Thermochimica Acta, 44 (1981) 235—237
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

Note

THEORETICAL STUDY OF THE KINETIC ANALYSIS OF THE DENSIFICATION OF CERAMIC POWDER COMPACTS BY "QUASI-ISOTHERMAL" DILATOMETRY

J.M CRIADO

Departamento de Química Inorgánica de la Facultad de Química de la Universidad de Sevilla and Departamento de Investigaciones Físicas y Químicas, Centro Coordinado del C S I.C., Seville (Spain)

(Received 16 August 1980)

Paulik and Paulik [1,2] have developed a new thermodilatometric technique, designated "quasi-isothermal dialtometry" (QID), that allows the monitoring of the temperature of the sample in such a way that the measurements are performed at a constant rate of change in length. These authors have applied this technique to the study of the thermal decomposition of anhydrous CaC_2O_4 and have concluded that QID allows discrimination of the two steps taking place in the thermal decomposition of this compound much better than the conventional thermodilatometry (TD) carried out at a constant heating rate.

It is noteworthy that the quasi-isothermal dilatometry has not been used to date for performing the kinetic analysis of shrinkage of compact powders. In the opinion of Sørensen [3] this technique is not useful in kinetic studies because the temperature increases continuously but not at a constant rate. Thus, Sørensen seems to understand that the drawback of QID is that, the temperature not being a known function of time, the densification of the compact cannot be represented as a simultaneous function of both temperature and time. A similar conclusion was reached by Paulik and co-workers [4] with regard to the kinetic analysis of thermogravimetric curves of the thermal decomposition of solids obtained at a constant decomposition rate. However, this interpretation does not agree with that of Criado et al. [5,6] who have successfully applied the thermogravimetry at constant decomposition rate to determine the decomposition mechanism of alkaline-earth carbonates.

The scope of the present paper is to develop a method that permits the kinetic analysis of thermodilatometric data obtained by means of the so called quasi-isothermal heating technique.

Sintering is an activated process that can be described [3,7] by the following general equation

$$\frac{\Delta l}{l_0} = (kt)^n \qquad (1)$$

where Δl is the change in length of the specimen, l_0 is the initial length, n is an exponent which depends on the sintering mechanism, and k is the rate constant given by the Arrhenius law

$$k = A \exp(-E/RT) \tag{2}$$

where E and A are the activation energy and the pre-exponential factor of Arrhenius, respectively.

By differentiating eqn. (1) with respect to time t, we get

$$\frac{d(\Delta l/l_0)}{dt} = nk\left(\frac{\Delta l}{l_0}\right)^{1-(1/n)} \tag{3}$$

which, taking into account eqn. (2), becomes

$$\frac{d(\Delta l/l_0)}{dt} = nA \exp(-E/RT)\left(\frac{\Delta l}{l_0}\right)^{1-(1/n)} \tag{4}$$

If the thermodilatometric curve is recorded at a constant rate of change in length $C = d(\Delta l/l_0)/dt$, eqn. (4), after taking logarithms and rearranging, can be written as

$$\left(\frac{1}{n} - 1\right) \ln \frac{\Delta l}{l_0} = \ln \frac{nA}{C} - \frac{E}{RT} \tag{5}$$

or

$$\ln \frac{\Delta l}{l_0} = \left(\frac{n}{1-n}\right) \ln \frac{nA}{C} - \frac{E'}{RT} \tag{6}$$

where

$$E' = \left(\frac{n}{1-n}\right) E \tag{7}$$

The plot of the left hand side of eqn. (6) against $1/T$ should be a straight line whose slope and intercept permit the calculation of the activation energy and the pre-exponential factor of Arrhenius, respectively.

The method of kinetic analysis described above has the inconvenience that it does not allow determination of the value of n and, therefore, without prior knowledge of this parameter, the actual value of the activation energy, E, cannot be calculated. However, this drawback can be overcome by recording a series of dilatometric curves at different constant rates of change in length. Hence, it is very easy to deduce from eqn. (5) that, at a constant value of $(\Delta l/l_0)_c$, the following relationship must be accomplished

$$\ln C = B - \frac{E}{RT_c} \tag{8}$$

where $B[= \ln nA - (1/n - 1) \ln(\Delta l/l_0)_c]$ is a constant and T_c is the temperature at which the value of $(\Delta l/l_0)_c$, previously chosen, is reached on the thermodilatometric curve recorded at the constant rate of change in length C. Accordingly, the plot of $\ln C$ vs. $1/T_c$ should be a straight line whose slope gives the actual activation energy E.

The value of n can be calculated by comparing [by means of eqn. (7)] the E' value determined from eqn. (6) with that of E obtained from eqn. (8).

In summary, we can conclude that the densification mechanism of ceramic powder compacts can be characterized from the kinetic analysis of a set of quasi-isothermal dilatometric curves obtained at different constant rates of change in length.

REFERENCES

1 J. Paulik and F. Paulik, in H. Chihara (Ed.), Proceedings of the Fifth International Conference on Thermal Analysis, Heyden, London 1977, p. 75.
2 F. Paulik and J. Paulik, J. Therm. Anal., 16 (1979) 399.
3 O.T. Sørensen, in H.G. Wiedemann (Ed.), Proceedings of the Sixth International Conference on Thermal Analysis, Vol. 1, Verlag, Basel, 1980, p. 231.
4 M. Arnold, G.E. Veress, J. Paulik and F. Paulik, J. Therm. Anal., 17 (1979) 507.
5 J.M. Criado, Thermochim. Acta, 28 (1979) 307.
6 J.M. Criado, F. Rouquerol and J. Rouquerol, Thermochim. Acta, 38 (1980) 117.
7 F. Thummler and W. Thomma, Metall. Rev., 12 (1967) 69.