Study of the Kinetics of Recrystallisation of Dispersion-Strengthened (Al/Al₂O₃) Alloys

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The kinetics of recrystallisation of an SAP alloy containing 5.25 wt % oxide has been studied, mainly by metallographic observations and transmission electron microscopy. At the beginning of the process the isothermal reaction follows the Avrami law $x = 1 - \exp(-Bt^k)$ with $k \simeq 1.7$. A deviation from the above kinetics takes place with increasing time; it is shown by metallographic observations and from the effect of preliminary recovery that this behaviour results from competition between recovery and recrystallisation. The competing process has an activation energy close to the value of 1.57 eV, previously determined for the stage of dislocation recovery preceding recrystallisation.

Results reported by other authors have been analysed, and it is noticed that competition is a general feature of recrystallisation in these alloys; this effect becomes more pronounced with increasing oxide concentration, and can ultimately stop recrystallisation. The analysis of the kinetics of recrystallisation indicates that the dispersed phase not only reduces the driving force for grain boundary migration, but also affects mobility by raising the activation energy of the process.

1. Introduction

Extensive work has been carried out in recent years on the recrystallisation of metals containing a finely dispersed, stable second phase. The main points in this field have recently been reviewed by Cahn [1]. These observations show that precipitates or mechanically dispersed particles can hinder the recrystallisation process [2, 3]; the influence of inter-particle spacing in determining this effect has also been studied [4-6]. However, the recovery process in these alloys has not been extensively investigated although its study is important for a better understanding of recrystallisation.

The aim of the present work is to derive more detailed knowledge about the kinetics of recrystallisation in aluminium/alumina alloys, on the basis of the information derived from the earlier recovery experiments [7-9].

The study of different Al/Al₂O₃ SAP alloys

has shown that increasing the oxide content (resulting in a reduction of the mean linear inter-particle spacing to ~0.15μm) shifts the recrystallisation stage to higher temperatures, while the temperatures of the two stages of dislocation recovery preceding recrystallisation increase only slightly [7, 8]. These recovery stages have been studied in detail. The first has been attributed to a disentanglement process of screw dislocations through a stress induced cross-slip mechanism; and the second, centred at about 300° C and characterised by an activation energy of 1.57 eV, to dislocation climb through a self-diffusion process. The formation at this stage of new grains bounded by high angle boundaries, does not occur by the migration of sub-boundaries, but through another mechanism, probably sub-grain rotation and coalescence [8].

It has been shown that the introduction of artificial nuclei does not alter the recrystallisa-

tion behaviour of the work-hardened alloys. The physical process inhibited by the second phase must thus be the migration of grain boundaries [9]. On the factors affecting this process in two-phase alloys, few reliable experimental results are available. A growth rate decreasing with time has been observed in SAP [2]. It is generally accepted that in primary recrystallisation the migration rate depends on the free energy difference between the two sides of the boundary [10]. Thus the continuous decrease in the growth rate could well result from the existence of a concurrent recovery process taking place during recrystallisation. This is a point to clarify.

Another important point to be elucidated is whether the particles hinder boundary migration only through a reduction of the driving force, or also through a decrease of the boundary mobility. The usual treatments are restricted to an analysis of the reduction of the driving force [11, 12].

2. Experimental

The research was carried out with an SAP alloy with an alumina content of 5.25 wt %, whose detailed recovery behaviour has been reported in an earlier work [7]. Among the alloys studied on that occasion we have chosen that with the highest oxide content, so as to highlight the influence of this parameter on the recrystallisation behaviour.

The specimens were in the form of rolled sheets 100 μm thick, corresponding to about 98.8% reduction. They were available from the stock of sheets, stored in liquid nitrogen, used for the recovery determinations; their preparation has been detailed in the earlier paper [7].

