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QUASI-ISOTHERMAL DILATOMETRIC STUDIES OF THE INFLUENCE OF OXYGEN PRESSURE ON THE INITIAL SINTERING STAGE OF UO_2 POWDER COMPACTS

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Quasi-isothermal dilatometry (QID) is a useful technique for sintering studies of powder compacts. In the present work the principle of this technique and the method of calculating activation energies from the QID curves is first described; then, using this method, the sintering mechanism and the influence of oxygen pressure on the initial sintering stage of UO_2 *compacts are evaluated. The controlling mechanism was found to be grain boundary diffusion of uranium vacancies with an activation energy of 234 kJ/mole in accordance with literature data.*

Quasi-isothermal dilatometry /QID/ is a useful technique for sintering studies, since kinetic data, diffusion coefficients, as well as the optimum sintering conditions can be determined in a single experiment. This has been demonstrated in several previous publications [1,2] in which methods of calculating these data from the QID-curve are also described. Using the latest and most accurate of these methods [2], the influence of oxygen pressure on the initial sintering stage of UO_2 compacts is studied in the present work.

PRINCIPLE OF QID

The overall heating rate of the compact is characteristically determined by the shrinkage rate in this technique. This is

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obtained in the following way: The compact is heated in the dilatometer at a constant rate until the dl/dt-signal, which is proportional to the shrinkage rate, becomes larger than a preset limit, at which point the heating is stopped. Shrinkage now continues isothermally until the dl/dt-signal again becomes smaller than a second preset limit, at which point heating is resumed. The whole sintering cycle thus characteristically takes place in isothermal segments at different temperatures as shown in Fig. 1.

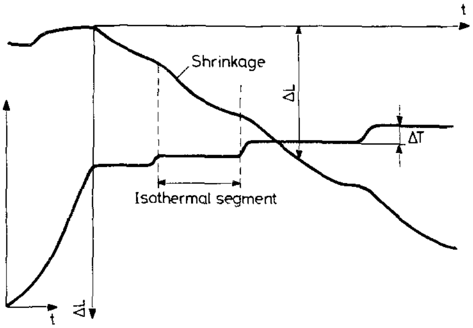

Fig. 1. QID /quasi-isothermal dilatometric/ curve

THEORY

For the overall shrinkage within the initial sintering stage, the following equation applies [2]:

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

where $y = \Delta l/l_o$, $\dot{y}$ = overall shrinkage rate, and $N = 1/n$ /n being a constant characteristic of the sintering mechanism/. $K(T)$ is the Arrhenius constant, which can be expressed as:

$$K(T) = K_o \cdot \exp(-Q/RT) \qquad (2)$$

Q being the activation energy.

Equation (1) can also be expressed as

$$(N-1)\ \ln y = \ln\ (K(T)) - \ln N - \ln \dot{y} \qquad (3)$$

and on plotting $\ln y$ versus $\ln \dot{y}$, both of which can be determined for each segment, a straight line will then be obtained from which N and thus n can be calculated from the slope. Finally, when N is known, $K(T)$ and therefore Q and D can easily be calculated.

EXPERIMENTAL

The QID measurements were performed in a horizontal Netzsch dilatometer in a sample holder of Al_2O_3. The optimum experimental conditions found in a previous study [3] were also used in this work. UO_2 pellets with green densities of 5.8 g/cm^3 were sintered in H_2-atmospheres containing 1 and 10% CO_2, respectively. The surface area of UO_2 powder used was 5.97 m^2/g.

RESULTS AND DISCUSSION

If the shrinkage rates /ln$\dot{y}$/ obtained in the sintering experiments in the two atmospheres are plotted versus the corresponding shrinkage, nearly parallel straight lines are obtained in accordance with Eq. 3 /Fig. 2/. From the slopes of these lines a mean value of n of about 0.3 can be calculated, indicating that grain boundary diffusion is the controlling mechanism. In a previous study [2] this mechanism was also found to control the sintering of UO_2 in pure H_2.

