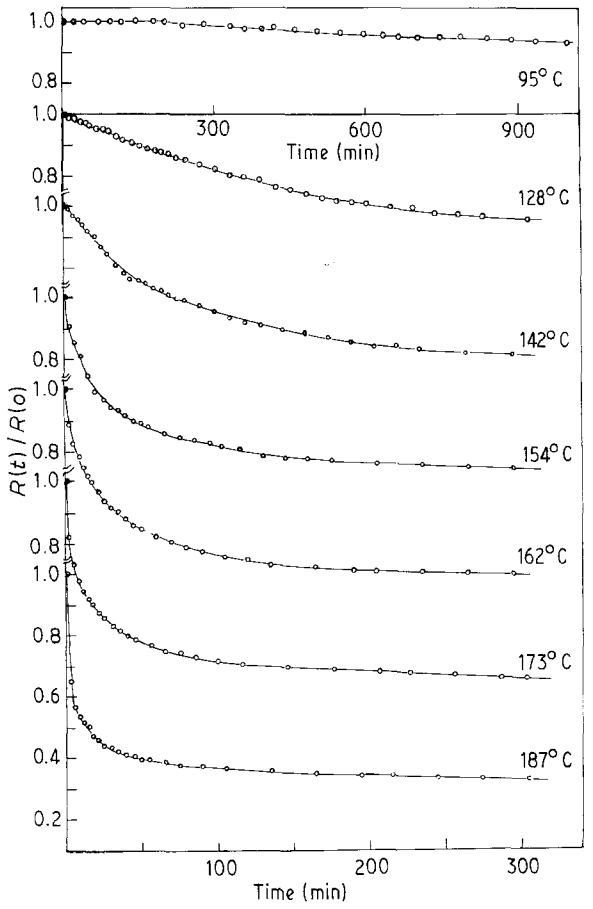

Figure 1 Variation of relative resistance $R(t)/R(O)$ with ageing time at different ageing temperatures for melt-spun Al–12.5 wt % Si, 20 μm thick ribbons.

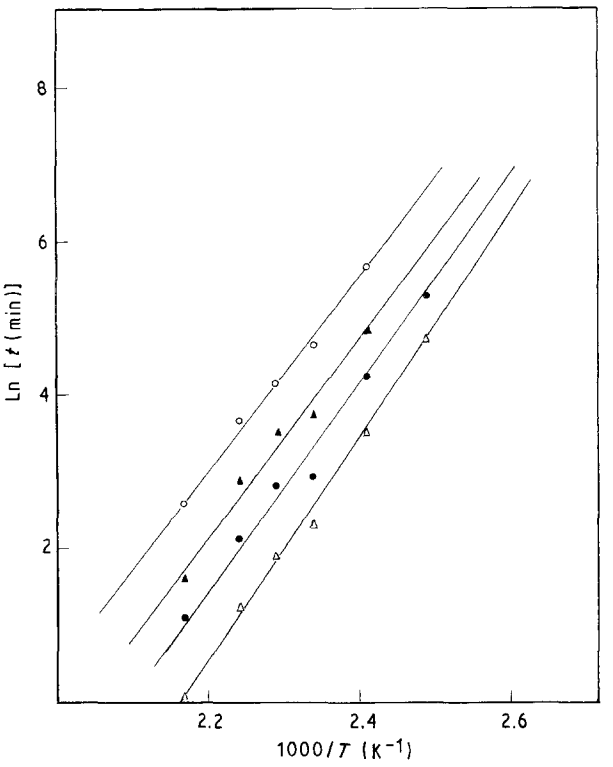

Figure 2 Determination of activation energy by plotting times to reach several values of $R(t)/R(O)$ versus the reciprocal of ageing temperature T for melt-spun Al–12.5 wt % Si, 20 μm thick ribbons: $R(t)/R(O)$ = (○) 0.5, (▲) 0.6, (●) 0.7, (△) 0.8.

over the curve as shown in Fig. 1. For ageing temperatures lower than 128 °C, the resistivity remains unchanged for a certain period of time. A representative plot at 95 °C is shown in Fig. 1 indicating an incubation period of 3 h. This incubation period increases with decreasing ageing temperature.

The measured resistivity of as-cast rods having 0.4 cm diameter and 2.5 cm length, and having the same composition as the ribbons, was 6.1 μΩ cm compared with 26.6 μΩ cm for the 20 μm thick as-spun ribbon.

3.1.1. Activation energy

From the isothermal annealing data (Fig. 1) the activation energy E was calculated. The time t taken to reach a given value of a property P is given by

$$\ln t = \frac{E}{kT} + \text{constant}$$

where k is the Boltzmann constant and T the absolute temperature.

A plot of the logarithm of the time to reach different values of $R(t)/R(O) = 0.8$, 0.7, 0.6 and 0.5 versus the reciprocal of the ageing temperatures is shown in Fig. 2. From the slope of the curves activation energies of 1.24, 1.11, 1.1 and 1.1 eV were obtained, corresponding to value of $R(t)/R(O)$ of 0.8, 0.7, 0.6 and 0.5, respectively, with an average of 1.14 ± 0.1 eV.

