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Surface mass transport of alumina

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The kinetics of thermal grooving at the intersection of rhombohedral twin boundaries with the (1 0 $\bar{1}$ 0) plane in aluminium oxide were measured from 1773 to 2273 K. Analysis of the data using the model of Mullins showed that surface diffusion was the dominant mechanism for mass transport. The results were compared with other similar published work on alumina, and the following equation for surface diffusion was determined:

$$D_s(\text{cm}^2\text{sec}^{-1}) = 4.05 \times 10^5 \exp - (452\,\text{kJ mol}^{-1}/RT).$$

1. Introduction

The kinetics of the changes in the topography of a crystal surface under the influence of capillary forces have been modelled in terms of various mechanisms of mass transport: surface diffusion, volume diffusion, and evaporation–condensation [1–4]. Surface modification by grain boundary grooving [5–7], the decay of sinusoidal surface features [8, 9], and the spheroidization of voids [10] have been used to measure diffusion kinetics in aluminium oxide in a variety of experimental conditions. The purpose of the present work was to measure the thermal grooving of twin boundaries in high purity single crystal alumina over an extended temperature range and to compare the results with those reported by other workers under other experimental conditions. The experimental variables from the literature and the present work are summarized in Table I.

Mullins' [1] theory of thermal grooving by surface diffusion predicts the following relation between boundary groove width, w, and time of annealing, t, at a constant temperature:

$$w = 4.6(Bt)^{1/4} \quad (1)$$

with

$$B = D_s\gamma\Omega^2 N/kT \quad (2)$$

where D_s is the surface diffusion coefficient. The other parameters in Equation 2 and their values for Al_2O_3 are as follows: γ, surface free energy (0.905 J m^{-2}); Ω, molecular volume (2.11×10^{-23} cm^3/molecule); N, surface concentration of diffusing species ($\Omega^{-2/3}$).

King and Mullins [11] derived a similar equation for the decay of a single symmetrical scratch by surface diffusion:

$$w = 6.9(Bt')^{1/4} \quad (3)$$

B is given by Equation 2 and t' is given by

$$t' = (t + t_0) \quad (4)$$

where t is the experimental time and t_0 is a fictitious time, the significance of which was discussed by King and Mullins [11].

There is some controversy in the literature regarding the appropriate analysis of grain boundary grooving [12–15]. The present work will follow previous authors and use the techniques proposed by Mullins [1–4] and Gjostein [15]. From Equation 1, a plot of log w against log t will have a slope of 1/4 for a surface diffusion mechanism. If volume diffusion mechanism is operating, the slope of such a plot will be 1/3. When both mechanisms are contributing to groove formation, the slope of log w against log t will be intermediate between 1/3 and 1/4, in which case corrections to the groove widths have to be carried out as discussed by Mullins and Shewmon [4].

2. Experimental procedure

High-purity aluminium oxide single crystals containing coherent rhombohedral twin boundaries (Union Carbide, Linde Division and H. Djevahirdjian SA) were used in this study. A typical analysis of these materials is given by Schackelford and Scott [7]. One specimen, cut from a Verneuil grown boule, contained two rhombohedral twins (four boundaries) which had been introduced by c-axis compression at 1973 K and 20 MPa. These will be called deformation twins. Another Verneuil grown boule contained one twin (two boundaries) as received. This twin was probably introduced by thermal stresses and was also a deformation twin, but will be designated here by "as-received". The crystals were cut such that twins met the free surface, the (1 0 $\bar{1}$ 0) plane, at about 65°. This particular surface plane was selected because it did not develop thermal facets during the heat treatments. The twin boundary traces on the (1 0 $\bar{1}$ 0) plane were 80, 115, and 35 μm apart respectively so they were independent in terms of thermal grooving behaviour.

