

THERMOGRAVIMETRIC AND DILATOMETRIC STUDIES USING STEPWISE ISOTHERMAL ANALYSIS AND RELATED TECHNIQUES

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The Stepwise Isothermal Analysis (SIA) technique, which was introduced by the author in the late seventies has proved to be very useful both in thermogravimetric and dilatometric studies. By this technique the heating and cooling programme is controlled by the rate of the reactions taking place in the sample, for instance thermal decompositions (TG) or sintering (dilatometry). By an advanced computer programme this control is achieved in the following way: The sample is heated at a constant heating rate until the reaction rate, i. e. the slope of the weight/length versus time curve, exceeds a preset limit at which point the heating is stopped. The reaction thereafter proceeds isothermally until the rate again becomes smaller than the limit where the heating is resumed. By this techniques the reactions thus characteristically take place in isothermal steps.

This technique is especially useful in studies of thermal decompositions and it is believed that the decomposition temperatures determined by SIA is much more accurate than those determined by other techniques even for materials involving consecutive and close-lying reactions. One typical application of this technique is establishment of optimum conditions for removal of organic binders from ceramic powder compacts prepared for instance by dry pressing or injection moulding.

The SIA technique is also very useful in kinetic studies and with the advanced computer systems available today rather sophisticated control and analysis of the data can be obtained. One example, which will also be discussed in the presentation, is a study of the decomposition of Ce-carbonate using first the standard technique described above by which the reaction mechanism could be established and then followed by the so-called Forced Stepwise Isothermal Analysis technique (FSIA) by which the activation energy could be obtained.

Finally the SIA technique is also very useful in dilatometric sintering studies and to demonstrate this the result obtained both using SIA and the related 'constant shrinkage rate' technique in a study of the initial sintering stage of CeO₂ will be presented.

Keywords: dilatometry, stepwise isothermal analysis, TG

Introduction

The Stepwise Isothermal Analysis (SIA) technique, which was introduced by the author in the late seventies [1, 2], has proved to be very useful in ther-

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mogravimetric and dilatometric studies. By this technique the heating and cooling programme is controlled by the rate of the reactions taking place in the sample – for instance thermal decomposition, evaporation, oxidation or shrinkage during sintering (dilatometry). By an advanced computer programme this control is achieved in the following way: The sample is heated at a constant heating rate until the reaction rate, which is calculated from the weightloss or change in length, exceeds a preset limit at which point the heating is stopped. The reaction thereafter proceeds isothermally until the rate again becomes smaller than this limit where the heating is resumed. By this technique the reactions thus characteristically take place in isothermal steps.

Historically the SIA-technique, was in fact developed from the so-called Quasi-Isothermal Analysis (QIA) techniques introduced by Paulik and Paulik [3] and by Rouquerol [4] respectively in the early seventies. The fundamental difference between these two techniques is that the reactions by the SIA technique takes place under strictly isothermal conditions at characteristic temperatures, whereas the QIA technique introduced by Paulik and Paulik and by Rouquerol essentially are constant reaction rate techniques in which the temperature, in principle at least, never can become constant. Compared to the conventional non-isothermal techniques SIA has the following advantages:

- (1) consecutive and close-lying reactions can easily be separated;
- (2) for each reaction the kinetics, i.e. the controlling mechanism and the activation energy, can therefore be determined without the interference of overlapping reactions;
- (3) the reactions take place under isothermal conditions and the data obtained are more suitable for kinetic studies than those obtained by non-isothermal methods, and finally
- (4) more accurate reactions temperatures are determined by this technique.

Based on the author's previous publication some examples of applications of the SIA technique both in thermogravimetric and dilatometric studies is presented in this review.

Thermogravimetric studies

Thermal decomposition of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ [5]

As an example of the ability of SIA to resolve consecutive and very closely lying reactions Fig. 1 shows the weight vs. temperature curve for

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ obtained using this technique. In conventional non-isothermal (constant heating rate of dynamic heating) techniques the removal of the first four water molecules is usually observed to take place in two overlapping steps at about 65 and 95°C whereas the SIA technique is capable of separating this reaction into four steps corresponding to the loss of one water molecule at 58 and 68°C respectively, the loss of 1.5 molecule at 75°C and finally the loss of the last half molecule of 85°C. To obtain this high resolution the preset rate limit used when the reaction is finished was ten times smaller than that used when the reaction is first detected, which ensures that a given reaction is properly completed before the system resumes the heating.

