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EVALUATION OF DILATOMETRIC TECHNIQUES FOR STUDIES OF SINTERING KINETICS

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Abstract. The kinetics of the initial sintering stage of CeO_2 is evaluated by three different techniques: constant heating rate dilatometry, constant shrinkage rate dilatometry and a new technique recently introduced by the authors called Stepwise Isothermal Dilatometry (SID).

Comparative measurements with these techniques showed that too high activation energies were obtained with the two first techniques, both of which can be termed as nonisothermal, whereas activation enegies comparable to those reported for cation diffusion in other fluorite oxides were obtained with the latter technique. Of the three techniques SID is thus considered to be the most accurate for studies of the sintering kinetics. In contrast to the two nonisothermal techniques SID has the further advantage that both the controlling mechanism and its activation energy can be determined in a single exper-

iment. From the SID-measurement it was concluded that the initial sintering stage of CeO_2 is controlled by grain-boundary diffusion.

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CONTENTS

1. INTRODUCTION

Shrinkage curves determined by isothermal dilatometric measurements have previously been used by Johnson (1) to study the kinetics of the initial sintering stage for many materials. For these measurements it is important that the samples be in thermal equilibrium right from the beginning of the sintering.

As this cannot be obtained in practice Johnson introduced a time and length correction technique and, furthermore, recommended the use of the differential form of the sintering equation which is insensitive to errors in time. However, kinetic analysis by this method is rather time consuming since it requires several measurements, each at a different temperature.

As a simple and quick method for studies of sintering kinetics Young and Culler (2) introduced the nonisothermal technique by which the sample is heated at a constant rate (see Fig.1-a). The shrinkage curve by this technique is evaluated under the assumption that a single mechanism is operating. An effective activation energy is calculated and this is used to distinguish among the various possible mechanisms. Parallel mechanisms of similar activation energies thus cannot be separated by this technique. By repeating the measurements using several heating rates Woolfrey and Bannister (3) however, showed that it is also possible to identify the mechanism and calculate its activation energy by this technique.

Recently, another nonisothermal technique was introduced by Criado (4). By this technique, which also has been used by Huckabee at al (5) in sintering studies on oxides powders, the sample is heated in such a way that the shrinkage rate is kept constant; this characteristically produces an oscillating temperaturetime curve as shown in Fig. 1-b. In order to identify the controlling mechanism and to determine its activation energy, this method also requires several measurements with different shrinkage rates.

Finally, a new isothermal technique calle? "Stepwise Isothermal Dilatometry" (SID) has recently been introduced by the authors (6,7,8). In contrast to the above-mentioned technique, SID has the advantage that both the controlling mechanism and its activation energy can be determined in a single experiment. As shown in Fig. 1-c by this technique the overall heating of the sample is controlled by the shrinkage rate, i.e. by the dl/dt-signal as measured by an electronic derivator. When this signal becomes larger than a preset limit, the heating is automatically stopped and the sintering now proceeds isothermally until the dl/dt-signal again becomes smaller than the preset limit at which point the heating is resumed. By this technique the sintering thus takes place in isothermal steps from which accurate kinetic data can be evaluated.

In the present work dilatometric measurements are described that use the constant heating rate, constant shrinkage rate and the stepwise isothermal techniques. These measurements were performed on the same material, cerium oxide, with the purpose of evaluating the variations among the three techniques. Only initial sintering stage kinetics is considered in this work.

2. THEORY

The equations describing the three techniques can be derived from the general shrinkage equation:

$$y = \Delta l/l_0 = (K_0/T)^n \exp(-nQ/RT) \cdot t^n \qquad (1)$$

where Δl = shrinkage

l_0 = initial sample length

K_0 = prexponential factor of Arrhenius equation

Q = activation energy

T = absolute temperature

R = gas constant

t = time

n = constant depending on the sintering mechanism.

The following equations were used to evaluate kinetic data for the three techniques:

1. Constant heating rate (3)

$$\dot{y} = (K_0 TR/n\beta Q)^n \exp(-nQ/RT) \qquad (2)$$

where β is the heating rate ($^\circ$C/min).