3. Techniques

Our determinations were carried out by quantitative optical microscopy, using the etching reagent reported in an earlier paper [9]. The recrystallised fraction was determined after isothermal treatments in a molten salt bath stabilised to $\pm 0.1°$ C. Before determination the samples were etched down to ~ 40 μm to avoid surface effects. Actually, it was observed that the original surface of the sheets recrystallises last, and that this effect vanishes when a depth of ~ 15 μm has been removed.

Measurement was effected by a statistical method based on heating individual samples for different periods of time; effects due to thermal cycling are thus avoided. Each treatment has

been carried out on several specimens, and each experimental point represents the mean arithmetical value of the recrystallised fraction on an area of ~ 50 cm^2.

For electron microscopy observations we have used the techniques of diffraction contrast already specified [7, 8]. Microhardness determinations were also carried out to follow recovery processes in the unrecrystallised portion of the matrix. As in our previous work we operated at constant load, using a Vickers microhardness apparatus mounted on a Reichert microscope [7].

4. Results

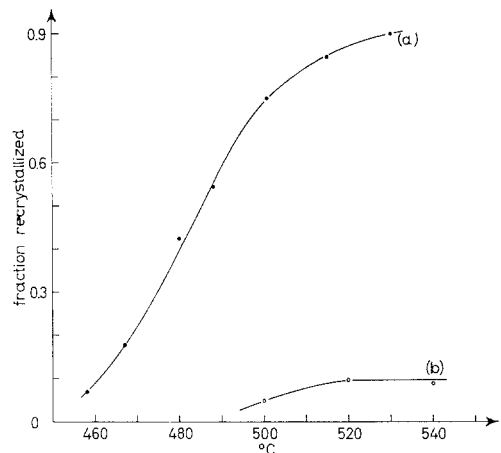The values of the recrystallised fraction after isochronal heating of 30 min are reported in fig. 1

Figure 1 Recrystallised fraction in SAP 5.25 wt. % oxide, deformed 98.8% by rolling, after isochronal heating of 30 min. (a) As-rolled specimens; (b) specimens heated in steps of 20° C, starting from 100° C.

[curve (a)]. Recrystallisation begins at $\sim 450°$ C. In fig. 2 we report the recrystallised fractions after isothermal treatments at 458.2, 467, 480, 488, and 497° C.

To verify whether the kinetics of recrystallisation follow the Avrami equation [13]

$$x = 1 - \exp\left[-Bt^k\right]$$

where x is the fraction recrystallised at time t, in fig. 3 we have replotted $\ln 1/(1 - x)$ versus $\log t$ for the isotherms at 458.2, 467, and 480° C. It is observed that Avrami's kinetics are in fact followed during the early stages of the process. The value of k is constant at ~ 1.7.
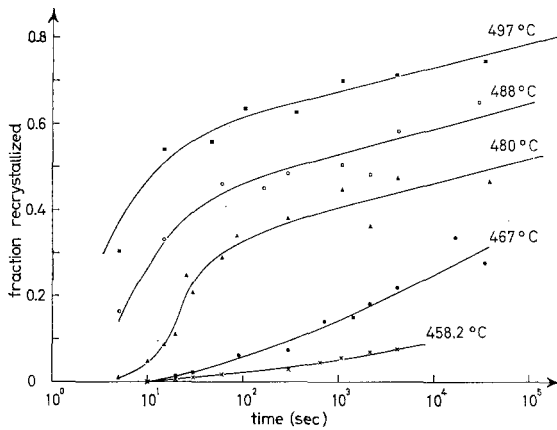
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Figure 2 Values of the recrystallised fraction, after isothermal heating, of SAP 5.25 wt % oxide, deformed 98.8% by rolling.
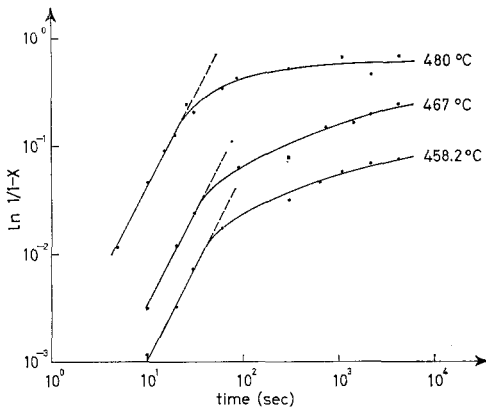

Figure 3 Plot of the values of the recrystallised fraction *x*, in fig. 2, in a log [ln 1/(1 − *x*)] versus log *t* scale.