3.2. X-ray diffraction

The X-ray diffraction patterns of the as-quenched Al–12.5 wt % Si ribbons (20 μm thick) for 2θ from 20 to 80 ° show the first three reflections from Al, but no Si lines were observed.

However, the X-ray diffraction pattern of ribbons annealed for 5 h at 200 °C show the presence of the first three Si lines which were absent in the as-prepared ribbons. Table I shows the intensities of observed reflections compared with the reported values [14].

From Table I it can be seen that in the as-quenched ribbons the relative intensities of Al lines do not conform with the published values, indicating some degree of preferred orientation. This can happen because, on quenching the melt, the direction of heat gradient and the way the ribbon separates from the melt affect the orientation of the Al crystals to a significant degree. The degree of preferred orientation decreases slightly after annealing. On the other hand, the relative intensities of the Si lines match the published values fairly well. This can be attributed to the fact that Si was present as a solid solution in Al in the as-quenched ribbons. When the ribbons are subjected to heat, it may be that Si starts precipitating randomly. So, the newly formed crystallites do not have any reason to show preferred orientation.

Although Si lines were absent in the as-prepaied ribbons, an estimate of about 2 wt % Si could be lost, without being observed, in the background in the X-ray diffraction pattern. So an amount of about 10 wt % Si present as solid solution is estimated.

TABLE I Intensities of X-ray lines from as-prepared and annealed Al–12.5 wt % Si ribbons compared with reported values [14]

d (nm)	Assignment (hkl)	Relative intensity		
		Reported [14]	Observed[a]	
			Quenched	Annealed
Al lines				
0.2338	(1 1 1)	100	100	100
0.2024	(2 0 0)	47	26	33
0.1431	(2 2 0)	22	9	10
Si lines				
0.3135	(1 1 1)	100	–	100
0.19201	(2 2 0)	55	–	53
0.16374	(3 1 1)	30	–	33

[a] Filtered CoK_α radiation.

From the X-ray diffraction patterns of as-quenched and annealed ribbons a shift of 0.05° was observed for the (2 2 0) Al line. This indicates a change of 0.00022 nm in the lattice constant of Al.

Calculations [15] based on the observed line intensities given in Table I give a value of 10 at % Si.

To determine the amount of Si retained in solid solution from the X-ray line shift Vegard's law can be used. However, there is a difficulty in using Vegard's law, namely the difference in crystal structure of the diamond Si and the f.c.c. Al. This difficulty was partly solved [16] by assigning an effective value of 0.3731 nm to the lattice parameter of an imaginary cubic Si. This implies a change in the lattice constant of Al by 3.18×10^{-4} nm per 1 at % Si in solid solution.

The observed shift gives a value of 0.63 at % as an estimate of the amount of Si in solid solution. This quantity is exceedingly low. It is inconsistent with the absence of all Si lines in the X-ray diffraction pattern of the as-quenched ribbons.

An alternative to determine the amount of Si present in solid solution from the X-ray line shift is to extrapolate Equation 1 of Bendijk *et al.* [12]. This relation gives the change in lattice parameter as 1.74×10^{-4} nm per 1 at % Si in solid solution. According to this relation an estimate of 1.3 at % Si in solid solution is obtained. This value is still too low.

The reason may be due to extrapolation of the relation to the high solubility values usually obtained in melt quenching, as compared to the very low solid solubilities (maximum 0.93%) used in obtaining this relation.

Finally, use is made of studies [7–12] of the variation of lattice parameter with the assumed amount of Si present in solid solution. Itagaki *et al.* [7] prepared Al–Si alloys by splat quenching with a cooling rate of 10^7–10^8 K s^{-1}. They obtained a lattice parameter shift of 1.16×10^{-4} nm per 1 at % Si. Shingu *et al.* [8], with a splat-cooling rate of 10^5–10^7 K s^{-1}, obtained a shift of 1.72×10^{-4} nm per 1 at % Si. The splat cooling result of Kobayashi *et al.* [8, 9] gives 1.77×10^{-4} nm per 1 at % Si at a cooling rate of 10^4–10^5 K s^{-1}.

The shifts obtained from melt-spun ribbons are much smaller than those obtained from splat-cooled foils. Bose and Kumar [11] prepared ribbons of thickness varying between 100 and 150 μm by melt spinning. Their results give a shift of 3.7×10^{-5} nm per at % Si. Bendijk *et al.* [12] prepared non-uniform ribbons ranging in thickness from 0.1 to 150 μm by melt spinning. They obtained a shift of 3×10^{-5} nm per 1 at % Si.

From the splat-cooling results of others [7–10], the amount of Si estimated to be in solid solution according to our measured shift is 1.9 [7], 1.3 [8] and 1.2 at % [9, 10]. However, the melt-spinning results give 5.9 and 7.3 at % Si according to Bose and Kumar [11] and Bendijk *et al.* [12], respectively. Although the melt-spinning results give a better estimation than that from splat cooling, the former estimation is still low.