The (1 0 $\bar{1}$ 0) faces were polished to a final finish of 1/4 μm diamond. The crystals were cleaned in detergent solution, distilled water and rinsed in isopropyl alcohol. To isolate the crystals from atmospheric

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TABLE I Summary of various conditions for surface topography experiments in alumina

Specimen	Reference	Method	Al_2O_3 Method	Orientation	Atmosphere	Container	Temperature (K)
5	Robertson and Chang [5]	Grain-boundary groove	Sintered, polycrystal 99.7% pure	Random	Air	Sintered Al_2O_3	1373–1993
6a	Robertson and Ekstrom [6]	Grain-boundary groove	Polycrystal, MgO doped (Lucalox)	Random	Air	Sintered Al_2O_3	1673–1953
6b	Robertson and Ekstrom [6]	Sub-grain boundary	Single crystal (Verneuil)	55° from c-axis	Air	Sintered Al_2O_3	1673–1953
7	Shakelford and Scott [7]	Grain-boundary groove	Pressure sintered bicrystal	$\{10\bar{1}0\}$	10^{-3} Pa	Tungsten	1813–2073
8a	Huang *et al.* [8]	Sub-grain boundary	Single crystal	$\simeq(11\bar{2}3)$	10^{-4} Pa	Sintered Al_2O_3	1873–2073
	Present work Gaddipati	Twin-boundary groove	Single crystal (Verneuil)	$(10\bar{1}0)$	$< 10^{-3}$ Pa	Sapphire	1773–2273
	Present work Gaddipati	Scratch decay	Single crystal (Verneuil)	$(10\bar{1}0)$	$< 10^{-3}$ Pa	Sapphire	1873
8b	Huang *et al.* [8]	Sinusodial decay	Single crystal	(0001)	10^{-4} Pa	Sapphire	1873–2023
8c	Huang *et al.* [8]	Sinusodial decay	Single crystal	$(11\bar{2}0)$	10^{-4} Pa	Sapphire	1873–2023
9	Monty and Duigou [9]	Sinosodial decay	Single crystal (pure and MgO doped)	(0001)	Air	Sintered Al_2O_3	1923–1973
10	Yen and Coble [10]	Spheroidization of voids	Single crystal (cracked)	–	Air	Sintered Al_2O_3	1923–2083

contamination, the anneals were done in a closed sapphire crucible made by core drilling a single crystal boule. A polished sapphire plate was used as a crucible lid. Annealing was carried out in a vacuum induction furnace with a tungsten susceptor. The specimens were heated to 1523 K in about 40 min and then to the final isothermal anneal temperature in about 5 min. The pressure was maintained at less than 10^{-3} Pa.

Groove profiles were analysed from interference images obtained using a Normarski attachment on a Reichert microscope. The objective had a numerical aperture of 0.818 and the final lateral magnification of the photomicrographs was × 1250. After a complete set of isothermal anneals at various times, the crystals were repolished to remove at least 10 μm before proceeding to the next anneal at a new temperature.

One experiment was carried out on the kinetics of scratch smoothing. Isolated scratches were placed on the surface parallel to the twin traces by a Tukon diamond indentor with a 10 g load. The scratches were pre-annealed at 2073 K for one hour to smooth out irregularities in the scratch profile. The scratches were then annealed at 1873 K for various times and the width of the scratch was measured by interferometry after each anneal.

3. Results and discussion

Log width against log time data are plotted in Fig. 1. Each data point is an average for the two boundaries of a single twin, and, at each time there are three data points from each of the three twins. The crystal containing the as-received twin was annealed in three independent series at 2073 K to check the reproducibility of the method. This result is shown in Fig. 2. Each line is marked with the slope obtained from a least squares best fit. With only two exceptions, the slopes were all less than 0.25, indicating that the surface diffusion model rather than the volume diffusion model (Slope = 0.33) is appropriate. Investigations 5 through 8 (Table I) and the present work report a total of 25 values for slopes which were obtained using similar plots. The average of the 25 values is 0.238 with one standard deviation = 0.032, and the values show no systematic correlation with temperature.

In analysing the scratch decay results, a value of t_0 = 13 h was found to be consistent for the surface diffusion. The plot of log w against log t' is shown in Fig. 3. The slope of the line through these data is 0.23, again indicating that surface self diffusion is dominant at 1873 K.

