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Surface Diffusion in $CaTiO_3$

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The surface diffusion of $CaTiO_3$ was examined using grain-boundary grooving. Measurements of groove widths were taken over the temperature range 1200 to 1500° C on dense, sintered polycrystalline samples. A new approach for measuring groove widths on polycrystalline samples is described. For the temperature range from 1200 to 1350° C grooving was found to proceed by a surface diffusion mechanism. The activation energy for surface diffusion of $CaTiO_3$ is $330 \pm 30\,\mathrm{kJ\,mol^{-1}}$. At 1450° C and above, grooving occurs by a volume diffusion mechanism.

1. Introduction

Surface diffusion can contribute to such processes as sintering, pore migration and grain growth. The study of surface diffusion and its dependence on parameters such as temperature, composition, surface orientation and ambient atmosphere can be of fundamental importance to understanding the kinetics of the sintering processes in oxide materials. In our work, surface diffusion of $CaTiO_3$ was studied using the grain-boundary grooving method [1, 2]. This method does not yield data on the diffusivity of specific species. However, formation of the groove involves mass transport mechanisms near the surface and is therefore a practical method for measuring surface transport. Surface diffusion studies using the grain-boundary grooving method were made for MgO [3, 4], ZrO_2 [5], Si and SiO_2 [6] and UO_2 [7]. A review of surface diffusion coefficients for oxides was given by Robertson [8].

2. Determination of D_s from grain-boundary grooving

Under the action of surface tension forces, a groove will develop at the intersection of a grain boundary with a sample surface as a result of matter transport during heat treatment (Fig. 1). For a grain boundary perpendicular to the surface with a groove width initially equal to zero, the groove can grow by several mechanisms: surface diffusion, volume diffusion in the solid, volume diffusion through the external phase and evaporation-condensation in the dilute vapour phase of the material. If surface diffusion is responsible for mass transport during boundary grooving, the width of the grain-boundary groove, i.e. the distance (w) between the profile maxima on the two sides, increases according to Mullins' equation [9–11] as

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

where

$$B = \frac{D_s \gamma \omega^2 n}{Tk} \tag{2}$$

in which D_s is the surface diffusion coefficient, γ is the surface energy, ω is the molecular volume of the diffusing species, n is the number of molecules/cm^2 of surface, k is the Boltzman constant and T is the experimental temperature. By convention, n is taken to be $\omega^{-2/3}$. The value of D_s can be calculated from the measured value of B. In principle, this model provides a convenient method for the study of the comparative rates of surface diffusion. The major assumption in its use is that other forms of mass transport, notably volume diffusion, are relatively slow during the heat treatment. A plot of ln (w) against ln (t) is used to verify the predominant mechanism of grain-boundary grooving. According to Mullins' theory, if the plot yields a slope of 1/4, surface diffusion is the predominant mechanism of grain-boundary grooving. However, if the slope is near 1/3, grain-boundary grooving occurs by volume diffusion. If humps do not develop at the edge of the groove, evaporation–condensation is considered to be the main mechanism for grain-boundary grooving.

3. Determination of the groove width

In the usual experimental procedure for determining surface diffusion coefficients according to Mullins' model, a bicrystal of a given material is used. The bicrystal is cut normal to the plane of the grain-boundary so that the surface orientation of the bicrystal is known. After polishing, the specimen is prepared for heat treatment. The groove width is then measured using interference microscopy. Very often it is difficult to obtain suitable bicrystals, whcih is also true for preparing bicrystals of $CaTiO_3$. Therefore, a new method is described for determining groove width

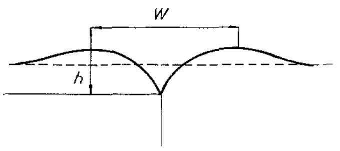

Figure 1 Schematic profile of grain-boundary groove of width, *w*, and depth, *h*.

