

Yttrium Diffusion in α -alumina single crystal

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Abstract

Yttrium bulk diffusion in single crystals of α -alumina is investigated by the SIMS technique, in the temperature range 1150–1500°C. The bulk diffusion coefficients obey the relation: $D(Y)(1150\text{--}1500^\circ\text{C}) = 1.2 \cdot 10^{-10} \exp(-295(\text{kJ mol}^{-1})/RT)$ ($\text{m}^2 \text{s}^{-1}$). These values are close to those of chromium diffusion in alumina, although the size of Y^{3+} ion is significantly higher than that of Cr^{3+} ion. The results are used to calculate the parameters of yttrium grain boundary diffusion in alumina, from the penetration profiles obtained in a previous work in polycrystals by the radiotracer technique. © 1998 Elsevier Science Limited. All rights reserved

1 Introduction

In a previous work,¹ yttrium diffusion in undoped α -alumina was investigated by means of the radiotracer ^{88}Y . The experiments on single crystals were unsuccessful because of the sharp decrease of the radiotracer activity for very low penetration depths. The SIMS technique offers the possibility to measure penetration profiles on small depths, i.e. lower than $1 \mu\text{m}$. This technique has been adapted to experiments on insulators. Bulk diffusion coefficient data of silver, copper and chromium have been published.^{2–4} Interesting results are expected by combining both the radiotracer and the SIMS techniques. In this case the flatter profiles resulting from dislocation or grain boundary diffusion, extending over a few μm to tens μm , may be analyzed.

The first objective of this study is the determination by SIMS of yttrium bulk diffusion coefficients in α -alumina. From the data, it would be possible

to calculate the grain boundary diffusion coefficients through the radiotracer penetration profiles obtained on polycrystalline samples.¹ The second is to compare the kinetics of diffusion of yttrium ions Y^{3+} to those of other ions such as Cr^{3+} and Al^{3+} .^{4,5} These ions, identical by their charge, exhibit different atomic radii and electronic structures. The comparison of the results will allow us to specify the importance of the size effect on the diffusion of foreign cation in alumina.

2 Experimental Procedure

2.1 Preparation of materials

Specimen of dimensions $7 \times 7 \times 1 \text{ mm}^3$ were cut from an α -alumina monocrystalline boule grown by flame fusion and provided by Baikowski Chimie (Annecy, France). The impurity content of the starting powder, given by Baikowski, was less than 100 ppm. A chemical analysis of the samples, the results of which are reported on Table 1, showed that the calcium and the silicon impurity concentrations increased during the elaboration. The samples were polished with diamond pastes down to $1 \mu\text{m}$. Samples were pre-heated in air at the temperatures and times of the subsequent diffusion conditions.

Yttrium was deposited on alumina through an yttrium chloride solution ($7 \cdot 10^{-4} \text{ mol l}^{-1}$). A drop of this solution, (about 0.1 cm^3) was deposited on one large face of the specimen which was then covered by a piece of polycrystalline α -alumina of dimensions equal to those of the monocrystalline sample. Yttrium was then stabilized as Y_2O_3 after a short heat treatment at 500°C in air.

In these conditions, owing to the higher solubility of yttria in polycrystalline material as compared to that in the monocrystalline form,⁶ it can be assumed that only a small amount of yttrium will diffuse in the single crystal, and that no precipitation will occur in the specimen.

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Table 1. Impurity content of the powder and of the α -alumina single crystal

Impurity	Powder (wt ppm)	Single crystal (wt ppm)
Si	50	450
K	40	
Ca	15	300
Mg	10	30
Fe		15

2.2 Diffusion anneals

Diffusion anneals were carried out in a lanthanum chromite furnace (Pyrox) in air. The annealing temperatures and times are shown on Table 2. After the diffusion treatment, the penetration profiles were determined by the SIMS technique using a Cameca IMS 4f apparatus. The conditions of analysis were the following:

- the samples were coated with a 50 nm thick gold layer and an electron flood was used to prevent a charge-up during the sputtering process;
- the incident ions O_2^+ were accelerated to 10 kV, the beam current was 100 nA. The secondary ions were accelerated to +4.5 kV;
- the scanned area was $100 \times 100 \mu m^2$, and the diameter of the analyzed zone was $30 \mu m$

These conditions gave sputtering rates lying in the range 1 to $2 \cdot 10^{-10} m s^{-1}$.