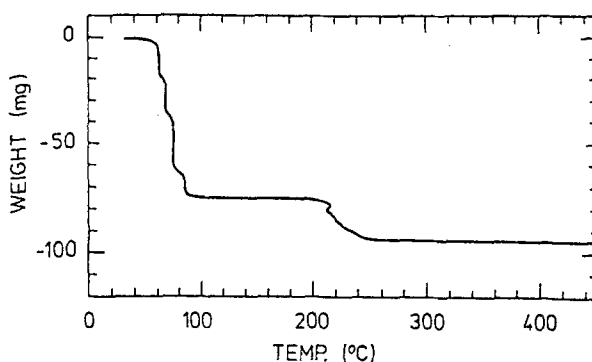


Fig. 1 SIA curve for $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ [5]

It is also interesting to note that the dehydration temperatures obtained using the SIA technique are generally lower than those observed both when dynamic heating or the quasi-isothermal technique is used. The main reason for this is of course, is that the dehydrations generally are reversible reactions which therefore depend on the water vapour pressure of the surrounding atmosphere. Measurements in closed crucibles or in a labyrinth crucible as used by Paulik and Paulik [1] will thus retard the reaction and the dehydration temperature determined under these conditions are generally too high. In the case of SIA the pressure of the water molecules in the sample holder does not, however, affect the measurement as the first reaction temperature detected by the system, which will be maintained constant throughout the whole reaction, correspond to the temperature of the sample near the crucible wall. Actually this dehydration temperature can be considered as the true 'decomposition temperature' whereas the temperatures determined by the other techniques are more close to what could be termed as 'equilibrium dehydration temperatures'.

Binder removal from injection moulded ceramic parts

A general technique for production of ceramic parts is injection moulding ceramic powder plasticised with organic binders. In order produce sound and crack free parts during the high temperature firing these binders have to be removed effectively. This is usually done by subjecting the injection moulded parts to a controlled heating programme which depend on the composition of the binder system used.

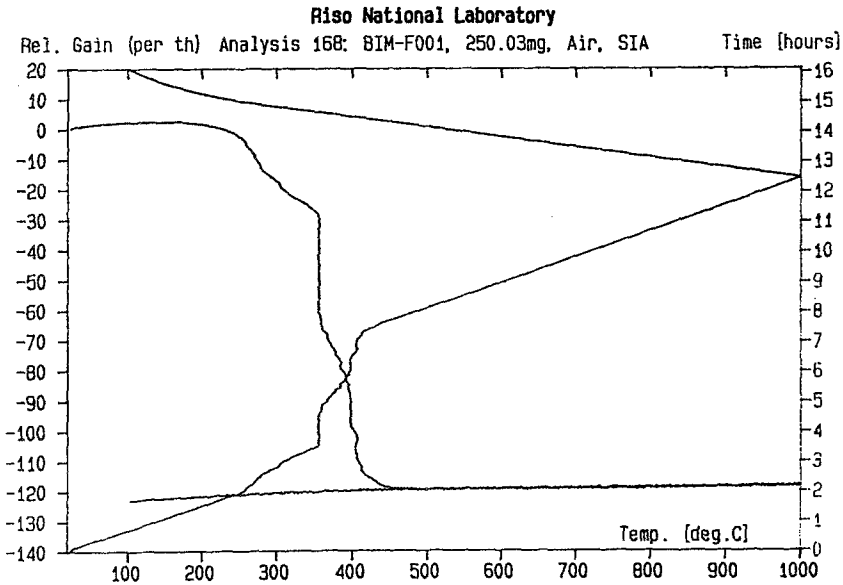


Fig. 2 SIA curve for binder removal from ceramic compact

The SIA techniques has proved to be a powerful tool to establish the optimum conditions for binder removal from injection moulded parts. One example is showed in Fig. 2, which gives the SIA-curve i.e. the weightloss versus temperatures, for the removal of a charateristic binder system. As will be noted the decomposition temperatures of the compounds involved can be easily determined from this curve. The SIA technique can also be used to control the binder removal directly and the advanced computer programme developed for these measurements is now used in a commercially available industrial furnace system.

Kinetic studies

As mentioned in the introduction, one of the greatest assets of the SIA-technique is that the data are obtained under isothermal conditions. This technique is thus particularly well suited for kinetic studies as demonstrated in [7-8].

