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Determination of kinetic parameters for nucleation and growth from DTA data

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Abstract

A mathematical model has been derived for non-isothermal kinetic analysis from overlapped exotherm and endotherm DTA effects occurring due to simultaneous nucleation and growth processes.

In the course of the mathematical treatment the refinement of the initial values of the kinetic parameters is performed.

The procedure for the determination of kinetic parameters from DTA has been demonstrated on a model system and on a kinetic analysis of mullite formation from diphasic gel.

INTRODUCTION

Nucleation and crystal-growth processes under non-isothermal conditions may proceed in two different ways. (i) Growth follows after the nucleation has been completed. (ii) Nucleation and growth processes take place simultaneously.

In the former case the DTA curve exhibits an exothermic strictly asymmetric maximum which corresponds to the crystal growth from previously formed nuclei. For such a $\Delta T-T$ relationship, the fraction of the crystalline phase at DTA peak temperature T_P is $\alpha_P = 0.63$.

In the latter case the thermal effect of nucleation and the thermal effect of growth overlap. Consequently, the DTA maximum belonging to the crystallization process deforms, the asymmetric feature is less pronounced, and $\alpha_P < 0.63$.

For processes with separate nucleation and growth, the non-isothermal kinetic analysis has already been worked out; numerous treatments for the

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determination of the crystal growth parameter n and the activation energy of crystal growth E_G have been described [1–7]. In the majority of treatments integral or differential equations have been used.

In the case of superimposed DTA effects, however, the α values obtained are not correct, and this impedes the successful use of the integral equation. Moreover, for a DTA curve of deformed shape the basic differential equation is not applicable.

This work describes a newly developed procedure for the determination of kinetic parameters from the DTA curve with superimposed effects, and from the apparent $\alpha - T$ relationship.

THEORETICAL

If the nucleation and growth processes take place simultaneously, kinetic analysis should be carried out by taking into account two basic functions $g(T)$ and $f(T)$. $g(T)$ is the integral function and for growth it is given by

$$g_G(T) = -\ln(1 - \alpha_G) = \exp[(a_G/T) + b_G] \tag{1}$$

where α_G is the degree of crystallization, $a_G = -(nE_G + qE_N)(1.052/R) = -mE(1.052/R)$ [1, 8], E_G is the activation energy of growth, E_N is the activation energy of nucleation, $n = p/s$, p is the number of crystal growth dimensions ($p = 1, 2, 3$), s equals 1 for linear and 2 for parabolic growth, q equals 1 for a constant nucleation rate and 0 for quenched nuclei ($0 < q < 1$ for retarded nucleation and $q > 1$ for accelerated nucleation), $m = n + q = (p/s) + q$ [10], $E = (nE_G + qE_N)/m$ [1, 8], and $b_G = \ln(K_0/\beta^m)$ ($\beta = dT/dt$).

In eqn. (1) Doyle's [9] approximation for $\int_0^T \exp(a/T)\,dT$ has been used, as proposed by Matusita et al. [6]. The appropriate differential function $f(T) = d\alpha/dT$ in this case is

$$f_G(T) = -a_G g_G(T) \exp(-g_G(T))/T^2 \tag{2}$$

Analogously, for the nucleation process we can write

$$g_N(T) = -\ln(1 - \alpha_N) = \exp[(a_N/T) + b_N] \tag{3}$$

$$f_N(T) = -a_N g_N(T) \exp(-g_N(T))/T^2 \tag{4}$$

In order to apply DTA data to eqns. (1)–(4) it is necessary to define the relationship between the experimentally obtained values of α and the corresponding α_G and α_N values. If P denotes the total area under the experimentally obtained DTA curve, P_G the total area under the DTA curve of growth and P_N the total area under the DTA curve of nucleation we have

$$P = |P_G| - |P_N| \tag{5}$$

and for areas up to temperature T

$$P_T = |P_{GT}| - |P_{NT}| \tag{6}$$

Now $\alpha = P_T/P$, $\alpha_G = P_{GT}/P_G$ and $\alpha_N = P_{NT}/P_N$ so

$$\alpha = \alpha_G K_G - \alpha_N K_N \tag{7}$$

where $K_G = |P_G/P|$ and $K_N = |P_N/P|$.

