Thermochimica Acta, 58 (1982) 261–270
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

QUASI-ISOTHERMAL DILATOMETRIC SINTERING STUDIES ON UO_2 POWDER COMPACTS: METHOD OF EVALUATION AND INFLUENCE OF EXPERIMENTAL PARAMETERS

LARS HÄLLDAHL

ASEA-ATOM, Box 53, S721 04 Västerås 1 (Sweden)

(Received 10 March 1982)

ABSTRACT

The influence on the results of a quasi-isothermal dilatometry (QID) sintering experiment on UO_2 powder compacts by the setting of the experimental parameters has been investigated. A large value of the shrinkage rate that stops the heating decreases the number of steps, and also delays the definition of the first step to a higher temperature. A large difference between the shrinkage rates that stops, or resumes, the heating will decrease the number of steps.

An attempt has been made to evaluate kinetic data from QID curves and it has been found that only truly isothermal steps can be used, and that a step has to have a certain length to be able to give an acceptable accuracy in this evaluation.

INTRODUCTION

Quasi-isothermal dilatometry (QID) was introduced by Paulik and Paulik [1]. It is based on the same principle as quasi-isothermal thermogravimetric analysis, which has been described by Paulik and Paulik [2–4] and Sørensen [5,6], and used by Hälldahl and Sørensen to analyse the decomposition of ammonium uranyl carbonate [7]. Sørensen has demonstrated the advantages of this technique in sintering studies [8], and a first attempt to reveal the influences of experimental parameters on the QID results from sintering of some UO_2 powder compacts was presented by Hälldahl and Sørensen [9]. In this paper, a refined method to evaluate the kinetics involved in the initial stage of sintering is described, and in using this method the influence of experimental parameters upon the QID results are analyzed. An attempt has also been made to use a constant experimental setting to reveal differences in sintering kinetics, depending on different green densities in UO_2 powder compacts.

0040-6031/82/0000–0000/$02.75

TECHNIQUE AND EXPERIMENTAL PARAMETERS

The principle of the QID technique has been described in refs. 6, 8 and 9, but a brief resumé will also be given here. The specimen (powder compact) is heated at a constant rate, while the length of the sample and the corresponding temperature is recorded. When the derivative of the length with respect to time becomes larger than a preset value, the heating is stopped. This value is called an 'outer' limit. The temperature is held constant while the reaction, the densification, continues. When the densification rate decreases, and becomes smaller than another preset value, the reaction is defined as being completed, and heating is then resumed. This latter preset value is called an 'inner' limit. The densification thus characteristically takes place in isothermal steps, as shown in Fig. 1. The specimen is considered to sinter under conditions close to equilibrium by this technique [8]. The setting of the two limits then determines the number of temperature steps and the time at each step.

The following parameters are important.

(1) The magnitude of the 'outer' limit, that is, the dl/dt signal that stops heating. An increase in magnitude of this signal can be expected to result in a smaller number of steps, and in a higher onset temperature of the first isothermal reaction.

(2) The difference in magnitude between the dl/dt signals at the outer and the inner limit, respectively. A large difference will increase the time at each step, and will tend to reduce the total number of steps.

The method's ability to resolve close-lying or overlapping reactions is dependent on the total number of steps. With many small steps, it is more easy to differentiate between close-lying reactions, but on the other hand, a step has to have a certain length to be able to give an acceptable accuracy in the kinetic evaluation. The problem comes down to an optimalization between these two demands.

THEORY

To describe the densification of a real powder compact, the equation proposed by Thümmler and Thomma [10]

$$\frac{\Delta l}{l_0} = (Kt)^n = (Z\,e^{-Q/RT})^n t^n \tag{1}$$

can be used, where Δl is the change in length, l_0 the initial length, t the time, n is a constant that characterizes the densification process, and K is the Arrhenius constant. At each temperature step, the length changes can be normalized according to

$$l_N = \frac{l_0 - l_t}{l_0 - l_f} \times 100 = \frac{\Delta l}{l_0 - l_f} \times 100 \tag{2}$$