Generally the reactions mechanism can be evaluated from the SIA data using the standard kinetic equation for heterogeneous solid state reactions:

$$kt = F(\alpha) \quad (1)$$

where t is the reaction time, k the rate constant ($= A \exp(-E/RT)$) and $F(\alpha)$ is a characteristic function of the fraction reacted, α . As it is well known, $F(\alpha)$ depends on the type of rate-limiting process, i.e. the slowest process controlling the overall reaction. $F(\alpha)$ is given in [8] for some typical controlling mechanisms.

A general and recognized method in kinetic studies is to evaluate the controlling mechanism(s) from an $F(\alpha)$ vs. t plot, which is shown in Eq. 1 should be linear for the correct mechanism. With the computerprogramme developed for kinetic studies $F(\alpha)$ can be calculated from the measured isothermal weight changes involving seventeen different standard kinetic equations [9].

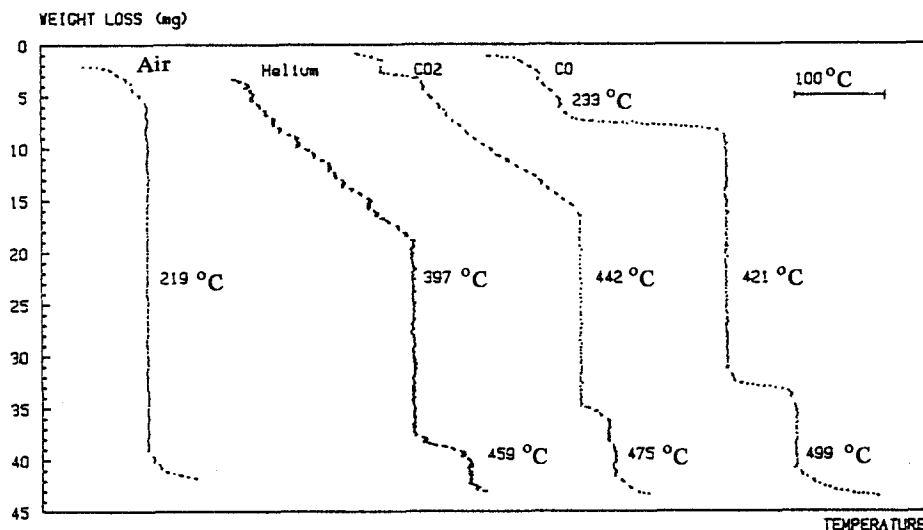
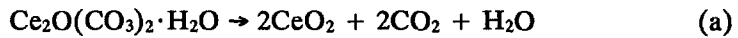


Fig. 3 SIA curves for Ce-carbonate in different atmospheres [8]

A typical SIA curve obtained for the thermal decomposition of Ce-carbonate ($\text{Ce}_2\text{O}(\text{CO}_3)_2 \cdot \text{H}_2\text{O}$), which is a precursor for the production of CeO_2 , is shown in Fig. 3. In this study [8] the SIA measurements were performed in different atmospheres and from Fig. 3 it will clearly be noted that the decomposition temperature as well as the number of steps strongly depend on the type of atmosphere used. In air, for instance, decomposition takes place in only one step at a relatively low temperature (219°C), whereas several steps at higher temperatures are involved in the other atmospheres studied. In reference 8 we propose that the reason for this difference is that the thermal decomposition, which must involve an oxidation takes place in air according to the reaction:



whereas the two isothermal steps observed at higher temperatures for the other atmospheres indicates a two-step decomposition according to:

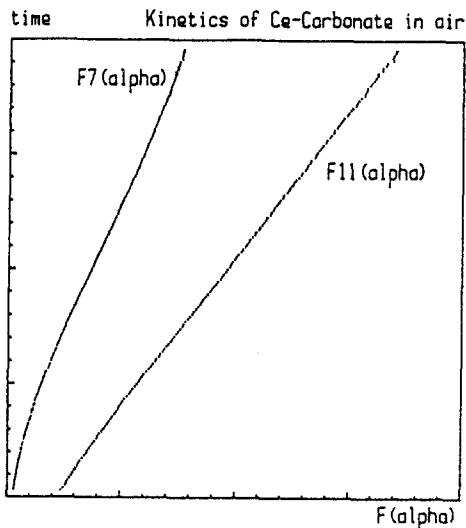
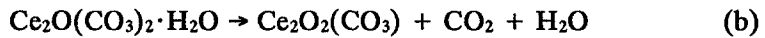


Fig. 4 $F(\alpha)$ vs. time plots for isothermal decomposition of Ce-carbonate in air [8]

Taking the data obtained in air as an example Fig. 4 shows that a nearly perfect linear plot could be obtained using the F_{11} (α) equation which has the form

$$F_{11}(\alpha) = 1/2(-\ln(1-\alpha))^2$$

and which describes a mechanism involving nucleation followed by two-dimensional growth controlled by phase boundary movement [9]. From this study it was therefore concluded that this mechanism is controlling the thermal decomposition in air in contrast to the decomposition in CO, which take place at higher temperature, where it was found that the controlling mechanism only involved phase boundary movement nuclei growth (in three dimensions). The nucleation is apparently so fast at these higher temperatures that it cannot control the thermal decomposition.