4. Discussion

The high observed resistivity value of 26.6 μΩ cm for the 20 μm thick ribbon cannot be explained by the mere presence of excess vacancies occurring on rapid solidification during melt quenching. This is because the vacancy resistivity is known to be low (of the order of 1 μΩ cm per 1 at % vacancies). However, it is possible that this supersaturation of vacancies helps initiation of a state of disorder on rapid cooling. Another possible contribution is the presence of a high amount (~ 10 wt %) of Si in solid solution as deduced from X-ray diffraction analysis. The resistivity per wt % Si 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 quenched-in resistivity can be accounted for.

On thermal ageing the annealing-out of quenched-in vacancies provides the atomic mobility for the redistribution process. Si starts precipitating from the matrix, resulting in the formation of relaxed structures which give rise to lower resistivity values. The decrease in resistivity occurs in two stages. A fast stage is followed by a slower one. The acceleration of annealing in the first fast stage may be due to excess quenched-in vacancies. In the early stages of annealing, Si precipitation is accelerated by moving vacancies which have a large number of jumps before annihilation to sinks whose number is small at the start. On prolonged ageing the number of vacancy sinks increases and the number of vacancy jumps decreases, thus slowing down the reaction.

The activation energy has been determined by Itagaki *et al.* [7] and Cheverier *et al.* [17]. Itagaki *et al.* [7] made some kinetic measurements to establish the activation energy of silicon precipitation. Because of the irregular shape of the splat-cooled foils, they said that they excluded resistometric techniques. From the isothermal variation of lattice parameter of Al–11 at % Si, they obtained for the activation energy values ranging from 0.61 to 0.87 eV. Chevrier *et al.* [17] estimated an activation energy of 1.0 eV from a differential calorimeter scan of Al–20 at % Si prepared by melt spinning.

The average activation energy of 1.14 eV extracted from the present isothermal ageing curves is close to

the reported value of 1.3 eV for diffusion of Si in Al [18]. So, it is probable that single equilibrium vacancies are responsible for giving the Si or Al atoms the required mobility for redistribution. The lower value reported by Itagaki *et al.* [7] may be partly related to the expected difference in structure of rapidly quenched alloys prepared by different methods.

Before ending this part of the discussion, it is worth mentioning that under the same conditions of preparation, it was found by Bastawros *et al.* [19] that for Al–Cu with eutectic composition (33.3 wt % Cu), only 4 wt % Cu was retained in Al as a solid solution after melt quenching. The as-quenched Al–Cu ribbons had a resistivity of 16.6 μΩ cm. On ageing, the resistivity decreased to 9.3 μΩ cm with an activation energy of 0.5 eV.

Concerning the determination of the amount of Si present in solid solution for Al–Si alloys containing more than 1 at % Si from the X-ray line shift, misleading results may be obtained. This is due to the considerable discrepancies in the reported variation of the lattice parameter with the assumed amount of Si present in solid solution. Assuming that the data reported by the various authors are correct, then the discrepancies can be attributed to one or more of the following sources.

First, the various authors did not mention that they determined the amount of Si actually present in the alloy after rapid solidification. Instead, they assumed that it possessed the nominal composition.

Second, it is expected that the concentration of quenched-in excess vacancies increases with the increase in cooling rate. Furthermore, Kirin *et al.* [20] observed a decrease of lattice parameter with the increase in concentration of vacancies. These two statements may explain the larger decrease in lattice parameter with Si content for splat-cooled alloys as compared to their melt-spun counterparts.

Third, the rapidly solidified solid solution may have the nominal composition but this composition does not have a single value. This effect has been observed by Cahn *et al.* [21] in their study of splat-quenched Al–Cu alloys. Using a Guinier camera, they found from the line profile solid solutions of a range of compositions higher and lower than the nominal value. So, the centre of gravity of the line as reported from the diffractometer measurements will depend on the cooling rate. This may resolve the reported discrepancies.

5. Conclusion

1. For Al–Si with eutectic composition prepared by melt spinning, a cooling rate of about 10^6 K s^{-1} was enough for most of the Si to be retained as a solid solution in Al after melt quenching. The 20 μm thick ribbons had a high resistivity which decreased from a value of 26.6 μΩ cm for the as-quenched ribbons to a value of 8.1 μΩ cm after thermal ageing, approaching the bulk resistivity of 6.1 μΩ cm.

2. The presence of the high excess resistivity is attributed partly to disorder and to the presence of supersaturation of Si in solid solution caused by the high melt quenching rate. On thermal ageing, the quenched-in vacancies provide the atomic mobility for reordering and Si precipitation. The resulting structure possesses low resistivity.

3. Estimation of the amount of Si retained in solid solution from X-ray line shifts is not recommended since it might lead to inaccurate values. It is expected that calculations based on line intensities will give more realistic values.

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