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Initial Sintering Stage Kinetics of CeO_2 studied by Stepwise Isothermal Dilatometry

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**Risø National Laboratory, DK-4000 Roskilde, Denmark
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INITIAL SINTERING STAGE KINETICS OF CeO₂ STUDIED BY STEPWISE
ISOTHERMAL DILATOMETRY

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Abstract. The kinetics of the initial sintering stage of CeO₂ is studied by a new dilatometric technique in which the heating of the sample is controlled by its shrinkage rate. By this technique the shrinkage characteristically takes place in "isothermal steps" which allows both the mechanism and its activation energy to be determined in a single experiment. The basic equations necessary to evaluate the shrinkage data are described, and using these equations on the curves recorded for CeO₂ it is shown that the controlling mechanism for the initial sintering stage for this oxides is grain-boundary diffusion of Ce⁴⁺-ions with an activation energy of 119.4 kcal/mole (5.2 eV). The corresponding diffusion coefficient is estimated to vary between 8.5×10^{-17} - 3.1×10^{-15} cm²/sec (1005 - 1099°C).

INIS Descriptors: ACTIVATION ENERGY; CERIUM OXIDES; DILATOMETRY; ISOTHERMAL PROCESSES; KINETICS; POWDER METALLURGY; SHRINKAGE; SINTERING

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1. INTRODUCTION

Stepwise Isothermal Dilatometry (SID) is a new technique which has been proven to be very useful in sintering studies of ceramic powders (1,2). Compared to conventional dilatometry, where the sample is heated at a constant rate, SID has the advantage that both the controlling mechanism and the activation energy can be accurately determined for the initial sintering stage in a single experiment. This has been demonstrated in previous publications for UO_2 (1) and UO_{2+x} (2). The sintering behaviour of CeO_2 powders is studied in the present work. From the experimental results obtained by this technique, it is concluded that the controlling mechanism of the initial sintering stage for CeO_2 is grain-boundary diffusion of Ce-ions with an activation energy of 119.4 kcal/mole (5.2 ev).

2. STEPWISE ISOTHERMAL DILATOMETRY

A characteristic feature of the SID-technique is that the heating of the sample (powder compact) is controlled by the magnitude of the derived signal, i.e. the dimensional change signal dl/dt which can be produced by an electronic differentiator. When this signal is smaller than a preset limit the sample is heated at a constant rate, whereas the temperature is kept constant whenever the dl/dt -signal exceeds a second preset limit. The sintering thus characteristically takes place in "isothermal steps" (see Fig. 1) where the time span of each step depends upon the sintering rates and it can be controlled by the setting of the two threshold values. In the present study the setting was chosen according to previous experience (3) such that the time at the isothermal steps was sufficiently long to allow an accurate analysis of the recorded shrinkage to be made.

3. THEORY

For each "isothermal step" in the initial sintering stage the densification can be considered to follow the expression:

$$y = \Delta l/l_0 = (K(T) \cdot t)^n \quad (1)$$

where

$$K(T) = A \cdot \gamma \cdot \Omega \cdot D / k \cdot T \cdot r^p \quad (2)$$

In these equations

- l_0 = initial sample length at the start of sintering
- $K(T)$ = Arrhenius constant
- D = diffusion coefficient (cm/sec.)
- r = particle radius (cm)
- γ = surface tension (erg/cm²)
- Ω = vacancy volume (cm³)
- A, n, p = constants whose values depend on the sintering mechanism.
- k = Boltzmann constant

In order to apply this equation it is necessary that both the shrinkage and the time can be measured from the recorded curve. As the initial sintering stage, however, extends over several steps it is impossible to determine the absolute time involved in the single steps; thus the time variable must therefore be removed from Eq. (1) before it can be used directly. This can be done by differentiation, which gives

$$\dot{y} = (K(T)/N) \cdot y^{-(N-1)} \quad (3)$$

where \dot{y} is the shrinkage rate and $N = 1/n$.

Equation (3) can also be expressed as

$$\ln \dot{y} = \ln (K(T)/N) - (N-1) \ln y \quad (4)$$

and on plotting $\ln \dot{y}$ versus $\ln y$, both of which can be determined for any point on the recorded curve, a straight line will be obtained for each isothermal step. From these steps the value of N and thus n can be determined from the slope and $K(T)$ from the intercept with the $\ln \dot{y}$ axis.

On taking the logarithm on both sides of the Arrhenius expression, we obtain

$$\ln (K(T)) = \ln A - Q/RT \quad (5)$$

where A is the pre-exponential factor and Q the activation energy. Both can be determined by plotting the $\ln(K(T))$ values found for the isothermal steps versus $1/T$. Finally the diffusion coefficient can be determined from Eq. (2) when $K(T)$ and the particle size of the powder is known. In this work the latter is estimated from the specific surface area of the powder.