During the sputtering process, the Al and the Y signals were recorded. At the beginning, after a very short time (about 100 s), the Al signal reached a constant value. The corresponding point was then taken as the depth origin. The crater depths, which were generally lower than $1 \mu m$, were measured using a Tencor P1 profilometer.

3 Determination of Diffusion Coefficients

From the total crater depth and the total sputtering time, assuming a constant sputtering rate, the

Table 2. Diffusion conditions, mean penetration depths and bulk diffusion coefficients for yttrium diffusion in α -alumina single crystals

Temperature (°C)	t (h)	\sqrt{Dt} (m)	D ($m^2 s^{-1}$)
1150	135	$3.5 \cdot 10^{-8}$	$2.5 \cdot 10^{-21}$
1200	79	$2.9 \cdot 10^{-8}$	$3 \cdot 10^{-21}$
1400	10	$4.2 \cdot 10^{-8}$	$5 \cdot 10^{-20}$
1453	96	$1.9 \cdot 10^{-7}$	$1 \cdot 10^{-19}$
1453	25	$1.1 \cdot 10^{-7}$	$1.4 \cdot 10^{-19}$
1500	3	$7 \cdot 10^{-8}$	$4.5 \cdot 10^{-19}$

depths corresponding to the SIMS intensities were calculated. Hence, the plots of the yttrium signal as a function of the sputtering time were converted into penetration profiles.

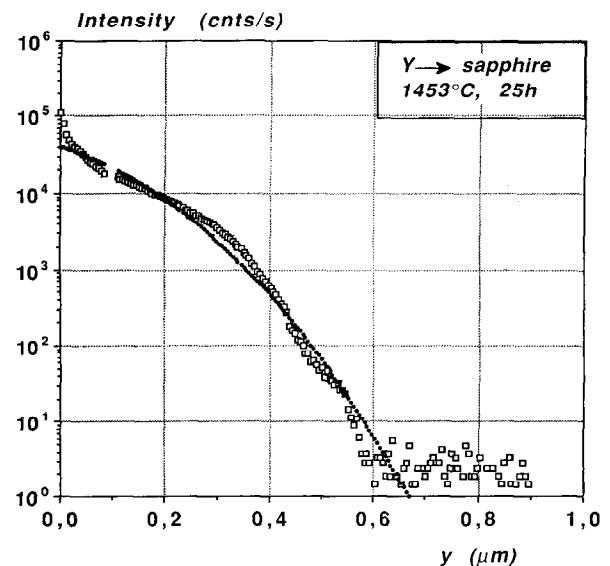
To analyze these curves, one has to take into account the low solubility of yttria in the bulk of alumina (< 10 ppm).^{6,7} As a result, we may assume that the yttrium surface concentration was constant. In this case, the dependence of the concentration, c , on the depth, y , is described by the relation:

$$c = c_0 \operatorname{erfc} \left(\frac{y}{2\sqrt{Dt}} \right) \quad (1)$$

In this equation, c_0 is the constant surface concentration, D is the bulk diffusion coefficient and t the diffusion time. The mean penetration depth \sqrt{Dt} characterizes the width of the zone affected by the diffusion process.

A typical experimental curve obtained after diffusion at $1453^\circ C$ for 25 h is shown in Fig. 1. When erfc plots were fitted to the curves, the mean penetration depths and the bulk diffusion coefficients, reported in Table 2, were deduced. The diffusion coefficients are plotted as a function of temperature on Fig. 2 which can be described by the following Arrhenius relation:

$$\begin{aligned} D(Y) (1150 - 1500^\circ C) \\ = 1.2 \cdot 10^{-10} \exp \left(-295 (\text{kJ mol}^{-1}) / RT \right) (m^2 s^{-1}) \end{aligned} \quad (2)$$

**Fig. 1.** Yttrium penetration profile in α -alumina single crystal (SIMS technique). $T = 1453^\circ C$, $t = 25$ h (dotted line = theoretical plot).