Assuming the validity of Equation 1, the width against time data were used to calculate the parameter B and D_s. The results from the present work are shown in Fig. 4. The data from the present work and from other investigators are summarized in Table II and Fig. 5.

Line A, Fig. 5 is all data from boundary grooving (and one scratch decay experiment) on pure single crystals. With the assumption that all the results from pure single crystals can be described by one line, the following experimental variables would appear to have no significant effect on the surface mass transport process: (i) Boundary type. These data include experimental results from pressure sintered bicrystals, grown-in lineage boundaries and rhombohedral twin boundaries. (ii) Air against vacuum. One set of four points (Number 6b) was done in air and is indistinguishable from others done in vacuum. (iii) Container. Scott [16] has shown that single crystals of alumina annealed in air at 1873 K in closed 99.5% pure sintered alumina crucibles collected surface deposits. On cooling, these deposits were in the form

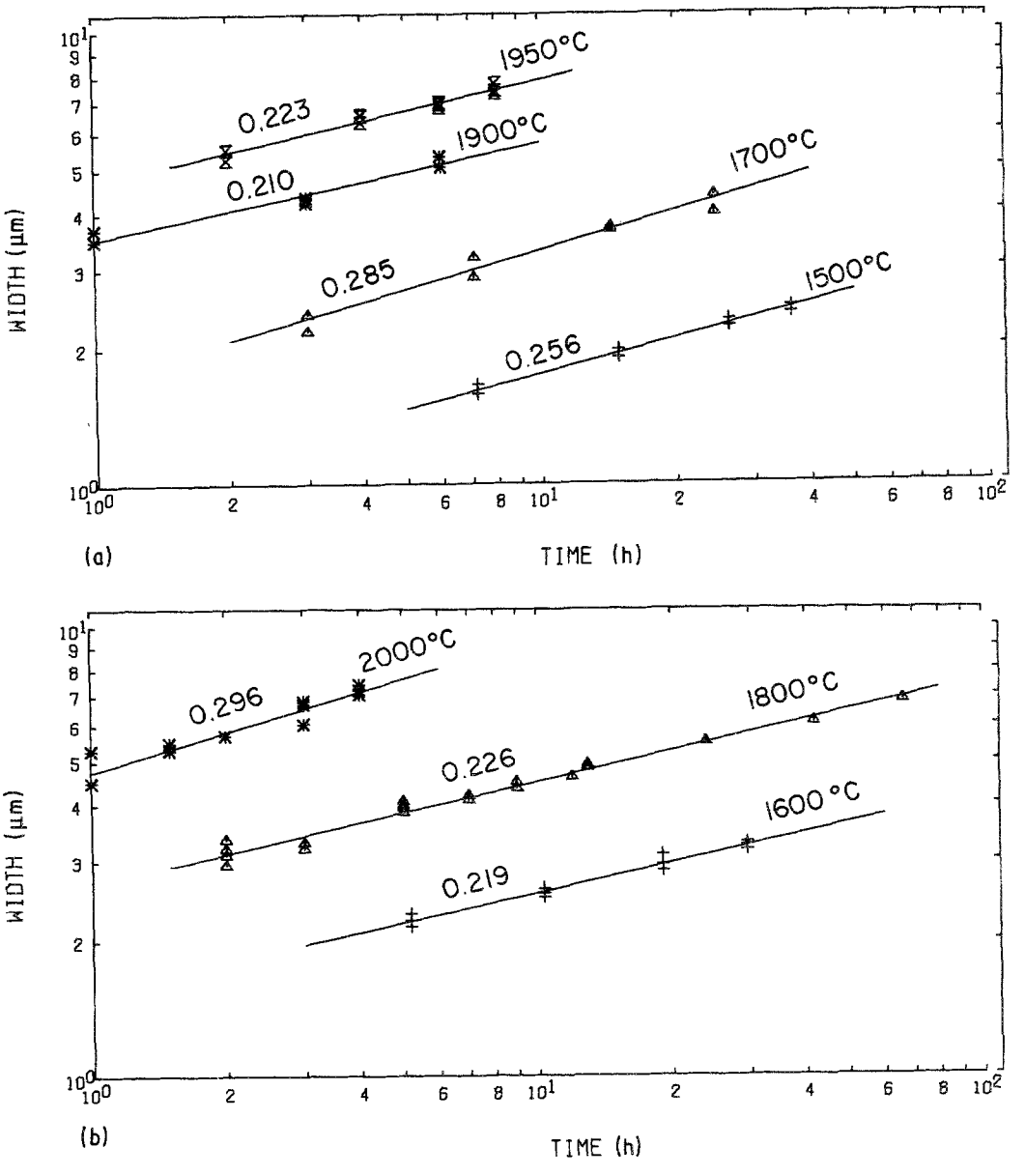

Figure 1 Groove width as a function of time at various temperatures.

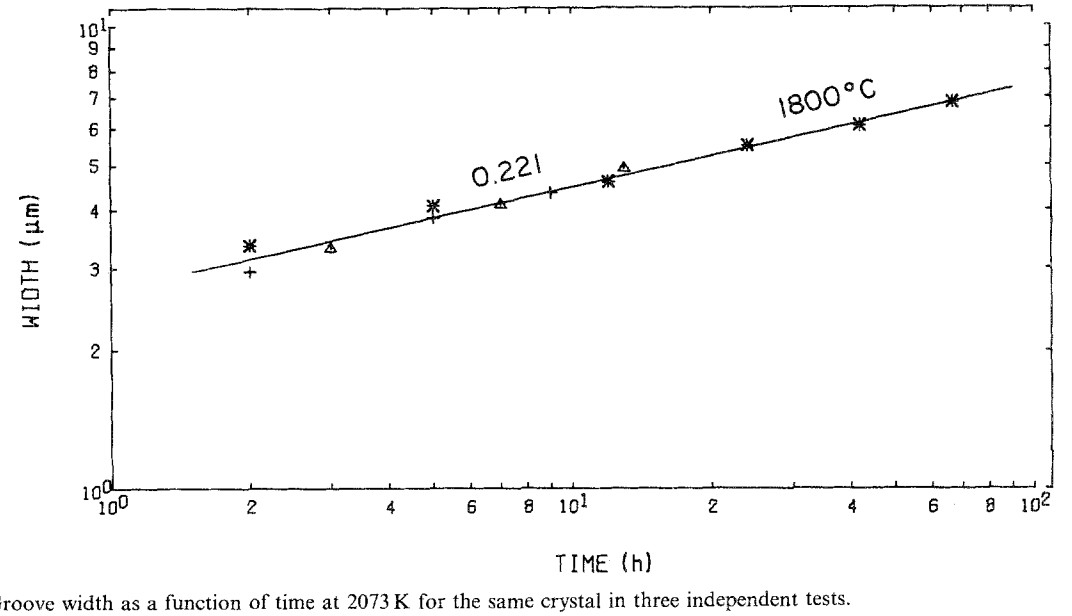

Figure 2 Groove width as a function of time at 2073 K for the same crystal in three independent tests.

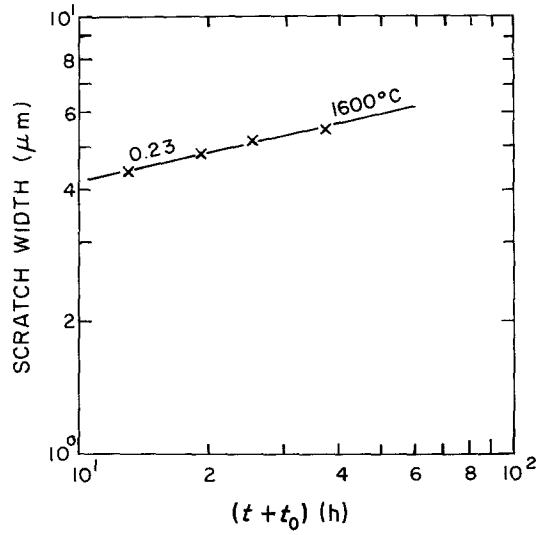

Figure 3 Scratch width as a function of time for t_0 = 13 h.