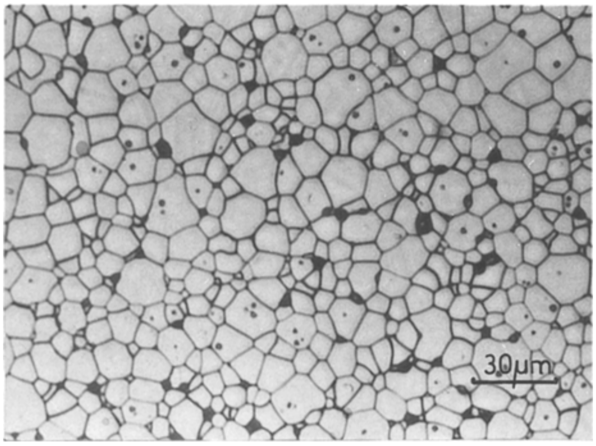

Figure 2 Microstructure of thermally etched $CaTiO_3$, $T = 1400°C$, $t = 8h$.

on polycrystalline samples using stereological analysis of the microstructure.

Thermal etching of dense polycrystalline $CaTiO_3$ will reveal grain boundaries on the surface after a certain time of etching. The microstructure of thermally etched $CaTiO_3$ (Fig. 2) is isotropic with almost straight grain boundaries between two adjacent grains. No faceting is noticed due to anisotropy of the surface free energy of different crystal planes. If a roughness analysis of this thermally etched surface is made using a surfometer (Talistep), a surface profile as shown in Fig. 3 is obtained. The humps on each side of the grain-boundary groove can be distinguished and the distance d_i measured. From the measurement of a few hundred d_i values the average groove width (a) at a certain temperature and time is calculated according to the equation

$$a = \frac{\sum_{i=1}^{N} d_i}{N} \qquad (3)$$

where N is the number of measured d_i values. The line analysis of the surfometer passes grooves at incident angles that range from 0 to 90°. In order to obtain the true value of groove width (w), the average angle θ between the grain-boundary grooves and the random line analysis of the surfometer must first be determined. The value of θ is obtained by stereological analysis of the microstructure in Fig. 2. This analysis is based on measuring the angles θ_i between the test line and the direction of the grain-boundary groove as shown in Fig. 4. From the results the average angle, θ, can be calculated. The true value of the groove width at a certain temperature and time is then given by the equation

$$w = a \sin(\theta) \qquad (4)$$

where a is the average groove width at a certain temperature and time of thermal etching, θ is the average angle of intersection between the grain-boundary groove and the random line analysis and w is the real groove width. The value of θ is constant for a specific microstructure.

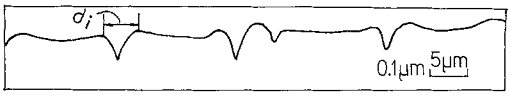

Figure 3 A segment of surface profile of thermally etched $CaTiO_3$ sample, $T = 1400°C$ and $t = 8h$.

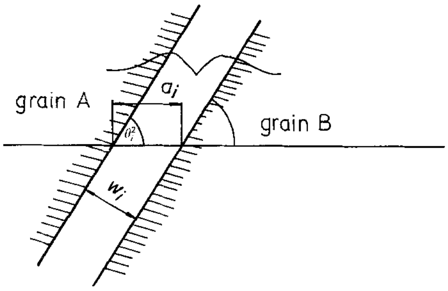

Figure 4 Schematic presentation of measuring angles, θ_i, between incident test line and the direction of the grain-boundary groove.

4. Experimental procedure

Pellets of $CaTiO_3$ (p.a. Ventron) were pressed and fired at 1630° C for 4 h: 98% theoretical density of the material was achieved. Polished surfaces were prepared by established metallographic techniques. The polished specimens were heat treated in a tube furnace at different temperatures from 1200 to 1500° C for 8, 16, 24 or 32 h. The furnace temperature was measured with Pt–Pt10% Rh thermocouple. The estimated precision of the temperature measurement was ± 5° C. After heat treatment at a certain temperature and time, roughness analysis of the surface of each specimen was made and the real groove width, w, was calculated according to Equation 4. A plot of ln (w) against ln (t) for different temperatures was drawn in order to determine the predominant mechanism of diffusion.

In this investigation the following values for the parameters in Equation 2 were used: $\gamma = 0.9\,J\,m^{-2}$, $\omega = 5.59 \times 10^{-23}\,cm^3$, $n = 6.84 \times 10^{14}\,mol\,cm^{-2}$ and $k = 1.38 \times 10^{-23}\,J\,K^{-1}$.