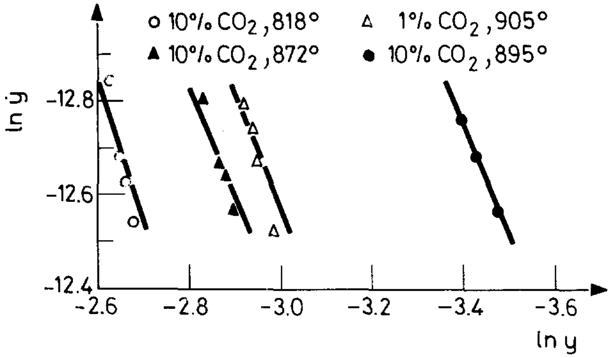

Fig. 2. Shrinkage rate versus shrinkage

Knowing n, and thus N, $K(T)$ can be calculated from Eq. 1. If the ln $K(T)$) values obtained are plotted against $1/T$, two nearly parallel lines are obtained, as shown in Fig. 3. The activation energy calculated from the slope of these lines /see Eq. 2/ is 234 kJ/mole, which is considerably smaller than the activation energy found in pure H_2 (390 kJ/mole, 94.75 kcal/ /mole, see Ref. [2]) where the composition is nearly stoichiometric.

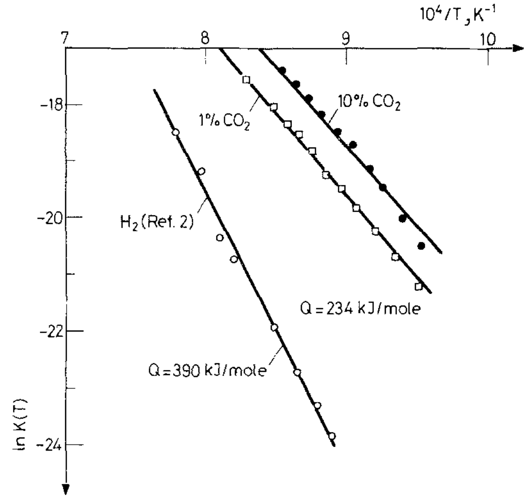

Fig. 3. Arrhenius plot of ln $K(T)$ versus $1/T$

The Q-value obtained in the present work corresponds closely to literature data obtained from initial stage sintering kinetics of UO_{2+x} [3÷5] and also to the estimated value of 45 ± 17 kcal/mole (188.3 ± 71 kJ/mole) for grain boundary diffusion [6]. Matzke's [7] atomistic model of the defect structure of fluorite type dioxides, predicts a value for the activation enthalpy for metal uranium diffusion in UO_{2+x} of 59.8 kcal/mole (250 kJ/mole), [2.6 ev] - which is close to the activation energy obtained in this work. This value of the activation energy, as shown from Fig. 3, is independent of the change in the composition of sintering atmosphere i.e. the percentage of added carbon dioxide in hydrogen. This agrees well with the model mentioned earlier which predicts this independency on degree of nonstoichiometry for hyperstoichiometric oxides. This model also predicts an increase in the concentration of uranium vacancies with x which, in turn, also agrees well with the observed increase in the shrinkage rate with increasing CO_2/H_2

ratio /see Fig. 2/. The initial sintering stage in these atmospheres thus seems to be controlled by the grain boundary diffusion of uranium vacancies as observed for stoichiometric $UO_{2.00}$ in a previous investigation [2].

CONCLUSION

The results obtained in the present work show that the initial sintering stage for slightly hyperstoichiometric uranium dioxide /UO_{2+x}/, which must be expected in the Co_2/H_2 atmospheres used here, is controlled by uranium vacancy diffusion along the grain boundaries formed. The activation energy found for this process is 234 kJ/mole.

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ZUSAMMENFASSUNG - Die quasi-isotherme Dilatometrie (QID) ist eine nützliche Technik für Sinterungsuntersuchungen von Pulverpresslingen. In der vorliegenden Arbeit werden zunächst das Prinzip dieser Technik und die Methode zur Berechnung von Aktivierungsenergien aus QID-Kurven beschrieben, danach werden, basierend auf mit dieser Methode erhaltenen Ergebnissen, der Mechanismus der Sinterung und der Einfluss des Sauerstoffdruckes auf das Anfangsstadium der Sinterung von UO_2*-Presslingen hergeleitet. Der geschwindigkeitsbestimmende Schritt ist die Korngrenzendiffusion von Uranfehlstellen mit einer Aktivierungsenergie von 235 kJ/mol, was in Übereinstimmung mit Literaturangaben steht.*

Резюме – Квазиизотермическая дилатометрия является полезным методом при изучении спекания порошковых материалов. В работе впервые описан принцип этого метода и способ вычисления энергий активации на основе кривых квазиизотермической дилатометрии. Используя этот метод установлен механизм спекания и влияние давления кислорода на начальную стадию спекания порошков двуокиси урана.Найдено, что определяющим механизмом спекания является диффузия вакансий в уране на границе зерен. Энергия активации этого диффузионного процесса составляет 235 кдж/моль что согласуется с литературными данными.