A deviation from this law is observed with increasing values of *x*; the break occurs at lower values of the recrystallised fraction, for lower temperatures of isothermal treatment. This deviation may be attributed to a decrease in the driving force for grain boundary migration, owing to competing recovery processes taking place in the unrecrystallised portions of the matrix. Actually, if the recovery process is characterised by an activation energy lower than that for grain boundary migration, the deviation of the kinetics of recrystallisation from the Avrami equation should take place at lower recrystallised fractions, the lower the temperature of isothermal treatment [14].

To check this hypothesis we carried out electron microscope observations of the unrecrystallised regions at different times during the isothermal treatments: figs. 4 and 5 represent typical situations after 10 sec and 3600 sec respectively at 480° C. A process of disentanglement is evident at short times, leading to a reduction in the dislocation density. Only in some rare cases, associated with local concentrations of oxide particles, does the density of dislocations remain considerable, as is shown in fig. 6, even after prolonged heating. By way of comparison fig. 7 represents the structure after annealing 1800 sec at a lower temperature, 380° C. This treatment corresponds to the recovery of about 75 % of the extra resistivity in the stage preceding recrystallisation [7]. The situation observed is intermediate between those in figs. 4 and 5.

This recovery phenomenon has also been followed by microhardness determinations in the unrecrystallised portion of the matrix. In fig. 8, the hardness is plotted as a function of re-

Figures 4, 5 Structural features of the unrecrystallised portions of SAP 5.25 wt % oxide specimens, heated at 480° C. (4) After 10 sec heating; (5) after 3600 sec (×18000).
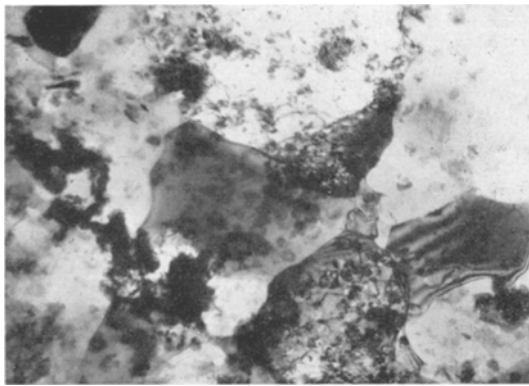
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Figure 6 SAP 5.25 wt. % oxide; region of high oxide concentration showing still high density of dislocations in the unrecrystallised matrix, after heating 3600 sec at 480° C (×18000).

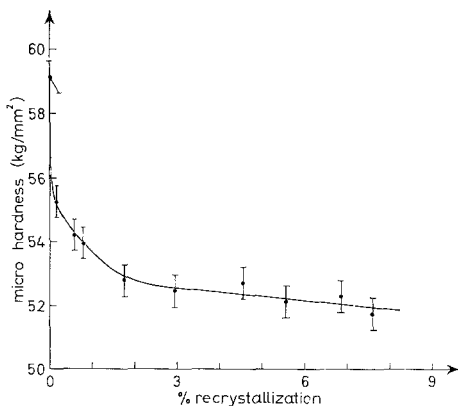Figure 7 Recovery structures in SAP 5.25 wt % oxide annealed 1800 sec at 380° C (×18000).