5. Results and discussion

A scanning electron micrograph of the intergranular fracture of a sintered polycrystalline $CaTiO_3$ pellet is shown in Fig. 5. The remaining pores are located at the grain corners and are spherical. It can be seen that

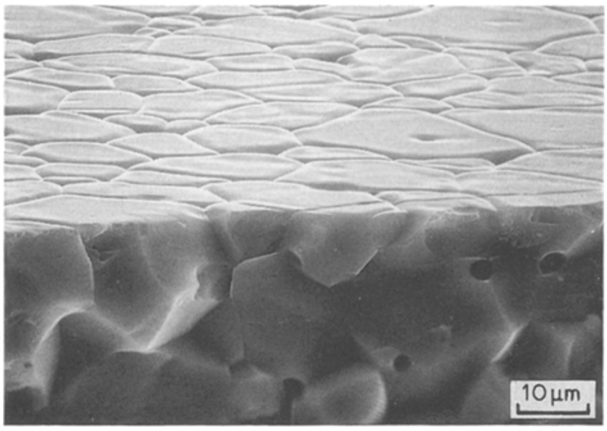

Figure 5 Scanning electron micrograph of thermally etched polycrystalline surface of $CaTiO_3$. $T = 1400°C$, $t = 8h$.

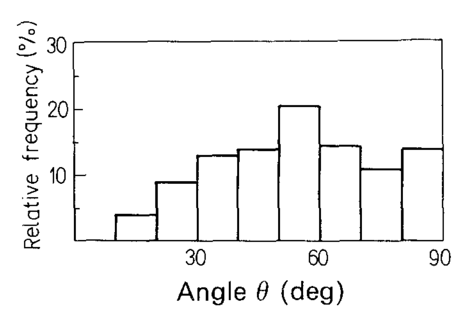

Figure 6 Distribution of angles between the random test line and the grain-boundary direction. $\theta = 53.5°$.

internal grain boundaries intersect the surface at random angles, depending where the grain has been cut through. On the surface, grain-boundary grooving caused by thermal etching can be observed. Grain boundaries with humps on both sides are clearly distinguished. The surface orientation of single grains is unknown, so presumably the surface energy of grains differs. This, and the fact that internal boundaries intersect the surface at random angles, probably caused a displacement of about 0.1 to 0.3 μm of some grains above the surface of the sample. The results of groove width measurement are given in Table I. The values of w at a particular temperature and time were calculated according to Equation 4. The indicated precision is given in terms of the standard deviation. The value a in Equation 3 was obtained on the basis of measurement of about 200 groove widths at each temperature and time. The average angle θ of the intersection between the direction of the grain boundaries and the random line analysis of the surfometer was determined on the basis of stereological analysis of the microstructure of $CaTiO_3$ to be 53.5° (Fig. 6). The indicated precision is again given in terms of the standard deviation. A plot of ln (w) against ln (t) for different temperatures of heat treatment is shown in Fig. 7. Straight lines with slopes between 0.22 and 0.26 were found for the temperature range from 1200 to 1350° C, indicating that surface diffusion was the predominant mechanism of grain-boundary grooving in the temperature range studied. For the temperature of 1450° C the slope of the line increased to a value close to 1/3, which is the characteristic value for volume diffusion mechanism. We can assume that at higher temperatures the volume diffusion mechanism is dominant. The derived surface diffusion coefficients for the range 1200 to 1350° C are shown in Fig. 8. A line of form

$$D_s = D_s^0 \exp(-Q_s/RT) \qquad (5)$$

was fitted by least squares analysis to the points, giving $D_s^0 = 1.8 \times 10^3\,\mathrm{cm^2\,sec^{-1}}$ and $Q_s = 330 \pm 30\,\mathrm{kJ\,mol^{-1}}$. There appears to have been no previous measurements of surface diffusion on $CaTiO_3$ or any related perovskites with which to compare the present results. Surface diffusion can occur by two mechanisms: surface vacancy, or adatom [8]. The adatom theory predicts that the activation energy of surface diffusion, Q_s, is approximately equal to two-thirds of the heat of evaporation of the material. Because there are no available data for the activation energies of bulk diffusion of $CaTiO_3$ and the enthalpy of sublimation, it is not possible to conclude whether surface diffusion in $CaTiO_3$ occurs by surface vacancy or adatom mechanism. Nevertheless, the value of the surface diffusion activation energy of 330 kJ mol^{-1} obtained is comparable with values of activation energies for surface diffusion of Al_2O_3 and MgO [6, 8].

