Bulk Diffusion Enhancement due to Grain-Boundary Migration

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This paper reports bulk diffusion enhancement under conditions where grain-boundary migration and grain growth, or grain growth only take place during the time of the diffusion experiment.

Although a substantial contribution to diffusion takes place through grain-boundaries the penetration curves measured remain Gaussian, as suggested by Balluffi and Ruoff [3]. The apparent enhancement measured is about a factor of two. However, it is shown that the real enhancement due to migration of grain-boundaries during the diffusion experiment may be as large as a factor of fifty.

1. Introduction

It is a well-established fact that diffusion through grain-boundaries is considerably faster than in the lattice; the activation enthalpy for diffusion in the boundary is approximately half that of the lattice. A similar effect occurs for dislocations. An indication of the type of diffusion, i.e. whether in the lattice, intergranular or along dislocations, is given by the type of penetration curves. Bulk diffusion is characterised by a curve which involves a Gaussian relationship. For the case of a thin film of tracer atoms which diffuses from one end of a semi-infinite bar, the penetration curve is a straight line when a plot of the logarithm of the solute concentration is plotted as a function of x^2, x being the penetration distance [1]. A straight line is obtained in a plot of the logarithm of the solute concentration vs. x for diffusion through boundaries or dislocations. Hart [2] has shown that under certain conditions dislocations can enhance the bulk diffusion coefficient, leaving the penetration curve still Gaussian. The relevant condition is that the time spent by a tracer atom in going from one dislocation to another is small compared with the total time of the experiment, and thus $(2D_\mathrm{v}t)^{1/2} \gg L$, where L is the mean distance between dislocations, D_v is the bulk diffusion

coefficient and t the time of the experiment.

A similar effect could occur with grain-boundaries, where the grain diameter plays the role of the distance between dislocations. The measured diffusion coefficient is given by $D \simeq D_\mathrm{v} (1-f) + fD_\mathrm{b}$, where D_b is the diffusion coefficient across the grain-boundary and f is the fraction of atoms contained in the boundary. Recently Balluffi and Ruoff [3] have objected to some strain-enhanced diffusion experiments by suggesting that the enhancements measured could be due to grain-boundary migration during deformation. Although the condition $(2D_\mathrm{v}t)^{1/2} \gg L$ does not apply, the situation is quite the same, for now the boundaries move to the atoms, instead of the atoms moving from one boundary to the other. In this way substantial diffusion enhancement could be obtained due to grain-boundary short circuits, while the penetration curve remains Gaussian. The equation $D = D_\mathrm{v}(1-f) + fD_\mathrm{b}$, under this circumstance, gives an upper limit to the measured diffusion coefficient.

It is the purpose of this note to report some bulk diffusion enhancement found under conditions where grain-boundary migration and, in some cases, recrystallisation occurred during the time of the diffusion experiments.

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2. Experimental Results

The material used was a 74 at. % Ni, 26 at. % Fe alloy and the tracer used was Ni^{63}. A spectrographic analysis of the material showed the following impurities: Ca = 0.0001%; Cu = 0.0001%; Mg = 0.0001%; Si < 0.0001%; Na < 0.0001%.

Three types of diffusion samples, (a), (b) and (c), according to their condition prior to the diffusion annealing, were prepared:

(a) Cold-rolled 80% reduction plus heat-treatment for the same time and at the same temperature as the diffusion experiments performed later. This heat-treatment gave a stable grain size, so that no grain-boundary motion existed during the diffusion annealing.

(b) Cold-rolled 80% reduction plus 2 h at 800°C. This heat-treatment recrystallised the material completely, but extensive grain-boundary migration occurred during the diffusion annealing at temperatures greater than 800° C.

(c) Cold-rolled 80% reduction with no heat-treatment prior to diffusion measurements. During the diffusion annealing, recrystallisation and grain growth occurred.

The samples were electroplated with Ni^{63} and annealed at different temperatures under a dynamic vacuum of 10^{-6} torr. Temperature stability was within 1° C. Fig. 1 shows typical photomicrographs of samples before and after the diffusion anneal at 1056° C for 55.5 h.