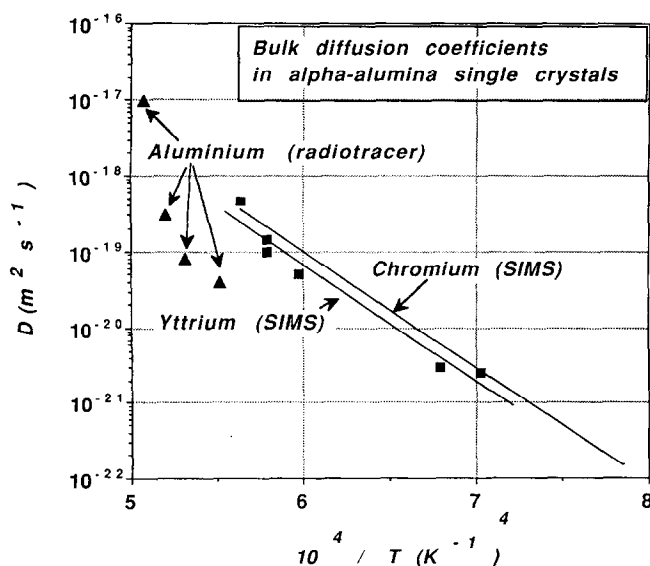


Fig. 2. Arrhenius diagram. ■, Yttrium (present work); ▲, aluminium⁵; —, chromium⁴.

4 Discussion

We can compare our results to those of Lesage *et al.*¹ for diffusion of radioactive yttrium (⁸⁸Y) in alumina single and polycrystals. These authors could not determine a true lattice diffusion coefficient in single crystals because of the very sharp profiles. Nevertheless they could estimate the lattice diffusion coefficient at 1588°C, $D = 10^{-18} \text{ m}^2 \text{ s}^{-1}$, which appears close to the extrapolation of eqn (1) at this temperature.

Their experiments in polycrystals showed that yttrium diffuses rapidly in grain boundaries. A typical curve obtained at 1408°C after a diffusion of 16.5 h is shown in Fig. 3. Yttrium is then present at depths larger than 100 μm . By using the

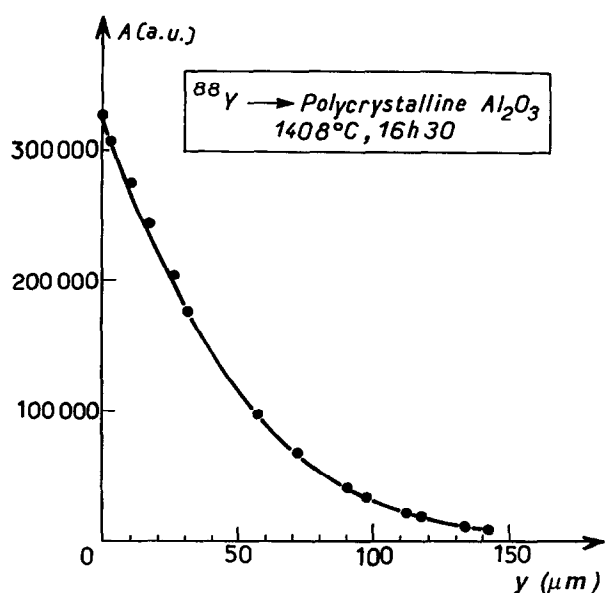


Fig. 3. Yttrium penetration profile in polycrystalline alumina (radiotracer technique).¹

lattice diffusion coefficient deduced from the present work and the Suzuoka analysis for the calculation of grain boundary diffusion parameter, $D' \times \delta \times \alpha$ where D' is the grain boundary diffusion coefficient, δ the grain-boundary width and α the segregation ratio, we obtain the values reported in Table 3. We have calculated also the $D' \times \alpha$ values (assuming $\delta = 1 \text{ nm}$) and the ratios $D' \times \alpha / D$.

The $D' \times \alpha / D$ values obtained at 1408 and 1292°C (respectively, 6.7×10^7 and 3.1×10^7) are rather high compared to those obtained by Le Gall *et al.* for Al sub-boundary diffusion in alumina ($D'/D \approx 10^5 - 10^6$).⁵ This can be easily explained if the segregation of yttrium at alumina interfaces is strong ($\alpha \gg 1$).^{6,8-10} Indeed, from their work on yttrium doped polycrystalline alumina, Loudjani *et al.*⁶ concluded that the yttrium concentration in the grain boundaries was 50 times greater than in the bulk. Considering $\alpha \approx 50$, the D'/D values are about 10^6 , close to the values found for self-diffusion.