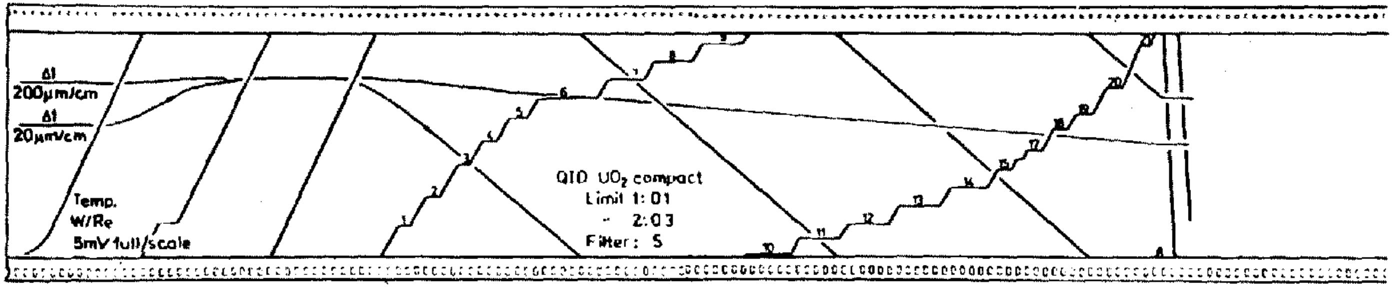

Fig. 1. QID curves (temperature and length) recorded during sintering of a UO_2 powder compact.

TABLE 1

Influence of experimental parameters

Experiment no.	$(dl/dt)_2$ (μm min^{-1})	$(dl/dt)_1$ (μm min^{-1})	$\Delta(dl/dt)$ (μm min^{-1})	First step (°C)	End, stage 1 (°C)	No. of steps stage 1
8	1.55	1.33	0.22	882	1045	11
1	1.62	1.50	0.12	892	1080	11
6	1.97	1.55	0.42	910	1060	7
4	1.98	1.50	0.48	912	1050	7
3	2.01	1.50	0.51	911	1080	7
2	2.03	2.03	~0			∞
9	2.81	2.41	0.40	945	1095	8
7	3.12	2.28	0.84	1161		0

where l_t is the specimen length at time t, and l_f is the final length obtained at a given temperature step. This equation makes l_N go from 0 to 100 for each step.

Figure 2 gives an example of a real temperature step, and will be referred to in the description of the evaluation method. At A, the outer limit stops the heating, but because of the heat capacity of the furnace, the temperature is not constant until point B is reached. It is only the truly isothermal part of a step that can be used for kinetic evaluation, in this case the part between B and C.

The length of the sample when the reaction starts corresponds to l_0, and the final length corresponds to l_f. The time for this reaction is t. By measuring the change in length for intermediate times, and by using eqn. (2), a set of corresponding $\ln l_N$ and $\ln t$ values can be calculated. From such a set, the n value in eqn. (1) can be determined, either by linear regression or graphical plotting.

As the l_N and t values are plotted on logarithmic scales, the l_N–t sets large enough to be measured with acceptable accuracy will yield points lying close together in this plot. As the n value is taken as the slope of this plot, the following procedure was used to improve the evaluation of the n value. To get l_N–t sets for very short reaction times, it is assumed that the reaction rate at point B (Fig. 2) is constant for a short period of time. The slope of the dilation curve at this point can be measured with high precision; multiplying it by a small value of t, a reliable l_N–t set can thus be obtained for the very first part of the reaction.

To calculate the K value in eqn. (1), this equation can first be written in logarithmic form

$$\ln \frac{\Delta l}{l_0} = n \ln K + n \ln t \tag{3}$$

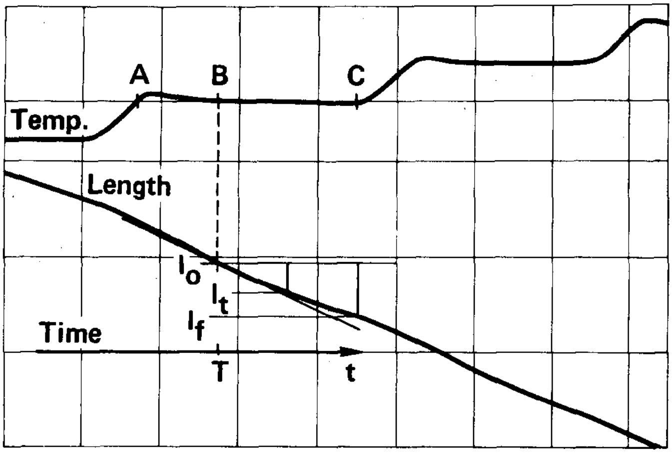

Fig. 2. Temperature and dilation track from one isothermal step.