On taking the logarithm on both sides of Eq. 2 we have

$$\ln y = -n\ln\beta + n\ln (K_0 RT/nQ)-(nQ/R)(1/T) \qquad (3)$$

where the two last terms on the right-hand side are constant at constant temperature. Plotting lny versus lnβ for constant temperature values should thus produce a straight line from which the n-value can be determined from the slope. When n is known Eq. 3 can also be used to calculate the activation energy Q.

2. Constant shrinkage rate

$$y(1/n-1)\dot{y} = (nK_0/T)\exp(-Q/RT)(1 + (Q/RT^2)t dT/dt) \qquad (4)$$

where $\dot{y}$ is the shrinkage rate. This equation is obtained on differenting Eq. 1.

If the second term is neglected, Eq. 4 can be reduced to the form used by Criado (4), which is

$$y^{(1/n\ -1)} \cdot C = (K_0/T)\exp(-Q/RT) \tag{5}$$

where C is the constant shrinkage rate used in these measurements. Equation 5 is thus valid only if the measurements are carried out isothermally, i.e $dT/dt = 0$, which, however, is not the case with this technique as discussed above.

3. Stepwise Isothermal dilatometry.

For SID the following equation has been derived previously (6,7.8):

$$\dot{y} = (nK_0/T)\exp(-Q/RT)y^{(1-1/n)} \tag{6}$$

Eqution 5 can be expressed also as

$$\ln y = \ln(K(T)/N) - (N-1)\ln y \tag{7}$$

where $N = 1/n$ and $K(T) = (K_0/T)\exp(-Q/RT)$ is the Arrhenius constant.

Plotting $\ln\dot{y}$ versus $\ln y$, both of which can be determined for any point on the recorded dilatometric curve (Δl vs. t), a straight line should thus be obtained for each isothermal step from which both N and thus n as well as the activation energy Q, can be determined.

3. EXPERIMENTAL

The measurements were performed in a horizontal dilatometer (Netzch type 402E) in oxygen in an Al_2O_3 sample holder. The electronic regulator used for the SID measurements has been described previously (1,2). For the measurements at constant shrinkage rate the Standard Netzsch programme regulator (401) was modified so that the sample was heated or cooled when the shrinkage rate was smaller or larger, respectively, than a preset value.

Cylindrical compacts were prepared by pressing CeO_2 (99,9% purity) powder at $3t/cm^2$. This powder had already been milled for 50 h, which is assumed to produce nearly spherical particles of uniform size which make the use of Eq. 1 reasonable. The BET surface area of the milled powder was 4.59 m^2/g and the green density of the pressed compacts was 61% TD.

4. RESULTS AND DISCUSSION

4.1 Stepwise Isothermal Dilatometry (SID)

The shrinkage curves recorded for each isothermal step were fitted polynomially and the shrinkage rate $,\dot{y}$, was calculated from the expression obtained. Plotting log $\dot{y}$ versus log y produced a set of nearly parallel straight lines (see Ref. 8) as predicted from Eq. 7. The average n value obtained from the slopes of these lines was 0.33 indicating that the controlling mechanism of the initial sintering stage is grain-boundary diffusion (9). The activation energy for this mechanism was found to be 119.4 kcal/mole (5.2eV). This activation energy corresponds well with the values reported by Matzke (10) for cation diffusion in other fluorite oxides (5.6eV for UO^2 for instance).

4.2 Constant heating rate measurements

Three measurements were performed using the heating rates: 0.6, 2.4 and 13.4°C/min. Figure 2 shows the ln y vs lnβ plots at four temperatures which according to Eq. 3 should give a straight line. Some scatter is observed indicating that this equation is not completely fulfilled. Furthermore, drawing the best line through the data points, two set of lines with different slopes are apparently obtained at low and high temperatures respectively. The n-values calculated from these lines are 0.36 and 0.31 corresponding to activation energies of 166.7 and 131.2 kcal/mole, respectively. Only the latter n-value agrees reasonably well with the results obtained with the SID technique, whereas the activation energy corresponding to the n-values is too large. It has been suggested that the observed change in slope could be due to surface diffusion effects (2). In a previous study by one of the authors it was observed that surface diffusion can affect only the very beginning of the initial sintering stage,which is also supported by the studies of Bannister et. al. (11) who concluded that surface diffusion is negligible. The variation in slope together with the scatter observed between data points may thus suggest a lack of equilibrium during the continuous heating of the sample.