The $D' \times \alpha / D$ value obtained at 1483°C seems 'abnormally' high. Although this single result must be considered with caution, and requires further work for verification, we have to keep in mind that 'abnormal' transport behaviour has already been observed between 1550 and 1650°C for yttrium doped alumina.^{11,12} A change in the grain-boundary structure induced by the diffusion of yttrium cannot be excluded.

We compare the diffusion coefficients obtained for yttrium to those of chromium⁴ and aluminium⁵ described by the Arrhenius relations (Fig. 2):

$$D(\text{Cr})(1000 - 1500^\circ\text{C}) \\ = 1.2 \times 10^{-10} \exp(-290(\text{kJ mol}^{-1})/RT) (\text{m}^2 \text{ s}^{-1}) \quad (3)$$

and

$$D(\text{Al})(1540 - 1697^\circ\text{C}) \\ \approx 1.6 \times 10^{-5} \exp(-510(\text{kJ mol}^{-1})/RT) (\text{m}^2 \text{ s}^{-1}) \quad (4)$$

The self-diffusion data were obtained by ²⁶Al radiotracer measurements, in a temperature range higher than those of chromium and yttrium. Considering that an extrapolation of data to much

Table 3. Parameters of yttrium grain boundary diffusion in alumina, deduced from radiotracer measurements on polycrystalline samples

Temperature (°C)	Time	$D' \times \delta \times \alpha$ ($\text{m}^3 \text{ s}^{-1}$)	$D' \times \alpha$ ($\text{m}^2 \text{ s}^{-1}$)	$D' \times \alpha / D$
1483	44 h 40 min	4.97×10^{-19}	4.97×10^{-10}	2.5×10^9
1408	16 h 30 min	4.00×10^{-21}	4.00×10^{-12}	6.7×10^7
1292	16 h 40 min	4.63×10^{-22}	4.63×10^{-13}	3.1×10^7

lower or higher temperatures may result in substantial error, the comparison between Al^{3+} and Cr^{3+} or Y^{3+} are carried out only around 1500°C. Some points arise from the comparison of the three sets of data: (1) the Y^{3+} diffusion coefficients are very close to those of Cr^{3+} in the whole temperature range, and (2) around 1500°C, Y^{3+} and Cr^{3+} diffusion coefficients are one order of magnitude higher than those of Al^{3+} . From the similarity of Y^{3+} and Cr^{3+} diffusion coefficients and activation energies, we can conclude that these ions diffuse with the same mechanism. Moya *et al.*⁴ suggested that chromium diffuses through an extrinsic vacancy mechanism. In other words, the temperature dependence of vacancy concentration is negligible and the measured activation energy is almost equal to the migration energy of the impurity atom.

Diffusion coefficients of Y^{3+} and Cr^{3+} are about one order of magnitude higher than those of Al^{3+} . Theoretical calculation by Dienes *et al.*¹³ and by Jacobs and Kotomin¹⁴ give for the vacancy migration energy in alumina, respectively, 366 kJ mol⁻¹ and 357 kJ mol⁻¹. The measured migration energies of Y^{3+} and Cr^{3+} ions are about 65–70 kJ mol⁻¹ lower than those of Al^{3+} ions. This difference in the migration energies is consistent with the observed one order of magnitude higher diffusion coefficients.

The fact that chromium and aluminium diffusion coefficients differ only by an order of magnitude can be easily understood since the Cr^{3+} and Al^{3+} ions have close characteristics (same valence, ionic radii of 0.063 nm for Cr^{3+} and of 0.051 nm for Al^{3+}). Hence a complete solid solution is obtained. In contrast, the similarity between Y^{3+} and Cr^{3+} or Al^{3+} diffusion coefficients was unexpected. These ions have the same charge but the atomic radius of Y^{3+} (0.093 nm) is significantly larger. As a result, yttria solubility in alumina is low (<10 ppm). It is therefore surprising to observe such close diffusion properties for yttrium and chromium in alumina. We can conclude that the ion size is not a reliable criterion for predicting variations in foreign element diffusion coefficients

in alumina. More complex analysis, taking into account the ion polarizability as well as the defect energy in the equilibrium site and in the saddle point would be required.

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