A drawback with this technique is that it cannot be used to determine the activation energy – data are needed at different temperatures in order to determine E from the rate (Arrhenius) constant k in Eq. 1. A new version of the SIA technique was therefore introduced by which the temperature is forced to increase in predetermined steps during the reaction. The technique has been termed as 'Forced Stepwise Isothermal Analysis' (FSIA).

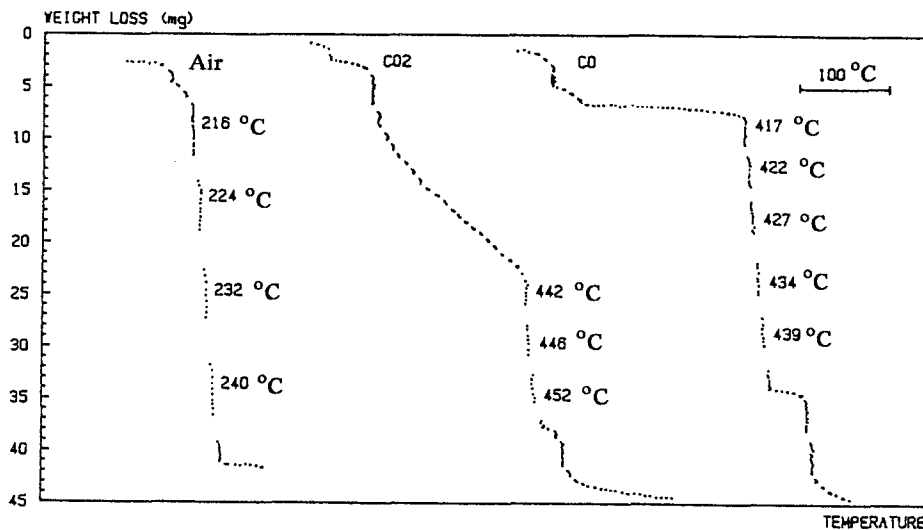


Fig. 5 FSIA curves for Ce-carbonate in different atmospheres [8]

Figure 5 shows the FSIA data obtained for the thermal decomposition of Ce-carbonate in different atmospheres. Plotting $F(\alpha)$ vs. t using these data

one single straight line will not be obtained as for the isothermal SIA-data but rather segments of lines with characteristic slopes depending on the temperature – see Fig. 6, from which the rate constant can be determined. The activation energy, E , can thus be determined in the standard way from an Arrhenius plot, i.e. $\ln k$ plotted as a function of $1/T$, which should give a straight line with a slope of E/R .

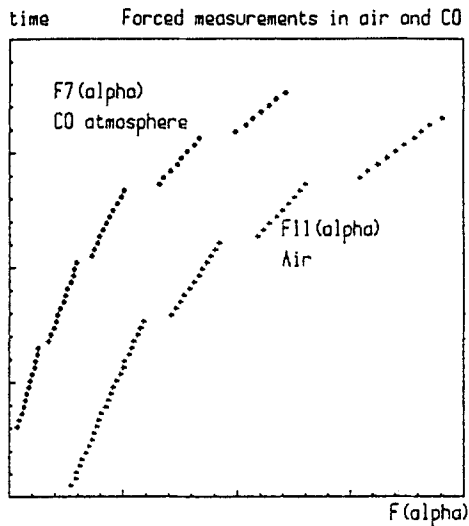


Fig. 6 $F(\alpha)$ vs. time plots for FSIA data obtained in air and CO [8]