TABLE I The results of groove-width measurement

T (° C)	t (h)	ln (t)	w ± S.D.(μm)	ln (w ± S.D.)
1200	8	2.079	1.54 ± 0.08	0.43 ± 0.02
	16	2.772	1.76 ± 0.07	0.57 ± 0.02
	24	3.178	1.90 ± 0.08	0.64 ± 0.03
	32	3.446	2.13 ± 0.09	0.76 ± 0.03
1250	8	2.079	1.70 ± 0.09	0.53 ± 0.04
	16	2.772	1.99 ± 0.11	0.69 ± 0.04
	24	3.178	2.19 ± 0.12	0.78 ± 0.04
	32	3.466	2.32 ± 0.13	0.84 ± 0.04
1300	8	2.079	2.27 ± 0.12	0.82 ± 0.04
	16	2.772	2.60 ± 0.12	0.96 ± 0.05
	24	3.178	2.91 ± 0.12	1.07 ± 0.04
	32	3.466	3.23 ± 0.16	1.17 ± 0.04
1350	10	2.303	2.88 ± 0.09	1.06 ± 0.04
	20	2.995	3.21 ± 0.09	1.17 ± 0.05
	30	3.401	3.55 ± 0.14	1.27 ± 0.05
	40	3.689	3.92 ± 0.13	1.37 ± 0.05
1450	8	2.079	4.04 ± 0.35	1.39 ± 0.09
	16	2.772	5.26 ± 0.35	1.66 ± 0.09
	24	3.178	6.02 ± 0.3	1.79 ± 0.09
	32	3.466	6.78 ± 0.35	1.92 ± 0.10

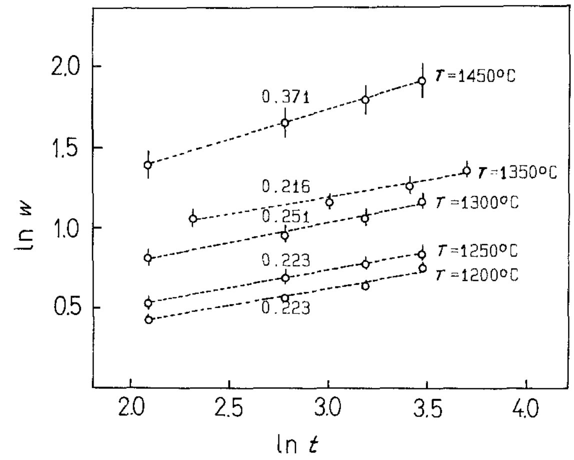

Figure 7 Ln (w) as a function of ln (t).

6. Conclusions

1. A new approach for measuring groove width on polycrystalline samples is described.

2. In the range from 1200 to 1350° C, grain-boundary

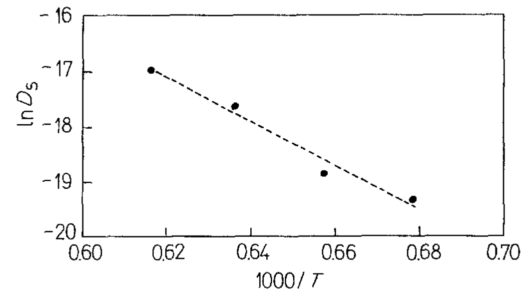

Figure 8 Ln (D_s) as a function of 1000/T.

grooving in $CaTiO_3$ occurs by a surface diffusion mechanism.

3. Surface diffusion in $CaTiO_3$ in air occurs according to the following relation

$$D_s = D_s^0 \exp(-Q_s/RT)$$

with $D_s^0 = 1.8 \times 10^3\,cm^2\,sec^{-1}$ and $Q_s = 330 \pm 30\,kJ\,mol^{-1}$.

4. At 1450° C and above, surface diffusion is suppressed. Grooving occurs by a volume self-diffusion mechanism.

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