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A QUANTITATIVE INVESTIGATION OF THE PHASE TRANSFORMATION OF GAMMA TO ALPHA ALUMINA WITH HIGH TEMPERATURE DTA

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ABSTRACT

The phase transformation of gamma to alpha alumina was studied with high temperature DTA. The results were analysed with the methods of Borchardt and Daniels, Freeman and Carroll, Coats and Redfern and Kissinger. The order of the reaction is one, indicating a nucleation and growth mechanism with one nucleus being formed per crystallite. The activation energy is 0.60 MJ mol^{-1}.

INTRODUCTION

Gamma alumina is widely used as a catalyst support because of its high surface area (200-300 m^2 g^{-1}) and its relatively large thermostability. However, during prolonged exposure to high temperatures ($> 800\,^\circ C$), especially in the presence of steam, a large surface-area loss occurs. The result is usually the deactivation of the catalyst. The surface-area loss is accompanied by the phase transformation to alpha alumina (corundum), which is the thermodynamically stable phase. According to some authors [1-4] this is the main cause of surface-area loss of gamma alumina at high temperatures. Therefore, it is interesting to investigate this phase transformation in more detail.

Gamma alumina is a cation deficient spinel, consisting of cubic close-packed oxygen anion layers, with cations occupying octahedral and tetrahedral sites. Alpha alumina has the corundum structure: hexagonal close-packed oxygen anion layers, with cations occupying octahedral sites. The phase transformation of gamma to alpha alumina requires a rearrangement of both cations and anions and occurs only at high temperatures. It should be noted that this phase transformation may proceed via several other

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modifications (delta, theta). Since the crystal structures of these modifications resemble that of gamma alumina it is convenient to represent the series of transitions as one phase transformation, of gamma to alpha alumina.

Previous investigations [5–8] have used scanning electron micrography to show that the phase transformation proceeds via a nucleation-and-growth mechanism. There is little agreement in the literature on the kinetic parameters of this reaction. Several authors determined these parameters from quantitative X-ray diffraction measurements: Wilson and McConnell [6] found an activation energy of 600 kJ mol^{-1}; Drobot et al. [9] calculated activation energies of 225–410 kJ mol^{-1}; Steiner et al. [10] found zero order kinetics with an activation energy of 485 kJ mol^{-1}; earlier work by Clark and White [11] gives kinetic results from specific gravity measurements, they found first-order kinetics and an activation energy of 330 kJ mol^{-1}.

The discrepancy in these results may be due to the insufficient accuracy of these analysis methods. Therefore, it is interesting to apply other techniques. Since the phase transformation is a slightly exothermic reaction (reaction enthalpy −20 kJ mol^{-1} [12]) it can be investigated by differential thermal analysis (DTA). Up to now this method has mainly been used for qualitative studies of the phase transformation [5,13–17]. Only Yoldas [18] determined the activation energy from DTA experiments, without stating which calculation method he used. He found a value of 557 kJ mol^{-1}.

Several methods are available for the determination of kinetic parameters from DTA curves. These are based on the common kinetic equation for a solid-state reaction

$$\mathrm{d}\alpha/\mathrm{d}t = Z\exp(-E_a/RT)(1-\alpha)^n \qquad (1)$$

where α is the fraction of the sample that has reacted up to time t. Only reactions with $n = 0$, 1/2, 2/3 or 1 have a theoretical justification [19].

If a DTA curve is considered as a plot of $\mathrm{d}\alpha/\mathrm{d}t$ vs. T, values of α may be obtained by integration. In this case kinetic parameters can be obtained by the methods of Borchardt and Daniels [20], Freeman and Carroll [21] or Coats and Redfern [22]. Table 1 lists the functions that are plotted on the x-axis and y-axis in these methods.

If several DTA curves recorded at different heating rates are available, the method of Kissinger [23] can be applied. The activation energy can be calculated from the relationship between heating rate (ϕ) and temperature of maximum deflection (T_m), as given in Table 1. Kissinger [23] also gives a method to determine the order of the reaction (n) from a single DTA curve

$$n = 1.26\left[(\mathrm{d}^2\alpha/\mathrm{d}t^2)_1/(\mathrm{d}^2\alpha/\mathrm{d}t^2)_2\right]^{1/2} \qquad (2)$$

where subscripts 1 and 2 refer to the values of these quantities at the inflection points.