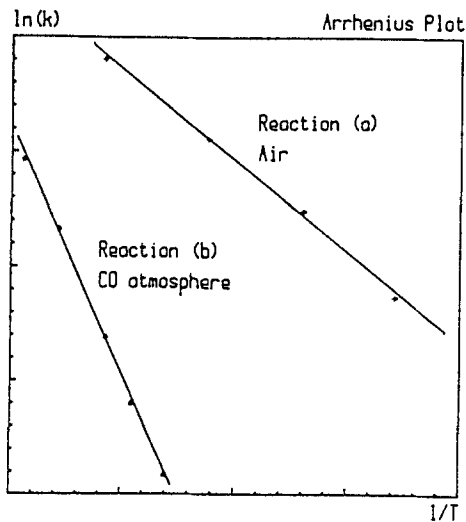


Fig. 7 Arrhenius plot obtained from FSIA data shown in Fig. 6 [8]

Figure 7 gives an example of an Arrhenius plot determined from the FSIA data obtained by performing the measurements in air and CO. The activation energies found were 104.9 and 297.8 kJ/mole respectively.

Dilatometric sintering studies

The stepwise isothermal technique has also proved to be very useful in dilatometric studies of the sintering behaviour of ceramic compacts. By this technique, which generally is designated as Stepwise Isothermal Dilatometry, SID, the temperature programme is controlled by the length changes (the shrinkage) of the sample and the temperature control is performed in the same way as for the SIA techniques, i.e. the sintering takes place in characteristic isothermal steps as found for the thermal decompositions described in the previous section. As an example Fig. 8 shows a typical SID curve obtained for sintering of yttria doped zirconia (typical structural high strength ceramic) in the temperature range 850° to 1450°C. In the following I shall demonstrate what information can be obtained from such a curve.

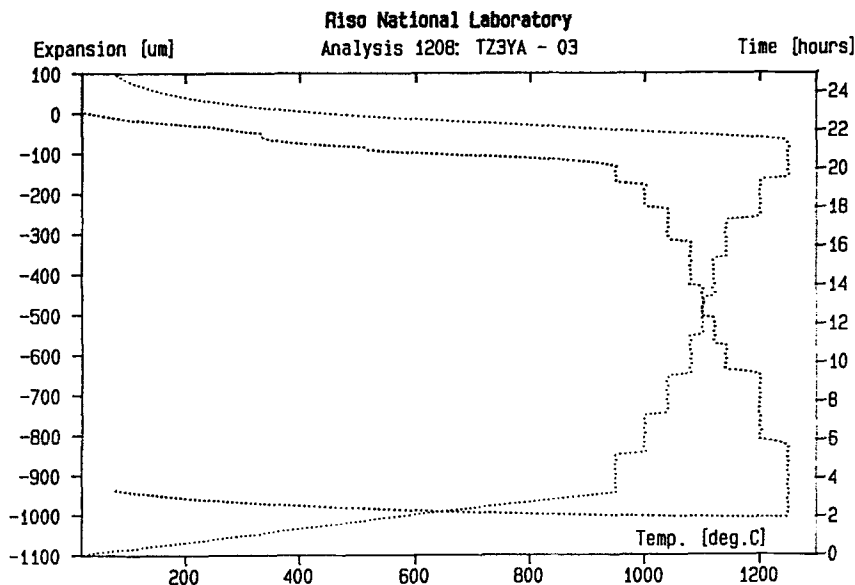


Fig. 8 SID curve for zirconia ceramics (specimen TZ3YA-07)

Evaluation of temperature of maximum shrinkage

If the shrinkage taking place at each step is plotted against the corresponding temperature the curve shown in Fig. 9 is obtained. The maximum of this curve correspond to the temperature at which the shrinkage rate is largest, which again correspond to the temperature where grain growth is initiated. By this technique sintering conditions producing fine grained materials can thus easily be established. This is particularly useful in the productions of ceramics for structural applications as the grain size to a large extent determine the mechanical strength of the sintered compacts.

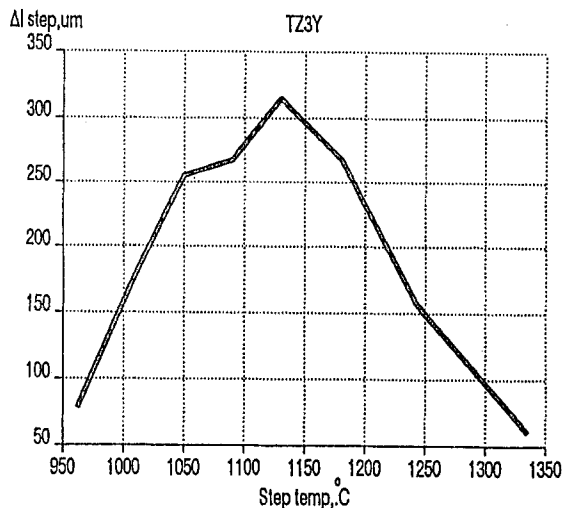


Fig. 9 Shrinkage at isothermal steps vs. step temperature obtained from SID measurements on yttria stabilized zirconia (TZ3Y)