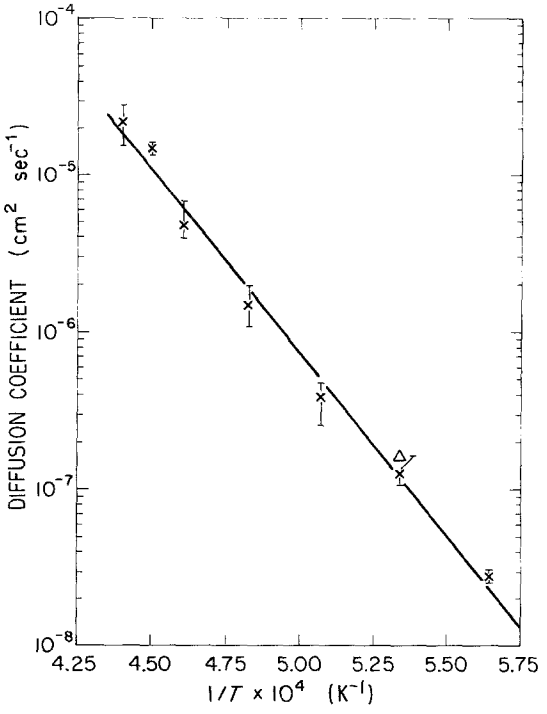

Figure 4 Arrhenius plot of surface self diffusion data for alumina from twin boundary grooving and one measurement of scratch decay (Δ). The vertical bars indicate the range calculated from each individual anneal time by Equations 1 and 2.

of transparent glassy droplets which were shown to contain silicon, calcium, and potassium. Huang *et al.* [8] also mention deposits containing silicon, calcium, and tantalum on specimens heated in vacuum in similar closed crucibles. Specimens from 6b and 8a would be expected to have this contamination, yet the data are consistent with that from specimens annealed in sapphire or tungsten crucibles.

Line B might also be included in Line A based on typical experimental scatter. However, this material was a polycrystalline, sintered, MgO doped alumina with random grain orientation. Since it was treated along with Number 6a, the variation between the points of 6a and 6b is probably significant. Monty and Le Duigou [9] found that magnesium doping reduced the kinetics of sinusodial surface decay relative to that for pure alumina. Therefore, the slight increase in the diffusion indicated by Line B may not simply be atrributed to the presence of magnesium.

Line C represents a merger of data measured by sinudoidal decay on two different crystalline planes in pure alumina. The merged data have an activation energy only 4% greater than Line A. The reasons for the reduction of D_s by a factor of three from that obtained by grain boundary grooving is not understood.

Line D is clearly in a different regime. The activation energy is 31% lower than for grain boundary grooving in pure single crystals, and the absolute value is a factor of 10 to 15 greater. This sintered material contained about 0.3% impurities which were probably segregated at the boundaries. The boundary grooving kinetics may be dominated by the surface transport of this impurity phase.

Line E is anomalous in that its activation energy is intermediate and the D_s value is close to that for impure material. This measurement was made on the spheroidization of internal voids in single crystals and it might be expected to fall closer to Line A.

TABLE II Summary of surface diffustion data for Al_2O_3

Specimen	Reference (Table I)	Number of data points	D_0 ($cm^2 sec^{-1}$)	ΔH ($kJm mol^{-1}$)	Merged data (plotted Fig. 5)	
					D_0	H
5	Robertson and Chang [5]	7	8.9×10^2	313	Line D	
6a	Robertson and Ekstrom [6]	4	1.07×10^9	558	Line B	
6b	Robertson and Ekstrom [6]	4	1.97×10^7	506		
7	Shackelford and Scott [7]	2	5×10^5	460	4.504×10^5	452
8a	Huang *et al.* [8]	3	1.45×10^7	513	Line A	
	Present work Gaddipati	7	3.217×10^5	445		
8b	Huang *et al.* [8]	4 (0001)	2.54×10^5	460	6.97×10^5	475
8c	Huang *et al.* [8]	4 (11$\bar{2}$0)	1.91×10^6	489	Line C	
10	Yen and Coble [10]	–	2.38×10^5	397 ± 25	Line E	