applicable only under strictly isothermal conditions. Two new quantities are now defined. If L is the sample length at the start of the very first reaction in the QID experiment, and τ is the time the reaction should have taken, if it had been carried out at the actual isothermal temperature for the QID step to be evaluated, starting from the initial length L, then insertion in eqn. (3) gives, at B

$$\ln \frac{(L-l_0)}{L} = n \ln K + n \ln \tau \tag{4}$$

and at C

$$\ln \frac{(L-l_0+l_f)}{L} = n \ln K + n \ln(\tau + t) \tag{5}$$

In these two equations, there are two unknowns, K and τ, which can then be calculated.

This way to calculate K is therefore based on two points in the original graph, and it should give a better K value than would be obtained by solving eqn. (3) for point C only.

From eqn. (1) it can be seen that the activation energy, Q, can be obtained by plotting $\ln K$ values versus inverse temperature. The slope of this plot times R, the molar gas constant, then gives Q. The plot should be a straight line for steps belonging to the same reaction.

EXPERIMENTAL

The QID measurements were performed in a Netsch dilatometer in a horizontal Al_2O_3 sample holder. The correction due to the expansion of this sample holder (30 μm at 1500°C, compared with 1.5 mm for the sample) is negligible. The electronic derivator and regulator developed for the simultaneous thermoanalyzer was used in these experiments.

The UO_2 powder compacts were pressed from a standard powder taken directly from the production line in ASEA-ATOM's fuel factory. The green densities of the compacts used for evaluating experimental parameters were in the 5.50–5.54 g cm^{-3} range, and for the compacts used for evaluating the influence of green densities on the kinetics, the range was 5.04–5.75 g cm^{-3}.

The UO_2 compacts were sintered in a 2:1 mixture of H_2 and He, in the temperature range 20–1450°C. The different settings used for the inner and outer limits for the dl/dt signals are given in Table 1. The heating rate between the steps was 2°C min^{-1}.

RESULTS

The first part of the investigation deals with the influence of experimental parameters on the overall appearence of the QID curves. In Table 1 the experiment number, the outer limit, the inner limit and finally, the difference between these two limits are listed.

The column labelled 'first step' gives the temperature of the first isothermal step. As can easily be seen, this temperature is a function of the magnitude of the $(dl/dt)_2$ signal. At a low magnitude, the system at an early time defines the start of a reaction and then terminates the heating. When the 'outer' limit is large, however, the first definition of a reaction is delayed, and the temperature is raised. Changing the 'outer' limit from 1.55 μm min^{-1} to 3.12 μm min^{-1} thus makes the temperature of the first reaction increase from 882 to 1161°C.

From the plots of $\ln K$ vs. $1/T$ (one example is shown in Fig. 3), it is clear that the sintering starts with an initial stage during which the calculated activation energy is constant. The end of this stage is characterised by a change of slope in the $\ln K$ vs. $1/T$ plot, and the corresponding temperature is listed in the column labelled 'end stage 1'. All values in this column are reasonably expected to be at the same level, except for experiments 2 and 7, which are the two extremes.

The last column in Table 1 gives the resulting 'number of steps' within this initial stage.