Sintering kinetics

As for the solid state reactions involving weight changes it is also of great interest to determine the controlling mechanism as well as the activation energy for the densification taking place during the sintering process. This can be done fairly straightforward for the first sintering stage – the neck growth stage – as was demonstrated for different materials in previous publications [10–14]. The general equation describing the linear shrinkage during this stage can be expressed as

$$y = \Delta l / l_0 = (k(T)t)^n \quad (2)$$

which by differentiation heads to

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

In these equations:

l_0 = initial sample length at start of sintering

$k(T) = A \exp(-E/RT)$ = Arrhenius constant

n = constant depending on the sintering mechanism

$N = l/n$

Eq. 3 can also be expressed as

$$(N-1)\ln y = \ln k(T) - \ln N - \ln \dot{y}$$

and on plotting $\ln \dot{y}$ vs. $\ln y$ a straight line should be obtained from which the value of N and thus n can be determined from the slope. Finally when N is known it is also possible to calculate $k(T)$ at different temperatures and this method thus also gives the possibility of determining the activation energy.

As an example a $\log \dot{y}$ vs. $\log y$ plot determined for the first six isothermal steps involved in the sintering of CeO_2 is presented in Fig. 10. As will be noted nice and straight lines were observed from which an average value of $n = 0.33$ could be calculated indicating that the shrinkage kinetics for the initial sintering stage for this oxide is controlled by grain boundary diffusion [15].

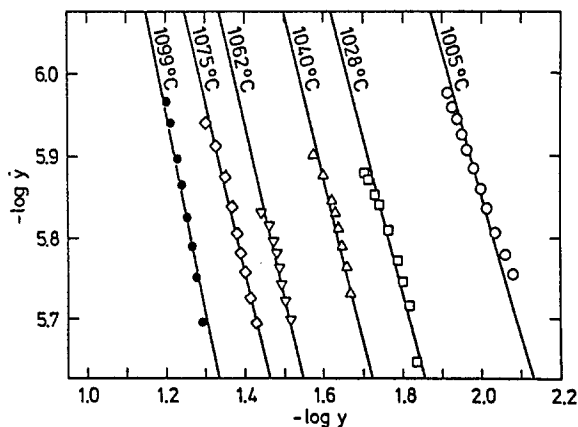


Fig. 10 Shrinkage rate vs. shrinkage for isothermal steps obtained from SID data for sintering of CeO_2 -powder compacts [13]

Furthermore the $\log(k(T))$ values determined from the intercepts of the lines in Fig. 10 are plotted against $1/T$ in Fig. 11. A straight line was again ob-

tained from which an activation energy of 499.6 kJ/mole (5.2 eV) could be obtained. This value corresponds very well to the activation energies for cation diffusion in other oxides with the same structure (the fluorite structure) [16] and it can be concluded that it is grain-boundary diffusion of the Ce-ions that is the rate controlling mechanism for this oxide.

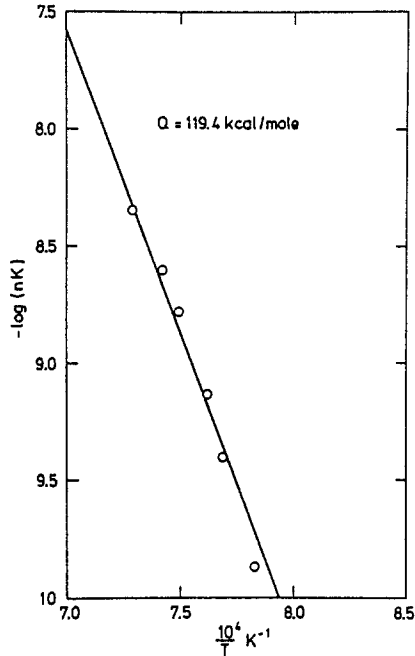


Fig. 11 Arrhenius plot for sintering of CeO₂-powder compact from SID-data shown in Fig. 10

Finally the Arrhenius constant can also be expressed as

$$k(T) = A \gamma \Omega D / k T r^p$$

where

A, p = constants depending on the controlling mechanism

γ = surface tension (erg/cm²)

Ω = vacancy volume (cm³)

D = diffusion coefficient (cm/scc)

k = Boltzmann constant

T = absolute temperature

r = radius of particles in the powder compact (cm)

Inserting the relevant values for the constants and estimating the average particle size from the surface area of the CeO_2 starting powder the diffusion coefficient for the Ce-ion diffusion was calculated to be 8.5×10^{-17} – $3.1 \times 10^{-15} \text{ cm}^2/\text{sec}$ for the temperature range considered (1005–1099°C). These values are comparable to those obtained by the author from sintering studies of other oxides with the fluoride structure, for instance UO_2 [12].