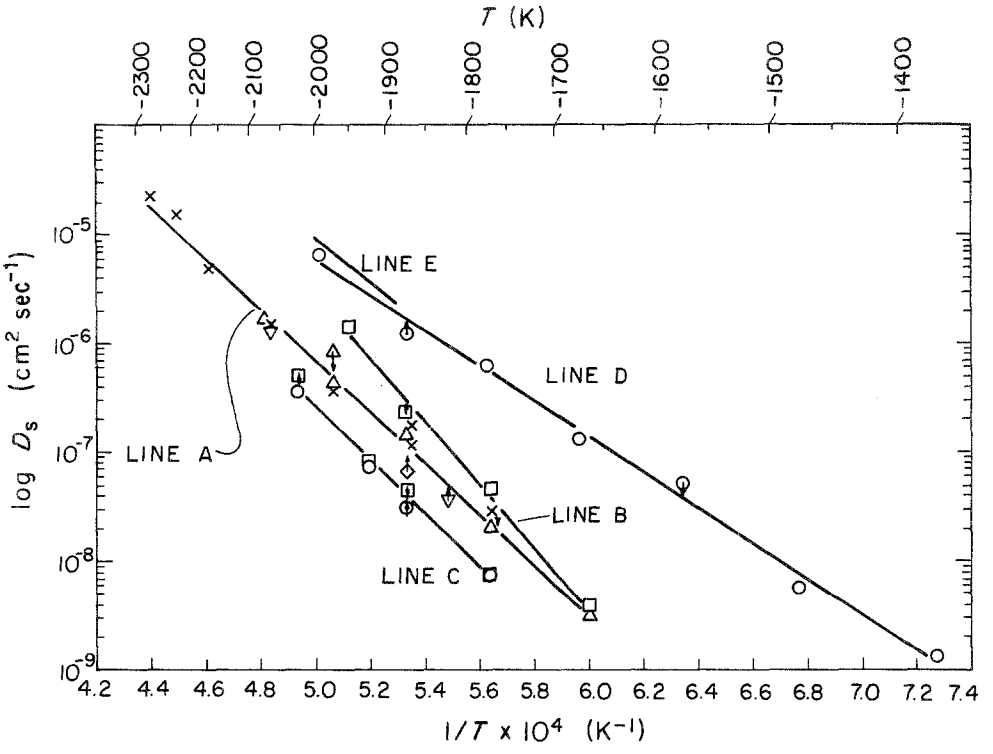

Figure 5 Plot summary of literature data and the present work on surface self diffusion for alumina. The lines are least square best fit and the resulting parameters are given in Table II. Data from other investigators were recalculated where possible or else measured from large scale figures. Line A: △ 6b, ▽ 7, ◇ 8a, × Gaddipati. Line B: □ 6a. Line C: ○ 8b, □ 8c. Line D: ○ 5, Line E: 10.

4. Summary and conclusions

Grain boundary grooving by diffusion at high temperature follows the model of Mullins for surface diffusion. When analysed using this model, 17 data points for boundaries between pure single crystals from four investigators may be described by the equation

$$D_s(\mathrm{cm^2\,sec^{-1}}) = 4.504 \times 10^5 \times \exp - (452\,\mathrm{kJmol^{-1}}/RT). \quad (5)$$

The value of D_s does not appear to be sensitive to air or vacuum or to conditions where some surface contamination by silicon, calcium and potassium is to be expected. The measured boundary types included pressed bicrystals, rhombohedral twins, and lineage boundaries in single crystals.

Published data for decay of a sinusodial surface features give an activation energy 4 to 8% greater and a D_s about a factor three lower than for grain-boundary grooving.

Published data for grain boundary grooving of 99.7% pure sintered alumina give an activation energy 31% lower and a D_s 10 to 15 times higher than that for pure crystals.

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