DISCUSSION AND CONCLUSIONS

In experiment 8, the $(dl/dt)_2$ signal is set at the lowest value producing the lowest starting temperature. As even the $(dl/dt)_1$ signal is low, this requires many steps, 11. In experiment 1, the $(dl/dt)_2$ signal is increased, which should give fewer steps, but this is compensated for by a higher

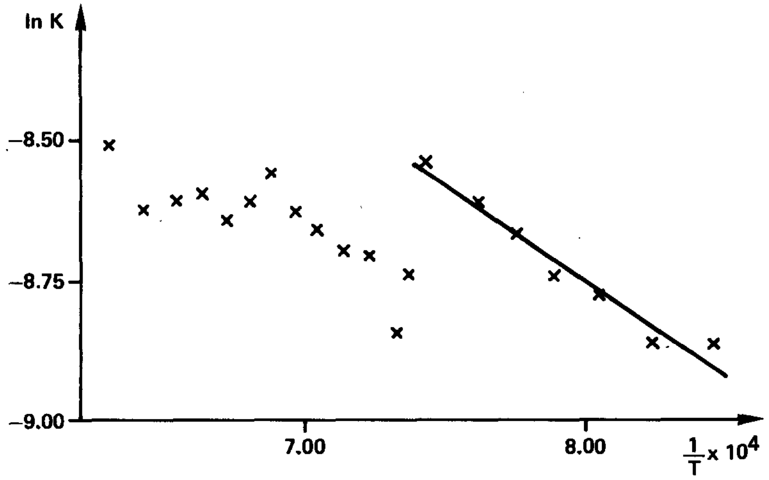

Fig. 3. Example of a $\ln K$ vs. $1/T$ plot (from experiment 3).

TABLE 2

Calculated activation energy

Experiment no.	Q (kJ mole^{-1})	r^2
8	7.44	0.27
1	24.0	0.85
6	23.7	0.94
4	26.2	0.99
3	28.2	0.96
2		
9	20.9	0.66
7		

$(dl/dt)_1$ signal, producing the lowest Δ (dl/dt) value, and this results in the same number of steps, 11.

The following three experiments were run with very small variations in $(dl/dt)_2$ and $(dl/dt)_1$ signals, and show the reproducibility of the QID method. The level of the $(dl/dt)_2$ signal is increased markedly compared with experiments 1 and 8. This yields a higher temperature for the first step, but should also give fewer steps. The increased $\Delta(dl/dt)$ value is expected to work in the same direction. The combined effect is that the number of steps are 7 for these three experiments.

Lowering of the $\Delta(dl/dt)$ value produces an increased number of steps and, as an example of this, experiment 2 is an extreme. The $\Delta(dl/dt)$ value equal to zero produces an infinite number of steps, which makes the appearence of the QID curve approach a constant heating experiment.

Experiment 9 shows that a certain $\Delta(dl/dt)$ value has a different influence at different levels of $(dl/dt)_2$ signal. By comparing experiment 9 and experiment 3, the larger $(dl/dt)_2$ signal in experiment 9 is expected to produce fewer steps but the simultaneous lowering of the $\Delta(dl/dt)$ value counteracts this strongly and the net result is an additional step.

The increase of both $(dl/dt)_2$ and $(dl/dt)_1$ signals in experiment 9 compared with 3, still gives roughly the same number of steps for the initial

TABLE 3

Influence of green density

Green density (g cm^{-3})	Q (kJ mole^{-1})	r^2	No. of steps stage 1
5.04	37.0	0.84	9
5.27	33.1	0.64	13
5.75	28.3	0.78	9

stage, but has other consequences. For the whole temperature range being analyzed, 20–1450°C, the total number of steps are 21 for experiment 3, and 25 for 9, but this takes 850 min for 3 and 600 min for 9. This has some influence on the kinetic evaluation, which shall be discussed below.

Experiment 7 is an extreme, as already pointed out. The highest $(\mathrm{d}l/\mathrm{d}t)_2$ signal combined with the highest $\Delta(\mathrm{d}l/\mathrm{d}t)$ value, gives at first the highest starting temperature, 1161°C, and also the fewest number of steps, only 7 for the whole temperature range. This parameter setting gives an analysis, not sensitive enough to resolve the initial stage.

Table 2 presents the kinetic data obtained during the initial stage. Q is the activation energy in kJ mole^{-1}, calculated from the slope of the $\ln K$ vs. $1/T$ plots, as outlined above. As an example, the plot from experiment 3 is shown in Fig. 3. r^2 is the regression coefficient from the linear regression analysis to obtain the slope from the plots. The value 1.00 corresponds to a perfectly straight line, and r^2 is here taken as a measure of validity for the Q value calculated.