Determination of activation energies by the jump method

The kinetics of any solid state reaction including sintering can be expressed by the general rate equation.

$$dy/dt = k(T) f(y) \quad (5)$$

where y for instance can be the linear shrinkage and where $f(y)$ depends on the specific controlling process. In the case of sintering, $f(y)$ is usually not known for the later stages as these involve several parallel reactions for instance removal of porosities and grain growth and for these stages it is impossible to use Eq. 5 to determine the activation energy. This can however be done by using the so called temperature jump method by which it is assumed first that the function $f(y)$ does not vary within a certain temperature range and secondly that $f(y)$ has the same value before and after a given temperature jump. This is actually what is obtained by SID when the temperature quickly jumps from one isothermal segment to the other. For two adjacent isothermal segment at T_1 and T_2 respectively we have from Eq. 5:

$$(dy/dt)_{1,y} / (dy/dt)_{2,y} = k_1/k_2 = \exp [-E(1/T_2 - 1/T_1)] \quad (6)$$

and E can therefore be obtained from the ratio of the slopes of the y - t curve on each side of the temperature jump. Activation energies determined using this method from SID-curves measured during sintering of $\text{ZrO}_2(\text{Y}_2\text{O}_3)$ (yttria doped zirconia) compacts are shown in Fig. 12 as a function of temperature. The difference between the two types of compacts examined is the density of the starting (green) compacts – the green densities were 44 and 49% – TD (theoretical density) for TZ3YA-03 TZ3YA-05 and TZ3YA-07 respectively. Apparently the activation energies determined for these compacts do not depend on the green density but rather on the temperature. Furthermore these compact increases showed a minimum in the activation energy near 1100°C whereas the compacts of higher starting densities

showed a gradual increase in activation energy with increasing temperature. The reason for this difference has not yet been clarified.

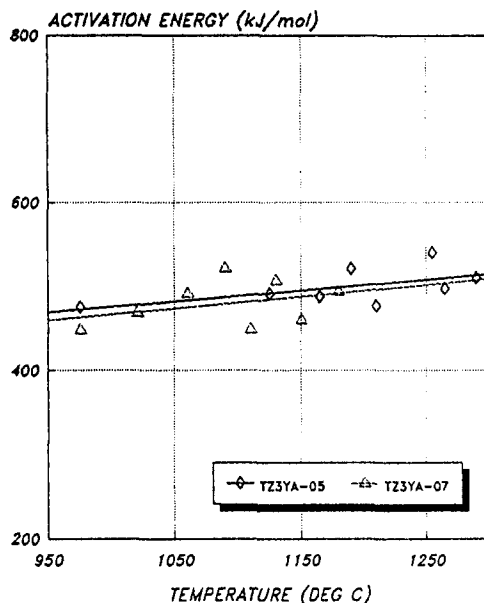


Fig. 12 Activation energies as a function of temperature calculated by the temperature jump method. Data obtained from SID data shown in Fig. 8

Related techniques

With the advanced software developed by the author for thermal analysis it is also possible to perform measurement at a controlled constant reaction rate either with one fixed rate throughout the whole measurement or with different rates in different temperature regimes. This method is thus especially suitable for activation energy determinations by the jump method. As demonstrated by Criado [17] and by the author [18] this method can also be used in dilatometric sintering studies to determine the activation energy. Assuming thermal equilibrium ($dT/dt = 0$) a full differentiation of the standard equation for the first sintering stage (Eq. 2) leads to the following equation

$$y^{(1/n-1)} c = n A/T \exp(-E/RT) \quad (7)$$

where A is the preexponential factor of the Arrhenius equation and c is the constant rate ($=\dot{y}$). Taking the logarithm on both sides of this equation and rearranging gives

$$\ln y = (n-1) \ln (n A/T c) - E (n-1)/RT \quad (8)$$

and as $n A/T c$ is nearly constant in the limited temperature range considered here a plot of $\ln y$ vs. $1/T$ should give a straight line from which E can be calculated from the slope provided the value of n is known.