EXPERIMENTAL

The dilatometric measurements were performed in a horizontal dilatometer* in an oxygen atmosphere. The sample holder used was made of Al_2O_3 . Cylindrical compacts were prepared by pressing CeO_2 (99.9% purity) powder at 3 t/cm^2 which had already been milled for 50 h. This treatment is assumed to produce nearly spherical particles of uniform size, which make the use of Eq. 1 reasonable. The green density of these compacts is 61%TD. The BET surface area of the powder was $4.59 \text{ m}^2/\text{g}$.

* Netzsch Dilatometer type 402E

4. RESULTS AND DISCUSSION

4.1. Controlling mechanism

The shrinkage curves recorded for each isothermal step were fitted polynomially and the shrinkage rate was calculated as a function of the shrinkage (y) from the expression obtained. Plotting these according to Eq. 4, i.e. in a $\log \dot{y}$ (shrinkage rate) versus $\log y$ (shrinkage) plot, a set of nearly parallel straight lines is obtained, as shown in Fig 2. From the slope of these lines an average value of $n = 0.33$ can be calculated from Eq. 4 indicating that the shrinkage kinetics of the initial sintering stage of CeO_2 is controlled by grain-boundary diffusion (5). This model has been recently reexamined and it was found to be still valid (6). A similar conclusion was reached in sintering studies on similar oxides with the fluorite structure (1,2,7,8).

In a previous study it was found by one of the authors that surface diffusion may contribute simultaneously with grain boundary diffusion (7). However this can affect only the very beginning of the initial stage. A technique has been described by D.L. Johnson (9) in which neck radius vs. shrinkage could reveal the surface diffusion contribution, but this technique is both time consuming and subject to experimental errors. Using this technique Bannister et al (10) found that surface diffusion is negligible which support our findings that surface diffusion only affect the very beginning of the initial sintering stage.

4.2. Activation energies

The $\ln(K(T))$ values determined from the intercepts of the lines shown on Fig. 2 are plotted against $1/T$ in Fig. 3. A straight line is again obtained as expected from Eq. 5, which shows that

the isothermal steps considered all are governed by the same process and that they all belong to the initial sintering stage. The activation energy calculated from the slope of this line is $Q = 119.4$ kcal/mole (5.2 eV) which corresponds well with values reported by Matzke (11) for cation diffusion in other fluorite oxides: 5.6 eV for UO_2 and 6.5 eV for ThO_2 . This activation energy is, however, much bigger than that reported for oxygen diffusion in CeO_2 (1.0 eV, see Ref. 12) and it can be suggested that it is grain-boundary diffusion of the Ce-ions that controls the sintering rate in the initial stage for this oxides. To the authors' knowledge activation energies for Ce-diffusion in CeO_2 have not previously been published.

4.3. Diffusion coefficients

The diffusion coefficients for Ce-diffusion were calculated from the $K(T)$ values determined for the isothermal steps according to Eq. 2 using the surface area of the CeO_2 powder to estimate the average particle size. The coefficients obtained ranged between $8.5 \times 10^{-17} - 3.1 \times 10^{-15}$ cm^2/sec for the temperature range considered (1005 - 1099°C). These values are comparable with those calculated from sintering studies for other fluorite structure oxides, for instance UO_2 (1).

CONCLUSIONS

The experimental data obtained by using stepwise isothermal dilatometry suggest that the rate controlling mechanism for the initial sintering stage of CeO_2 is grain-boundary diffusion of Ce-ions. The activation energy for this process was found to be 119.4 kcal/mole (5.2 eV) which agrees well with the values of the activation energies for cation diffusion in other fluorite oxides. For the temperature range 1005 - 1099°C the diffusion coefficients ranged between $8.5 \times 10^{-17} - 3.1 \times 10^{-15}$ cm^2/sec .

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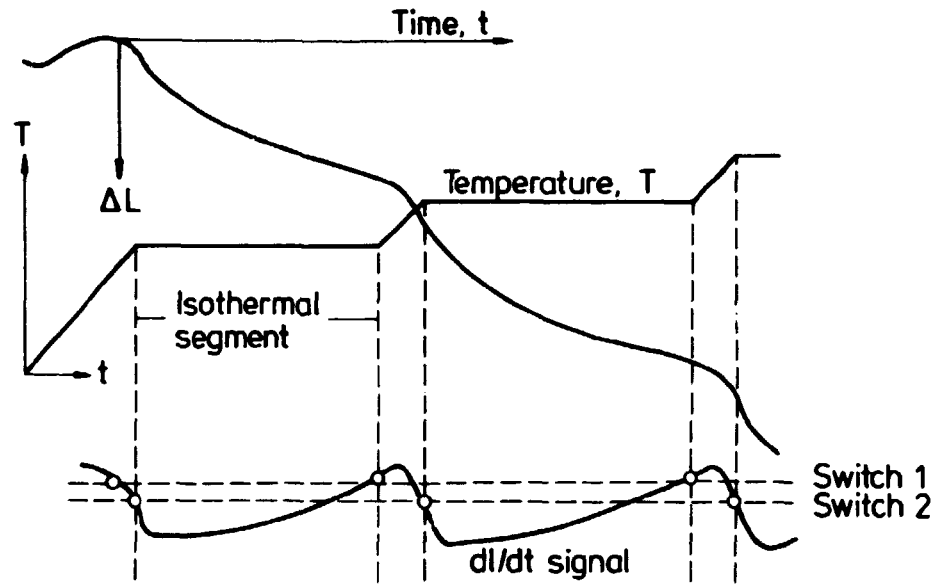


Fig. 1. Example of shrinkage and temperature curve recorded during stepwise isothermal dilatometry (SID) measurement.