TABLE 1

Survey of methods to determine kinetic parameters from DTA curves

Method	Plotted on x-axis	Plotted on y-axis	Slope	Intercept
Borchardt and Daniels [20]	T^{-1}	$\ln[(\mathrm{d}\alpha/\mathrm{d}t)/(1-\alpha)^n]$	$-E_a/R$	—
Freeman and Caroll [21] [a]	$A=\dfrac{T_r^{-1}-T_i^{-1}}{\ln[(1-\alpha_r)/(1-\alpha_i)]}$	$B=\dfrac{\ln[(\mathrm{d}\alpha/\mathrm{d}t)_r/(\mathrm{d}\alpha/\mathrm{d}t)_i]}{\ln[(1-\alpha_r)/(1-\alpha_i)]}$	$-E_a/R$	n
Coats and Redfern [22] ($n=1$)	T^{-1}	$C(1)=\ln[-\ln(1-\alpha)/T^2]$	$-E_a/R$	-
Coats and Redfern [22] ($n\neq 1$)	T^{-1}	$C(n)=\ln\{[1-(1-\alpha)^{1-n}]/(1-n)T^2\}$	$-E_a/R$	-
Kissinger [23]	T_m^{-1}	$\ln(\phi/T_m^2)$	$-E_a/R$	-

[a] This method used data sets $[T_i, \alpha_i, (\mathrm{d}\alpha/\mathrm{d}t)_i]$ and a reference set $[T_r, \alpha r, (\mathrm{d}\alpha/\mathrm{d}t)_r]$.

EXPERIMENTAL

The gamma alumina used in this investigation was provided by Ketjen catalysts in the form of 4 × 1.7-mm extrudates (type 000-1.5E). This support was selected because of its low impurity content: < 0.05 wt%, including < 0.0003 wt% Na_2O.

For the DTA measurements an apparatus of Bureau de Liaison was used. Approximately 20 mg of powdered samples were heated from 20 to 1400 °C in air. A linear heating rate between 4 and 40 °C min^{-1} was applied, using a Eurotherm temperature programmer. As reference material the same amount of alpha alumina was used. The temperature difference between sample and reference was measured with a Pt/Pt–10% Rh thermocouple, amplified and registered.

A parallel X-ray diffraction investigation was carried out. Samples of gamma alumina were heated in the DTA apparatus at a rate of 12 °C min^{-1} to the beginning of the peak (T_0), the maximum of the peak (T_m) and the end of the peak (T_e), respectively, and rapidly cooled to 20 °C. The qualitative phase composition was determined by X-ray diffraction, using an Enraf Nonius Guinier–de Wolff camera mark II. The sample taken at the maximum of the peak (T_m) was also studied by scanning electron microscopy, using a Jeol 200C microscope.

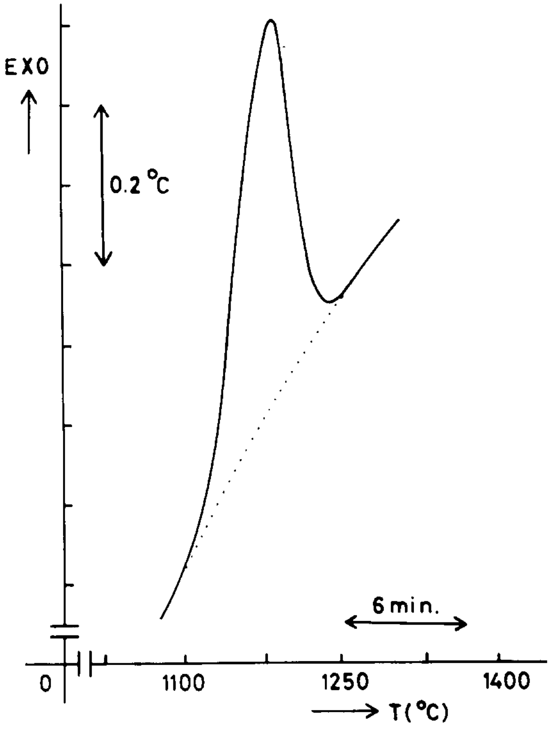

Fig. 1. DTA curve obtained by heating gamma alumina at a rate of 19 °C min^{-1}.