4.3. Constant shrinkage rate measurements

The variation of temperature, sample length and the dl/dt-signal during a constant shrinkage rate measurement is shown schematically in Fig. 3a. In order to keep the shrinkage rate constant the temperature typically oscillates around a mean value, which however, increases with time. Depending on the heating/cooling rate used, this temperature oscillation will inversely affect the shrinkage rate such that this rate generally becomes smaller when the temperature decreases than during a temperature rise. As illustrated in Fig. 3b, which shows sample length and temperature measured experimentally, this effect is very large at high heating rates, but even at 1°C/min a true constant shrinkage rate could not be obtained - the rate

during the heating period was nearly twice that obtained during the cooling period. The assumption for the simplified equation proposed by Criado (4) that $dT/dt = 0$ is thus generally not valid for these measurements.

Assuming that the sample can attain thermal equilibrium with the surroundings instantaneously dT/dt can be zero only at the maximum and minimum points of the oscillating temperature curve. Using the Δl values measured at these points and plotting these against $1/T$ the plot shown in Fig. 4 was obtained. Except for the point at the lowest temperature this plot appeared to be linear as predicted from Eq. 5, and using the value of n determined by SID (0.33) the activation energy calculated from this line was 151.5 kcal/mole. Compared to the SID technique, constant shrinkage rate measurements thus seem to give too high activation energies, and apparently neither equilibrium nor the condition that $dT/dt = 0$ is strictly obtained by this technique.

5. CONCLUSIONS

From the comparative measurements carried out on the same material, CeO_2, using Stepwise Isothermal Dilatometry (SID), constant heating rate dilatometry and constant shrinkage rate dilatometry it was shown that deviations from equalibrium in the two latter techniques may considerably affect the results obtained by the kinetic analysis. Only in the case of SID could activation energies comparable to those reported for cation diffusion for similar oxide systems be obtained and this technique thus seems to give the most accurate results. In contrast to the non-isothermal techniques, SID futhermore has the advantage that it can give informatin both about the controlling mechanism as well as its activation energy in a single experiment.