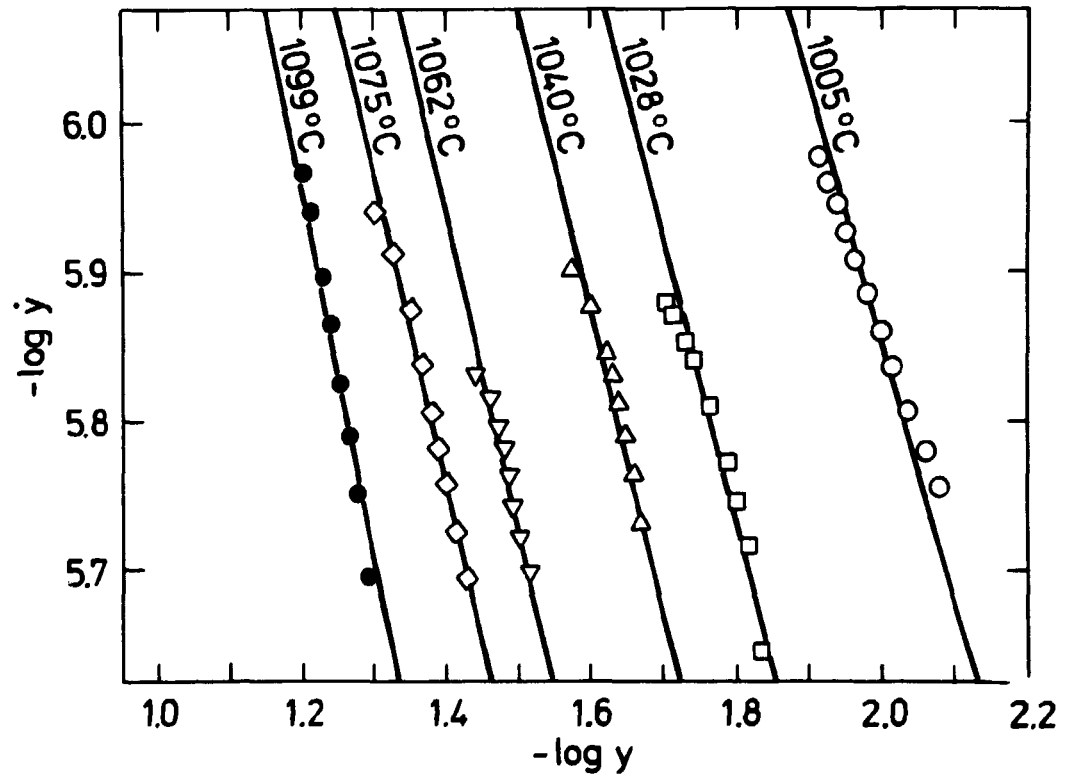


Fig. 2. Shrinkage rate versus shrinkage for isothermal steps during sintering of CeO_2 -powder compact.

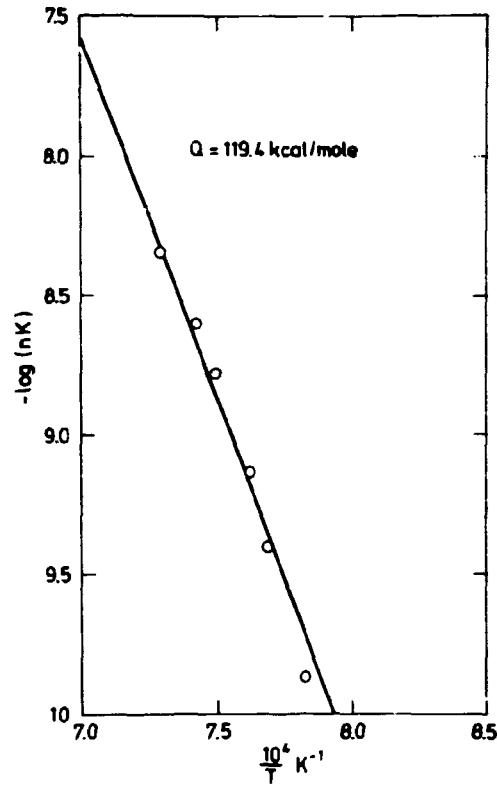


Fig. 3. Arrhenius constant ($K(T)$) versus reciprocal temperature, $1/T$, for sintering of CeO_2 -powder compact.

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