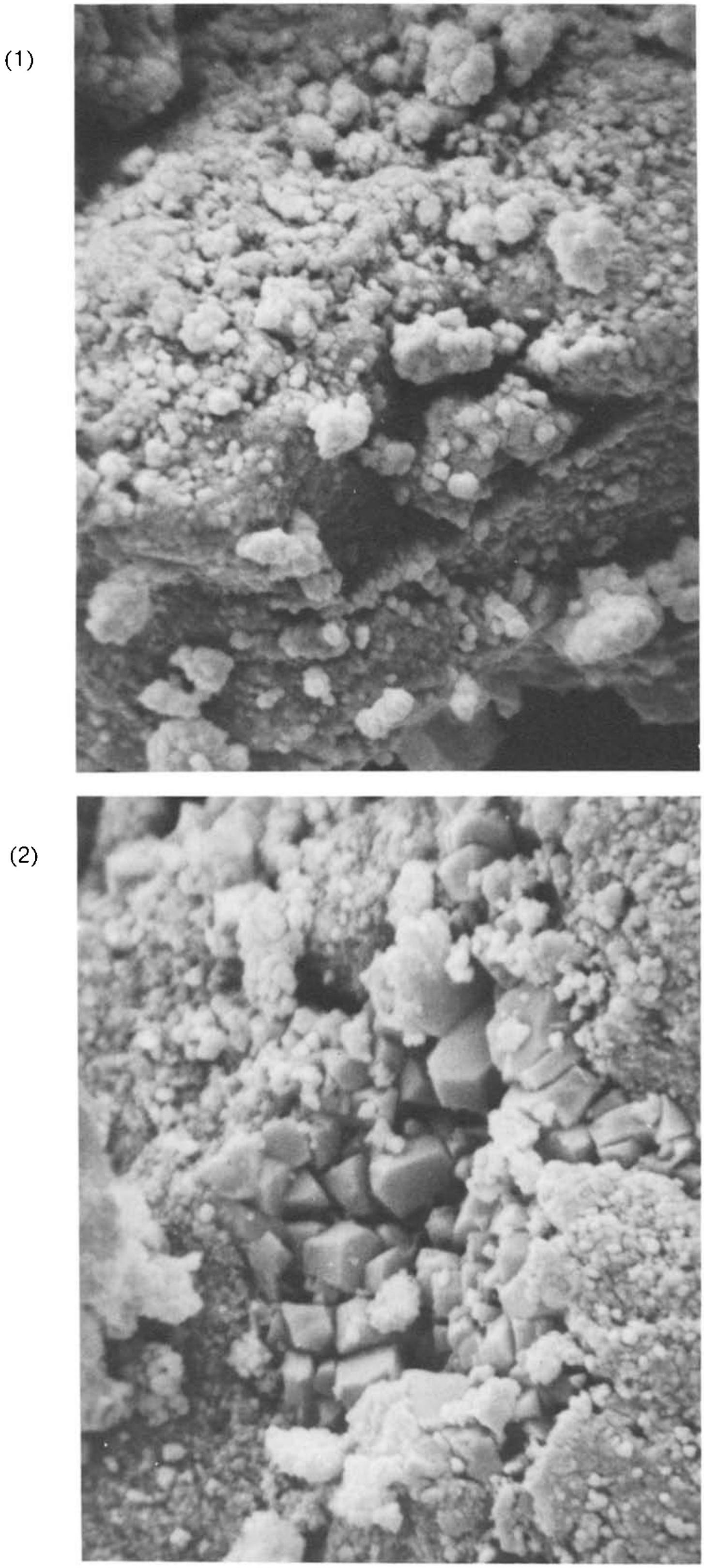

Fig. 2. Scanning electron micrograph (10000 ×) of (1) starting material, (2) sample C.