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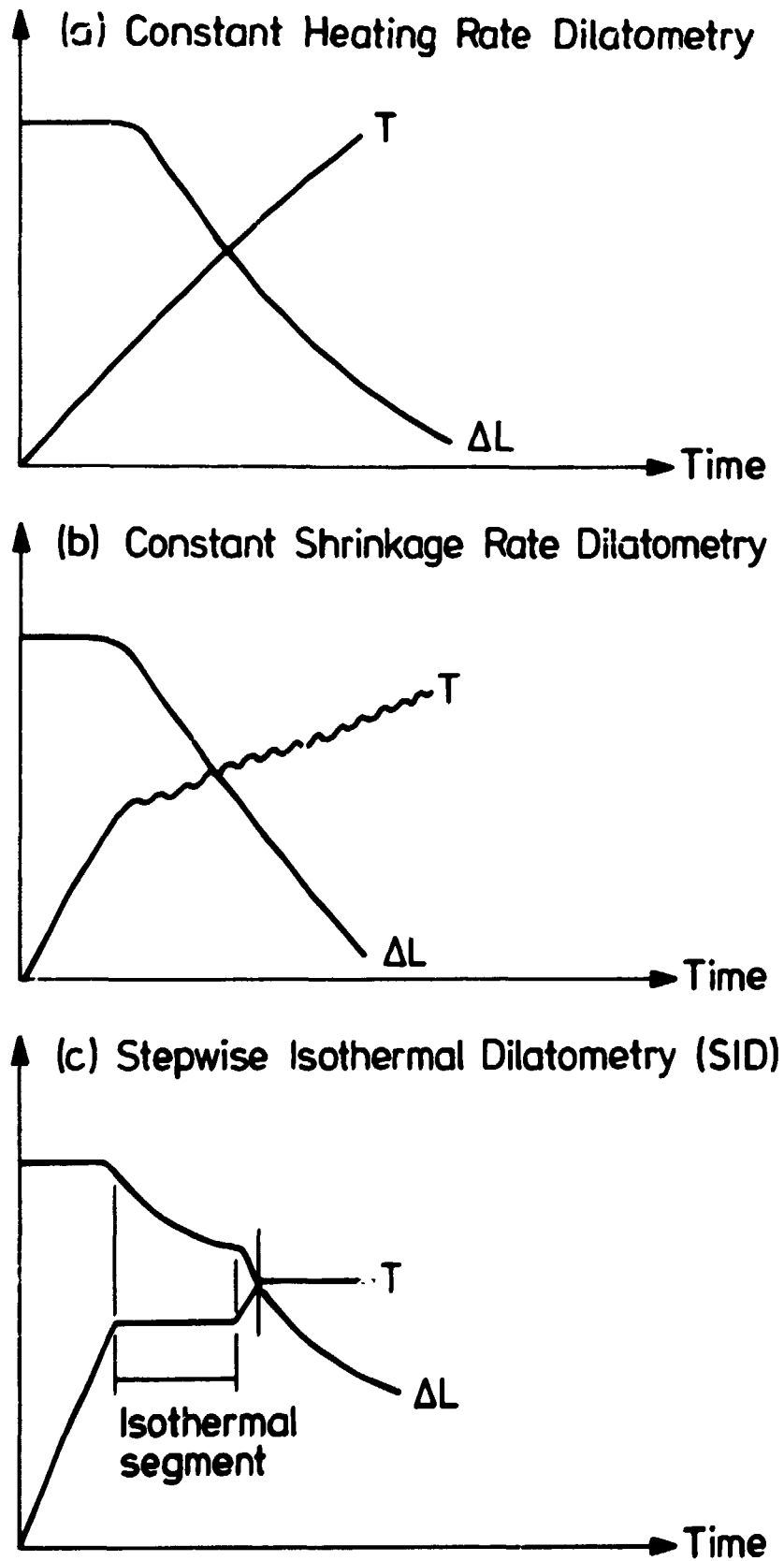
Fig. 1. Characteristic shrinkage and temperature curves for the three techniques considered.
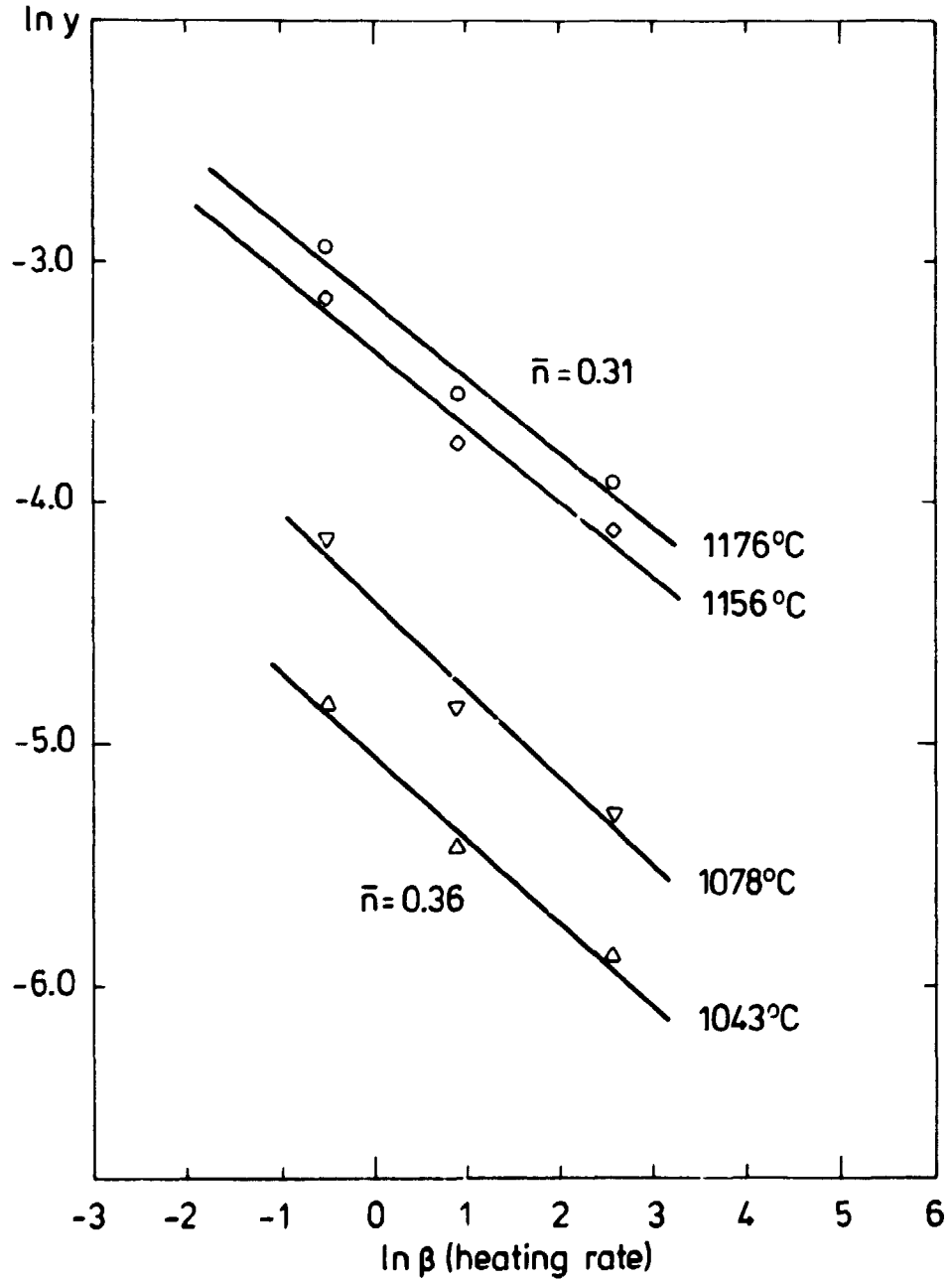
Fig.2. Shrinkage versus heating rate curves for sintering at various temperatures obtained by constant heating rate measurements.