Figure 8 Hardness decrease in the unrecrystallised portion of the matrix of SAP 5.25 wt % oxide, during recrystallisation at 458.2° C.

crystallisation during the isothermal treatment at 458.2° C. This plot confirms that some recovery precedes metallographically detectable recrystallisation. To establish the effect of a prior recovery treatment on subsequent recrystallisation kinetics we submitted specimens to low-temperature annealing treatments, and subsequently studied their recrystallisation behaviour.

We report in fig. 9 the values of the recrystallised fractions versus time after isothermal heating at 488° C. Curve (a) refers to unannealed specimens and is the same as in fig. 2. Curve (b) and closed circles (●) on curve (c) refer to specimens previously annealed 30 min at 406° C, and 10 min at 467° C, respectively. The effect of prior treatments and their dependence on temperature is evident.
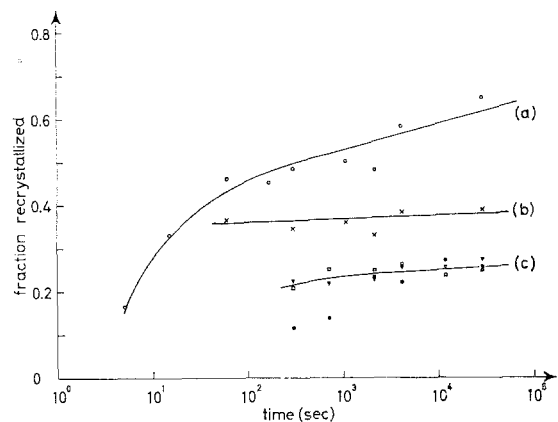

Figure 9 Values of the recrystallised fraction in SAP 5.25 wt % oxide, after isothermal heating at 488° C. Curve (a) as-rolled specimens (o); curve (b) specimens preannealed 30 min at 406° C (x); curve (c) specimens preannealed 110 min at 401° C (□), 36.3 min at 430° C (▽), 10 min at 467° C (specimens were recrystallised ~ 13%) (●).

An indication of the type of recovery process competing with recrystallisation can be derived by considering the results of our earlier work on the kinetics of recovery [7, 8], and the temperature and times for the onset of recrystallisation in fig. 2. This analysis suggests that the competing process is one that occurs in the stage immediately preceding recrystallisation. This stage (which we called stage B) has been attributed to dislocation climb, and is characterised by an activation energy of 1.57 eV. The above hypothesis is also consistent with the results of micro-

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graphic examinations as shown in figs. 4, 5, and 7.

To test this hypothesis, we studied the recrystallisation behaviour at 488° C after preliminary annealing (110 min at 401° C or 36.3 min at 430° C). These times were chosen so that if the competing process has indeed an activation energy of 1.57 eV then these pre-anneals, and that of 10 min at 467° C, should give rise to exactly equivalent reductions of the driving energy for recrystallisation.

The results of this experiment are also plotted in fig. 9. There is complete agreement of the effects of preliminary recovery anneals at the lower temperatures, and, for long heating times, also with those after treatment at 467° C.

According to the method of analysis proposed by Vandermeer and Gordon [14], an indication of the activation energy for the competing process can also be derived by comparing in fig. 3, at the different temperatures, the times giving rise to a fixed degree of deviation from the Avrami kinetic equation. Such times are plotted in fig. 10. The value of the activation energy thus determined is 1.5 ± 0.25 eV, in fair agreement with the above value, 1.57 eV, which is of course more reliable and precise.
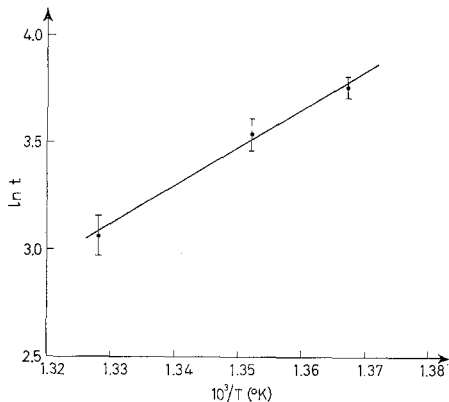

Figure 10 Times for deviation from the linear behaviour in fig. 3, plotted versus reciprocal temperature.