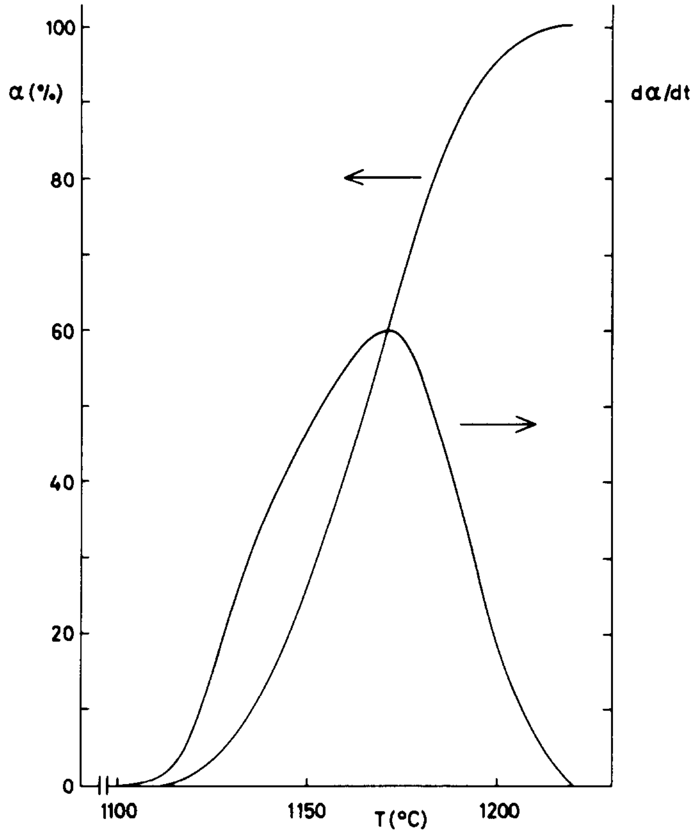

Fig. 3. Integrated DTA curve.

RESULTS AND DISCUSSION

Figure 1 gives the relevant part of the DTA curve, obtained by heating gamma alumina at a heating rate of 19 °C min^{-1}. All DTA curves show an exothermic peak in the temperature range 1100–1200 °C. The temperature of maximum deflection (T_m) was found to be reproducible within 3 °C for the same heating rate. The results of the X-ray diffraction measurements are given in Table 2. They show that the exothermic peak may be attributed to

TABLE 2

Results of X-ray diffraction measurements

Sample	Temperature	Alumina phases observed
A	20 °C	γ
B	T_0	θ, α (trace)
C	T_m	θ, α
D	T_e	α

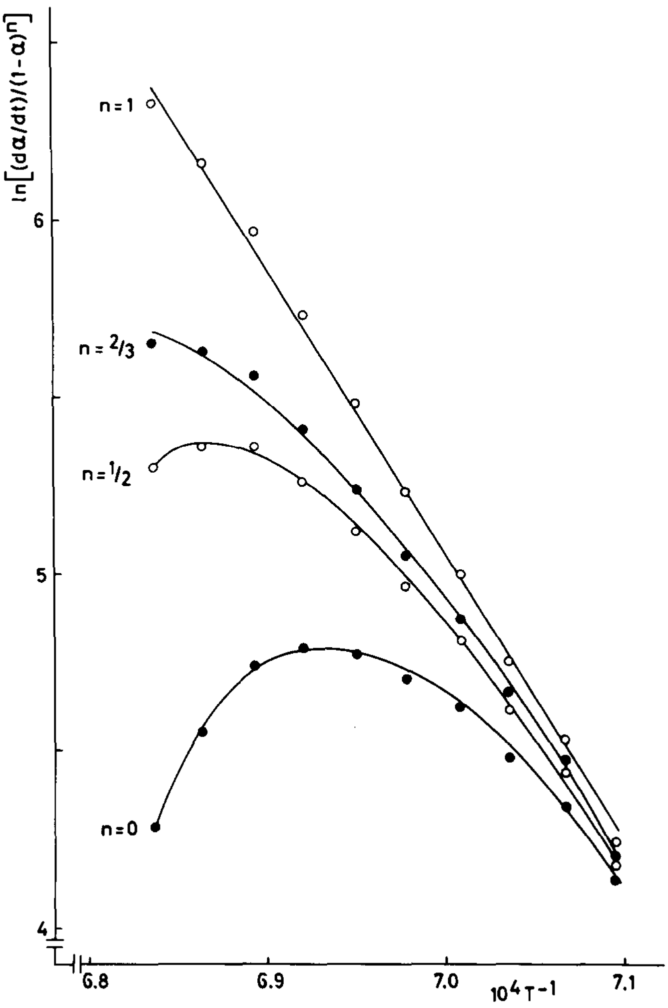

Fig. 4. Plot according to Borchardt and Daniels [20].

the phase transformation of theta to alpha alumina. This is confirmed by the SEM photograph of sample C, as presented in Fig. 2. This photograph shows hexagonal (alpha) alumina crystallites within a (theta) alumina matrix.