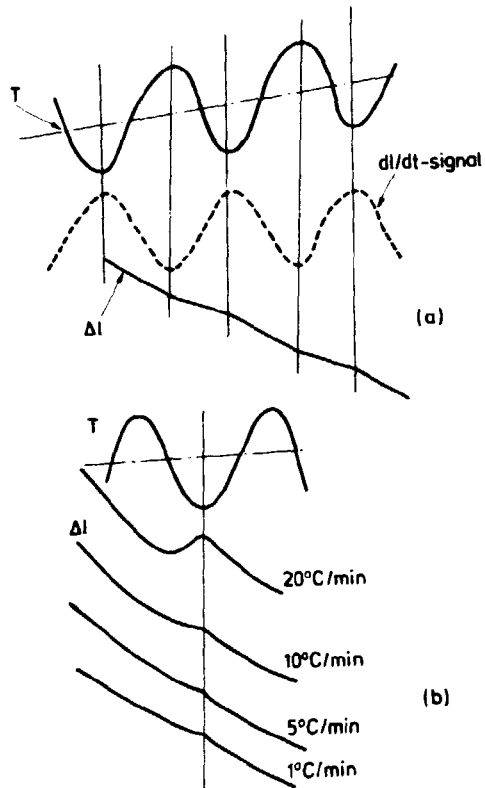
Fig. 3. Variation of temperature, shrinkage and shrinkage rate during constant shrinkage rate measurements.
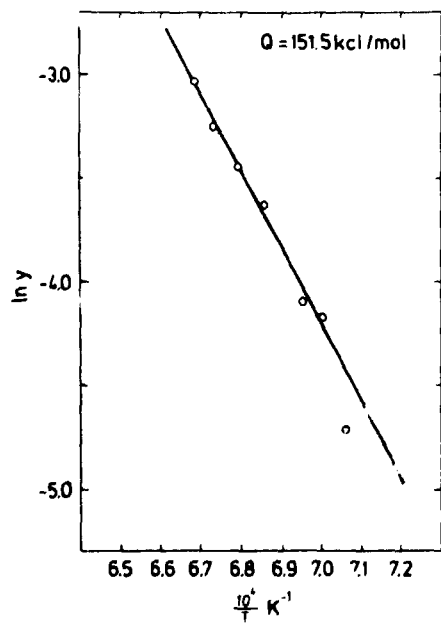
Fig. 4. Shrinkage versus 1/T plot for constant shrinkage rate measurements.