For experiment 8, the r^2 value is very poor, indicating that the Q value is not to be trusted. This depends on the smallness of each step and the resulting poor evaluation precision caused by the large number of steps.

Experiments 6, 4 and 3 seem to reproduce the same Q value with reasonably satisfactory r^2 values.

Experiment 9, compared with 3, shows agreement in the resulting Q value, but the r^2 value is poorer for 9. This depends on the aforementioned faster reaction during experiment 9. Roughly the same number of steps in shorter time makes each step shorter and thereby increases the difficulties of evaluating it from the graph.

Experiments 2 and 7 cannot be used for calculating the Q value for the initial stage. The steps in experiment 7 are too few and too large to resolve the different stages.

The result obtained from the eight experiments shows that for the type of green pellets used, the optimum conditions for QID sintering are those of experiment 1. The r^2 value is slightly lower than for experiments 3, 4 and 6, but the Q value is at the same level. The larger number of steps, compared with the number obtained for experiments 3, 4, and 6, gives a better resolution of closely lying and overlapping reactions. Experiment 1 thus offers a good compromise between the accuracy obtained in kinetic evaluation and good sensitivity.

From the experiments, some general conclusions can be drawn.

(1) Increasing the 'outer' limit decreases the number of steps.

(2) Increasing the difference between 'outer' and 'inner' limits decreases the number of steps.

(3) The effect of decreasing the $\Delta(\mathrm{d}l/\mathrm{d}t)$ value in creating more steps is more effective at a high $(\mathrm{d}l/\mathrm{d}t)_2$ level.

(4) The temperature at the start of the first reaction is determined by the

'outer' limit only. A low limit gives a low starting temperature.

(5) Only truly isothermal parts of the steps can be used for kinetic evaluation.

Table 3 gives the results from the sintering of pellets with different green densities. For all these measurements, the same set of experimental parameters has been used, corresponding to experiment 1. There seems to be a tendency for the activation energy to decrease by an increased green density, but the r^2 values are too poor and the number of experiments too few to really draw this conclusion.

The relatively low activation energies found in these experiments can indicate that the rate-controlling mechanism during the intial stage of sintering is oxygen surface diffusion. The initial stage has taken place between 900 and 1050°C and if the O/U ratio has been somewhat higher than 2.000 for stoichiometric uranium dioxide, for instance 2.005–2.007, the activation energies found can be realistic. For near stoichiometric uranium dioxide, Auskern and Belle [11] found the following data for surface diffusion.

$$\mathrm{O/U} = 2.004, \quad Q = 124 \text{ KJ mole}^{-1}$$

$$\mathrm{O/U} = 2.002, \quad Q = 273 \text{ KJ mole}^{-1}$$

By using the knowledge of the influence of the experimental parameters on the QID results obtained here, a more detailed study of the partial pressure of oxygen on the densification process is in progress.

ACKNOWLEDGEMENT

The author is very grateful to Dr. O. Toft Sørensen for many stimulating discussions on this subject.

REFERENCES

1 F. Paulik and J. Paulik, J. Therm. Anal., 16 (1979) 399.
2 J. Paulik and F. Paulik, Anal. Chim. Acta, 56 (1971) 328.
3 F. Paulik and J. Paulik, Thermochim. Acta, 4 (1972) 189.
4 F. Paulik and J. Paulik, J. Therm. Anal., 5 (1973) 253.
5 O.T. Sørensen, J. Therm. Anal., 13 (1978) 429.
6 O.T. Sørensen, Thermochim. Acta, 29 (1979) 211.
7 L. Hälldahl and O.T. Sørensen, Thermochim. Acta., 29 (1979) 253.
8 O.T. Sørensen, Proceedings of Sixth International Conference on Thermal Analysis, Bayreuth, F.R.G., Brikhaüser Verlag, Basel, 1980, p. 231.
9 L. Hälldahl and O.T. Sørensen, Proceedings of the Second European Symposium on Thermal Analysis, Aberdeen, U.K., Heyden, London (1981) p. 186.
10 F. Thümmler and W. Thomma, Metall. Rev., 12 (1967) 69.
11 A.B. Auskern and J.J. Belle, J. Nucl. Mater., 3 (1961) 267.