TABLE 3

Kinetic parameters of the phase transformation

Method	Figure	α-range	E_a (MJ mol^{-1})	n
Borchardt and Daniels [20]	4	0.10–0.90	0.67	1
Freeman and Carroll [21]	5	0.24–0.87	0.72	1.1
Coats and Redfern [22]	6	0.17–0.92	0.85	1
Kissinger [23]	7	–	0.60	1.0

The kinetic parameters of the phase transformation were determined by several methods. One DTA curve was integrated, as shown in Fig. 3. These data were analysed with the methods of Borchardt and Daniels, Freeman and Carroll, and Coats and Redfern. Several curves recorded at different heating rates were used to determine the activation energy according to Kissinger. The reaction order was determined from the shape of 20 DTA curves, using Kissinger's method. The results of these calculations are summarized in Table 3 and shown in Figs. 4–7. The values for the activation energy calculated by different methods do not show a good agreement. The first three methods are based on values of $d\alpha/dt$ and α obtained by integration of a DTA curve. These values are based on three assumptions: the DTA signal is proportional to the reaction rate; the baseline is straight; and the calibration factor is approximately constant in the temperature range of the peak. The last two assumptions are particularly doubtful. It is important to note that the largest deviation is found for the method of Coats and Redfern, which uses only values of α. These are expected to be less reliable than the $d\alpha/dt$ values. Kissinger's method is not based on calculated $d\alpha/dt$ and α values and has the further advantage that several DTA curves are used. Therefore, the value of 0.60 MJ mol^{-1} can be considered the most reliable value for the activation energy. This corresponds with some results in the literature [6,18].

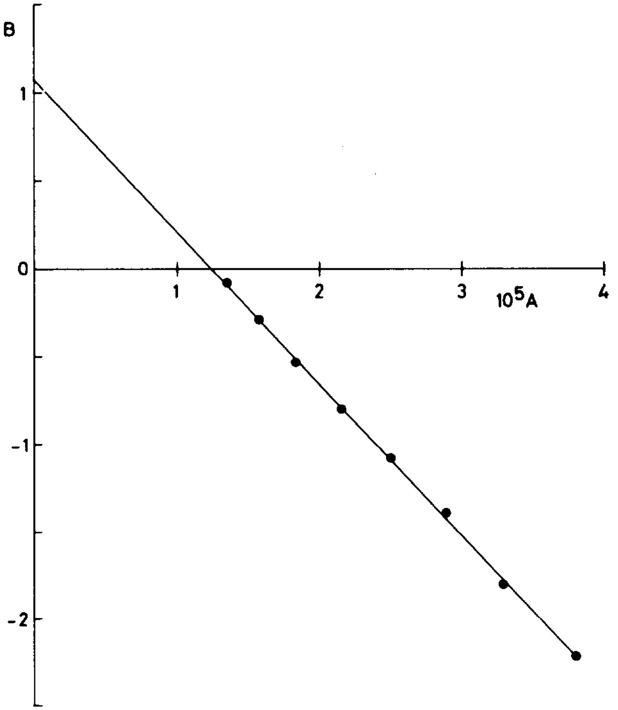

Fig. 5. Plot according to Freeman and Carroll [21].