The residual activity technique was used to evaluate the diffusion coefficients [4]. Briefly, if the free surface is abrased for a distance x_m, the measured activity I_m and the isotope concentration $C(x_m)$ at the new free surface are related by the differential equation $\mu I_m - (dI_m/dx_m) = K\,C(x_m)$, where μ is the absorption coefficient of the β-radiation of Ni^{63} in the material (10^4/cm), and K is a constant. As the β-radiation has a very low energy (0.067 mev) the relation $dI_m/dx_m \ll \mu I_m$ holds, then $I_m \simeq K\,C(x_m)$. For bulk diffusion $C(x_m) \sim \exp(-x^2/4Dt)$, where t is the diffusion time. Then $\ln(I_m) = Cte - x^2_m/4Dt$ and the tracer diffusion coefficient is obtained from the slope of the plot $\ln(I_m)$ vs. x^2_m. Fig. 2 shows a typical penetration curve for each type of sample at one temperature.
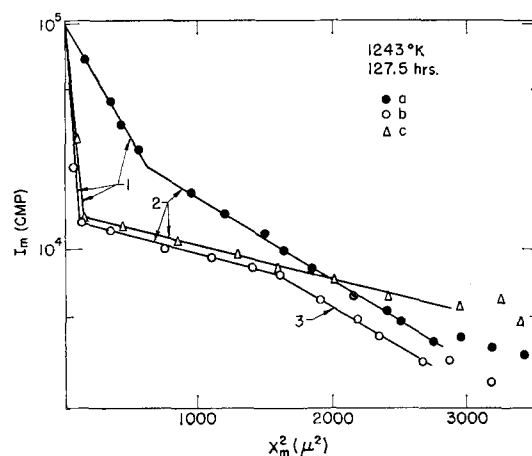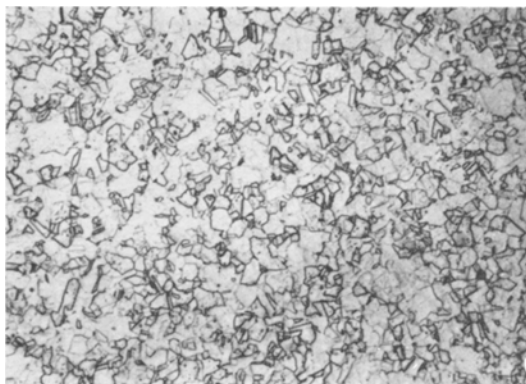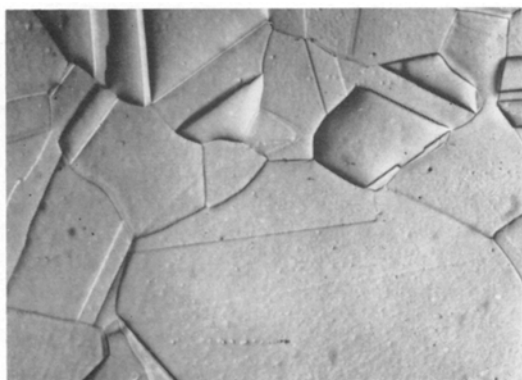

Figure 2 Typical penetration curves for each type of sample, at 1243° K for 127.5 h.

Note that it has been plotted as $\ln$ (activity) vs. x^2, so that a Gaussian penetration curve is

(a)   (b)

Figure 1 Photomicrographs of samples (a) before and (b) after the diffusion anneal at 1056° C for 55.5 h. (a) 2 h at 800° C; grain size $\simeq$ 27 μm ($\times$65). (b) Same as (a) plus 55.5 h at 1056° C; grain size $\simeq$ 220 μm ($\times$65).

TABLE I

T °K	Da_2 cm²/sec	Db_2 cm²/sec	Db_3 cm²/sec	Dc_2 cm²/sec	t sec
1243	6.61×10^{-12}	1.49×10^{-11}	6.67×10^{-12}	1.58×10^{-11}	4.59×10^5
1288	1.28×10^{-11}	2.43×10^{-11}	1.12×10^{-11}	2.39×10^{-11}	1.512×10^5
1329	2.30×10^{-11}	5.44×10^{-11}	2.25×10^{-11}	9×10^{-11}	1.998×10^5
1385	4.81×10^{-11}	1.04×10^{-10}	4.59×10^{-11}	1.19×10^{-10}	1.044×10^5

followed. The observations on the three samples are:

(a) Two zones named a_1 and a_2 appear at all temperatures. The first one, a_1, extends to about 25 μm at all temperatures. The second zone with a straight line, a_2 yields the lattice diffusion coefficient for Ni in the alloy. $Da_2 = D_1$ [5].

(b) Three zones named b_1, b_2, and b_3 appear at all temperatures. The first one, b_1, extends to about 12 to 14 μm. The second zone with a straight line, b_2, gives an enhanced diffusion coefficient Db_2 and extends from 12 to 13 μm to 39 to 45 μm. The third zone with a straight line, b_3, extends through the rest of the diffusion zone and yields a diffusion coefficient Db_3, which is equal to the lattice diffusion coefficient. As shown in fig. 1, there has been extensive grain growth during the diffusion annealing of specimens (b).

(c) Two zones appear at all temperatures. The first one, c_1, extends, as in (b) to about 12 to 13 μm. The second zone extends through all the rest of the diffusion zone yielding an enhanced diffusion coefficient Dc_2, which is approximately equal to Db_2. Recrystallisation followed by grain growth has occurred during the diffusion anneal.

The values obtained for the diffusion coefficients, annealing temperatures, and annealing times are summarised in table I.