5. Discussion

The results reported in fig. 9 show that competing recovery reduces the rate of recrystallisation, and can ultimately stop this process. Further evidence of the amplitude of this effect, which increases with the oxide content, is provided by the results of our previous determinations after isochronal annealing in steps [7]. In fig. 1 values of the recrystallised fractions after step-annealing are reported for comparison with the results of the

present study. We have confirmed that comparable reductions in the degree of recrystallisation also can be affected by slow continuous heating up to a given temperature.

As is shown by the results in figs. 9 and 10, the recovery process responsible for the deviation of the kinetics of recrystallisation in fig. 3 from the sigmoidal (Avrami) law, is that occurring in the stage (which we called stage B) immediately preceding recrystallisation. This conclusion is in agreement with earlier observations that the fraction of extra resistivity which recovers before recrystallisation increases with the oxide content, owing to the corresponding increase in amplitude of stage B [7].

Our conclusion can also explain the observations of Westerman and Lenel [2] that the growth rate of individual grains decreases with time. To test whether our conclusions have wide validity, and to confirm this point, we have analysed the data (recrystallised fraction as a function of isothermal heating time) presented by these authors for Al/Al$_2$O$_3$ alloys. It was particularly interesting to compare these different alloys because Westerman and Lenel examined transverse sections, instead of the surface of flat-rolled sheets as we did. The values of ln $1/(1 - x)$ versus log t for alloys with 3 % and 1.75 % oxide were plotted and analysed. Deviations from the sigmoidal law were again observed, with identical features as those in fig. 3. The value of k found was again 1.7. This confirms that competition between recovery and recrystallisation is a general feature of recrystallisation in these alloys. Owing to this effect the rate of grain boundary migration decreases with time, and the determination of the activation energy for grain boundary migration becomes difficult. We notice that in order for competition this activation energy for boundary migration must exceed that for the relevant recovery process, i.e. 1.57 eV. From observations of the growth rate of individual grains, Westerman and Lenel determined for boundary migration an activation energy of ~ 4 eV which (because of the diminishing rate of migration) must be rather higher than the true value. Nevertheless this true value appears to be much greater than 1.57 eV. The value of 1.57 eV corresponds to the activation energy for lattice self-diffusion in aluminium; thus our analysis suggests that besides reducing the driving force, the dispersed phase gives rise to an increase of the activation energy for boundary migration in recrystallisation.

Finally, we notice that recovery should affect the recrystallisation behaviour both by decreasing the internal energy and by reducing the energy difference between adjacent sub-grains. This last hypothesis is based on the consideration that the recovery rate should be higher in the grains of higher lattice distortion, owing to the influence of the internal stresses. This is suggested by the examination of the structure of fully annealed unrecrystallised regions, as in fig. 5.

6. Conclusions

The kinetics of recrystallisation of Al/Al_2O_3 alloys is characterised by a rate decreasing with time. It has been shown that this results from the existence of a competing process of dislocation recovery by climb, which decreases the driving energy for grain boundary migration, and can ultimately stop recrystallisation.

The activation energy for the competing process is 1.57 eV, i.e. that for self-diffusion in aluminium. Competition between recovery and recrystallisation increases with concentration of the dispersed phase.

The activation energy for grain boundary migration, in the presence of a dispersed phase, is found to be greater than that for lattice self-diffusion. This suggests that the dispersed phase not only hinders mechanically the displacement of a grain boundary, as in Zener's model [11], but also increases the activation energy for the process.

A more complete theory of the recrystallisation behaviour of two-phase alloys should thus be developed from the observation of this effect.

Acknowledgements

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