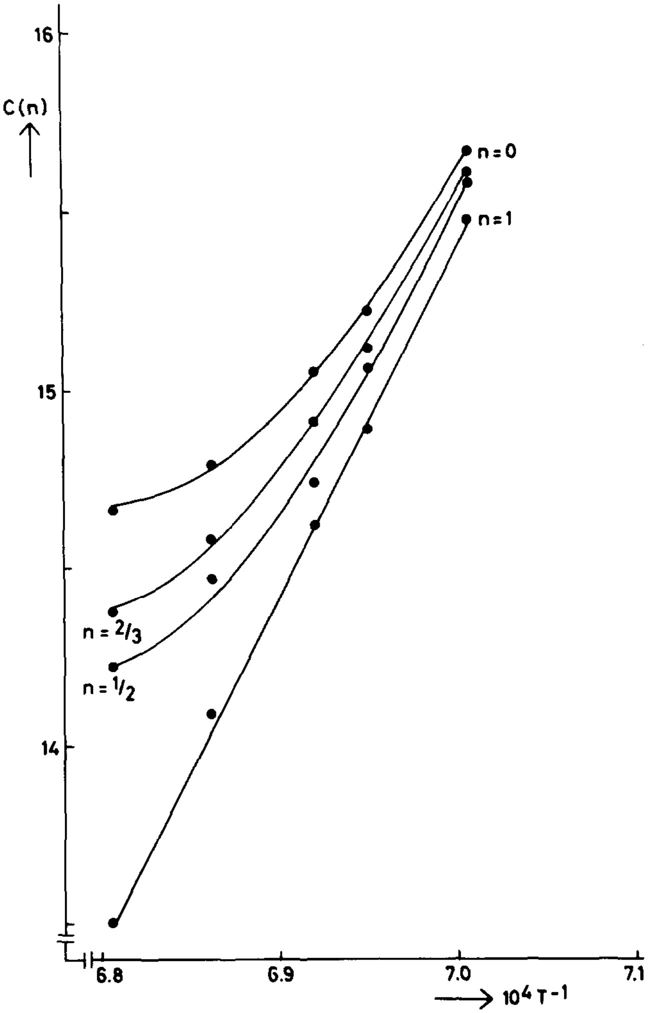

Fig. 6. Plot according to Coats and Redfern [22].

There is a very good agreement between the values of the order of the reaction determined by different calculation methods. If a nucleation-and-growth mechanism is assumed, a first-order reaction corresponds to random nucleation, with one nucleus being formed per crystallite [19]. This implies that the rate of nucleation is much smaller than the rate of growth. Similar results were reported by Dynys and Halloran [8].

Nucleation in solids is a much more complicated process than nucleation in a super-saturated solution. The activation energy of this process consists of several terms. The most important contribution is the activation energy of the jump frequency of the ions, which is identical to the activation energy of ion diffusion [24]. Since nucleation is a three-dimensional process, the activation energy of bulk diffusion will contribute to the activation energy of

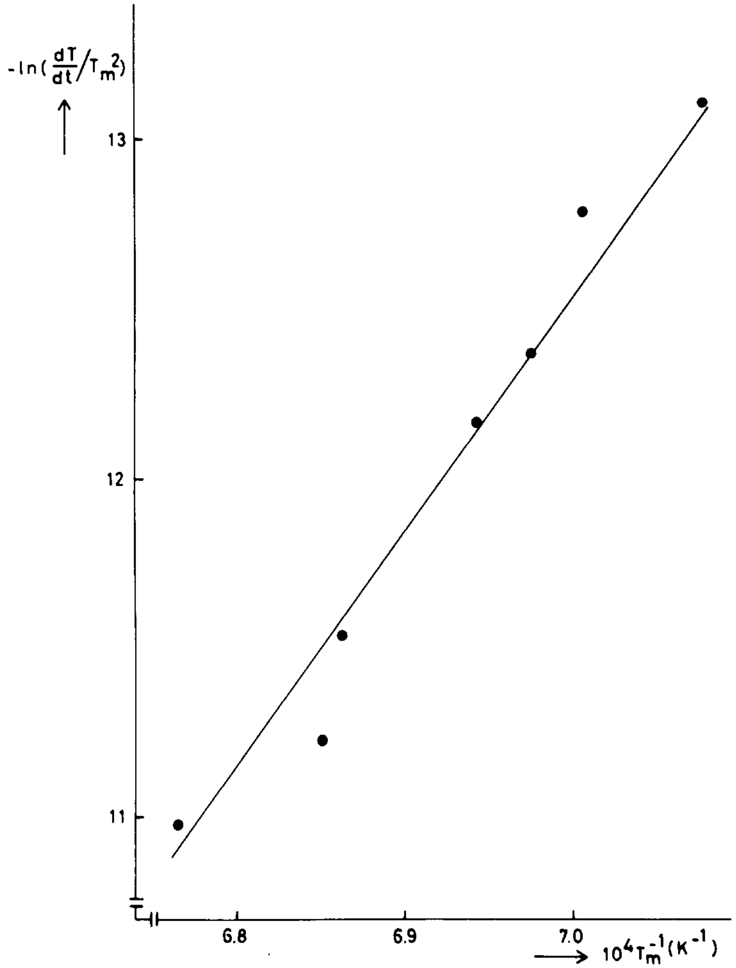

Fig. 7. Plot according to Kissinger [23].

nucleation. No quantitative data for bulk diffusion of aluminium and oxygen ions in gamma or theta alumina are available. For alpha alumina activation energies of 461 and 476 kJ mol^{-1} were reported [25,26] for bulk diffusion of oxygen and aluminium ions, respectively. As expected, these values are not very much lower than the activation energy for the phase transformation, as determined in this investigation.

CONCLUSIONS

(1) The phase transformation of gamma to alpha alumina can be studied quantitatively by DTA.

(2) The reaction order is one; this indicates a nucleation and growth mechanism with one nucleus per crystallite.

(3) The corresponding activation energy is 0.60 MJ mol^{-1}.

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