The first zone appearing in all three samples, at all temperatures, is well defined for sample type (a) only. For this sample, straight lines can be drawn through the points. This abnormally low diffusivity for small penetrations is found in a great number of penetration curves shown in the literature, it has been suggested that it is due to an oxide layer on the surface [6].

In fig. 3 we have plotted the logarithm of the diffusion coefficients for zones 2 and 3, i.e.: Da_2; Db_2; Db_3 and Dc_2 as a function of the inverse of the absolute temperature. From this plot it is seen that: all diffusion coefficients measured through the second slopes of the penetration curves of specimens where grain-boundary migration (Db_2) or recrystallisation
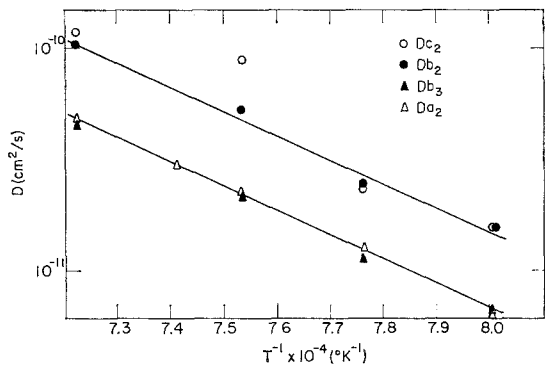

Figure 3 Logarithm of the diffusion coefficients as a function of the inverse of the absolute temperature.

and grain-boundary migration (Dc_2) took place, have approximately the same value, although the latter shows much more scatter. Diffusion coefficients measured through the third slope of specimens where grain-boundary migration occurred (Db_3) agree with the values for lattice diffusion (Da_2) [5]. It is also seen that a straight line may be drawn through the points for the values of Db_2. This line is parallel to that drawn through the points for Da_2 and Db_3 showing that over this period the activation energy is equal to that for lattice diffusion (Da_2) (47.7 kcal/mol [5]). The pre-exponential factor for Db_2 is a factor of two larger than that for Db_3 and Da_2 ($D_0 = 1.76 \times 10^{-3}$ [5]). For the specimens where recrystallisation also took place, the diffusion coefficients measured (Dc_2) show a scatter too large to allow a line through the points.

3. Discussion

The apparent enhancement of bulk diffusion found is about a factor of two. However, we note that in the diffusion experiments with samples prepared under conditions where grain growth, or recrystallisation and grain growth could occur, during the time after the grain-boundaries became immobile, diffusion took

987

place almost exclusively through the lattice, so that the measured coefficient $(Db_2 \simeq Dc_2 = D_m)$ is a weight average of the lattice diffusion coefficient $(Da_2 = D_l)$ and the true enhanced coefficient (D_e).
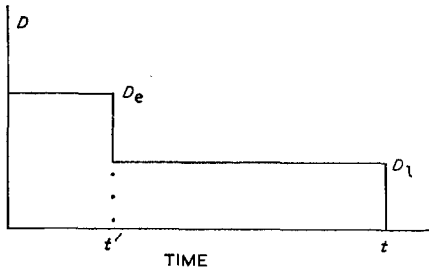

Figure 4 Assumed diffusion coefficient as a function of time.

Assuming that during the time t of the diffusion experiment, the diffusion coefficient of a specimen prepared for grain growth or recrystallisation and grain growth depends on time, as in fig. 4, where t' is the time after which there is no more grain-boundary motion, then the solution of the differential equation for diffusion with such a diffusion coefficient shows that $D_m t = D_e t' + D_l(t - t')$. Assuming $t' \ll t$ and as $D_m \simeq 2D_l$, then the true enhanced diffusion coefficient is $D_e \simeq D_l \frac{t}{t'}$:

Measurements of grain growth as a function of time at the different temperatures showed that t/t' is of the order of fifty, so that grain-boundary migration enhances bulk diffusion by that factor. A rough estimate of D_b/D_l is possible by using $D_e \simeq 50D_l$ and $D_e = D_b f + (1 - f) D_l$, and assuming for f a mean value calculated

from the data for grain growth as a function of time, through the relation $f \simeq 6b/L$, where b is the nearest neighbour distance and L the grain diameter. We find that D_b/D_l is of the order of 10^6, a value which is reasonable, although perhaps too high by a factor of ten, in view of the rather high temperatures used.

It is interesting to note that although it was found that after the first 5 to 10 min, depending on temperature, samples previously cold-rolled had the same grain size as those previously recrystallised, the penetration curve for this type of sample (c) does not show a third slope as in the sample, type (b), where only grain growth took place.

We believe the diffusion measurements made by annealing for times smaller than t', and therefore avoiding the estimation of t/t', followed by a careful measurement of grain size as a function of time to calculate a mean value of f, would provide an independent way of measuring D_b.

Acknowledgement

References
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