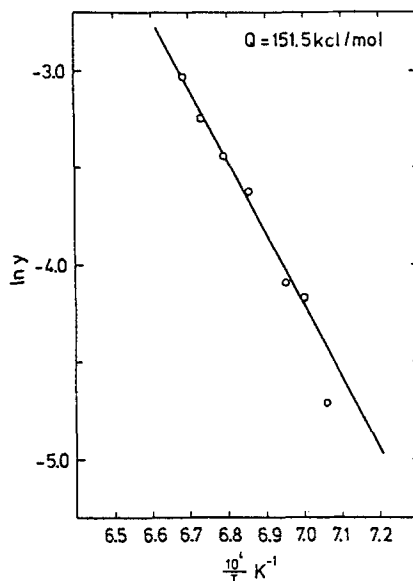


Fig. 13 Shrinkage vs. $1/T$ plot for constant shrinkage rate measurements [14]

As shown in Fig. 13 this was actually obtained in a preliminary constant shrinkage rate measurement on CeO_2 and using the value of n as determined by SIA discussed previously, $n = 0.33$ (grain boundary diffusion), an activation energy of $E = 634$ kJ/mole could be obtained. This value is of the right order of magnitude but it is somewhat larger than the E value obtained by SIA, which gave $E = 499.6$ kJ/mole. The reason for this difference could be that thermal equilibrium was not fully achieved in this measurement which was performed with a relatively primitive version of the temperature controller.

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Zusammenfassung — Das vom Autor Ende der siebziger Jahre eingeführte Verfahren der Stufenweisen Isothermischen Analyse (SIA) erwies sich sowohl bei thermogravimetrischen als auch bei dilatometrischen Untersuchungen als sehr nutzvoll. Bei diesem Verfahren wird das Heiz- und Kühlprogramm durch die Geschwindigkeit der in der Probe ablaufenden Reaktion – z.B. der thermischen Zersetzung (TG) oder des Sintern (Dilatometrie) – gesteuert. Diese Steuerung wird durch ein Computerprogramm auf folgende Weise erreicht: Die Probe wird mit einer konstanten Aufheizgeschwindigkeit aufgeheizt, bis die Reaktionsgeschwindigkeit, d.h. der Anstieg der Gewichts/Längen – Zeitkurve, einen gewissen Grenzwert überschreitet, wodurch der Aufheizvorgang gestoppt wird. Die Reaktion wird anschließend isotherm fortgesetzt, bis die Geschwindigkeit wieder kleiner als der Grenzwert wird, zu diesem Zeitpunkt setzt die Aufheizung wieder ein. Durch dieses Verfahren erfolgt die Reaktion somit in isothermen Stufen.

Dieses Verfahren ist besonders bei der Untersuchung von thermischen Zersetzungen nutzvoll und man nimmt an, daß die mittels SIA ermittelte Zersetzungstemperatur wesentlich genauer ist als im Falle von anderen Verfahren, besonders bei Substanzen mit konsekutiven und nahe beieinanderliegenden Reaktionen. Eine typische Anwendung dieses Verfahrens ist die Ermittlung der Optimumbedingungen für die Entfernung organischer Bindemittel aus Keramikpulverpreßlingen, die z.B. durch Trockenpressen oder Spritzgießen hergestellt wurden. Ein Anwendungsbeispiel dafür wird hier diskutiert.

Auch bei kinetischen Untersuchungen ist das SIA Verfahren sehr nutzvoll und mit den heute erhältlichen Computersystemen ist eine anspruchsvollere Überwachung und Analyse der Angabe ist möglich. Ein ebenfalls in vorliegender Arbeit diskutiertes Beispiel ist die Untersuchung der Zersetzung von Ceriumkarbonat, wobei zuerst die obenbeschriebene Standardmethode angewendet wird, wodurch der Reaktionsmechanismus abgeschätzt werden kann. Im Anschluß erfolgt eine sogenannte Erzwungene Stufenweise Isotherme Analyse (FSIA), wodurch die Aktivierungsenergie ermittelt werden kann.

Letztendlich ist das SIA Verfahren auch bei dilatometrischen Sinteruntersuchungen sehr nutzbringend. Um dies darzustellen, wird bei einer Untersuchung des ursprünglichen Sinterzustandes von CeO₂ sowohl das durch SIA als auch das durch das Verfahren der "konstanten Abschreckgeschwindigkeit" erhaltene Ergebnis dargestellt.