If $\alpha_G = 1$ and $\alpha_N = 1$ we also have $\alpha = 1$ and consequently

$$K_G - K_N = 1 \tag{8}$$

In the same way

$$K_{NG} = K_N/K_G = |P_N/P_G| = |Q_N/Q_G| \tag{9}$$

which means that K_{NG} is in fact the absolute value of the ratio of the heat necessary for the endothermic process and the heat developed in the exothermic process.

The relationship between the corresponding differential functions follows from eqn. (7) as

$$\mathrm{d}\alpha/\mathrm{d}T = K_G\, \mathrm{d}\alpha_G/\mathrm{d}T - K_N\, \mathrm{d}\alpha_N/\mathrm{d}T \tag{10}$$

i.e.

$$f(T) = K_G f_G(T) - K_N f_N(T) \tag{11}$$

The experimental DTA curve starts after detection of the difference between $K_G f_G(T)$ and $K_N f_N(T)$ becomes possible, which means that when $\alpha \approx 0$, $\alpha_G > 0$ and $\alpha_N > 0$. For the temperature interval T_s–T_o (Fig. 1), when

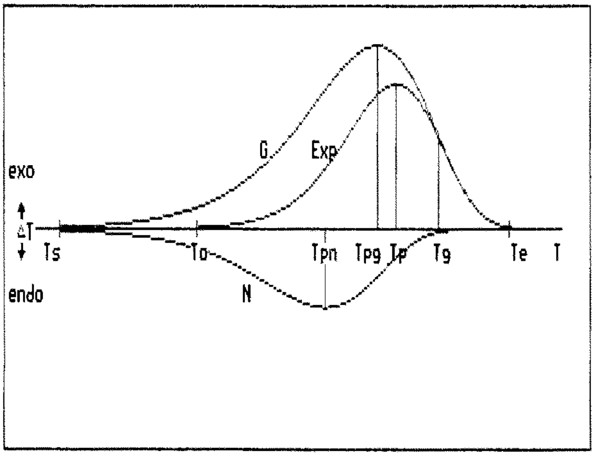

Fig. 1. Hypothetic superposition of exothermic (G) and endothermic (N) DTA effects and the experimental DTA curve (Exp). T_P, T_{pg} and T_{pn} are the temperatures of the maxima of the experimental curve $f(T)$, the growth function $f_G(T)$ and the nucleation function $f_N(T)$ respectively. For $T > T_g$, $f_N(T) \approx 0$. For the temperature interval T_s–T_o, $f(T) \rightarrow 0$.

$\alpha \approx 0$, $\alpha_G > 0$, $\alpha_N > 0$, according to eqn. (7)

$$K_G \alpha_G = K_N \alpha_N \tag{12}$$

and

$$K_G\{1 - \exp[-g_G(T)]\} = K_N\{1 - \exp[-g_N(T)]\} \tag{13}$$

or approximately, because of small values $g_G(T)$ and $g_N(T)$

$$K_G g_G(T) = K_N g_N(T) \tag{14}$$

Equation (14) shows that a_G and a_N in eqns. (1) and (3) are equal, i.e. that

$$a = a_G = a_N \tag{15}$$

which is acceptable because the processes of nucleation and growth are interconnected [8] and they have the same average activation energy E, with $m = n + q$. From eqns. (14) and (15) it follows that

$$K_G \exp(b_G) = K_N \exp(b_N) \tag{16}$$

Further, if

$$k_{ng} = \exp(b_N - b_G) \tag{17}$$

we have

$$k_{ng} = 1/K_{NG} \tag{18}$$

and in accordance with eqn. (14)

$$g_N(T) = k_{ng} g_G(T) \tag{19}$$

By introducing expressions (18) and (19) into eqn. (10) we obtain

$$f(T) = -aK_G g_G(T)\{\exp[-g_G(T)] - \exp[-k_{ng} g_G(T)]\}/T^2 \tag{20}$$

which because $\mathrm{d}Q/\mathrm{d}t = \text{const} \times \mathrm{d}\alpha/\mathrm{d}T$ represents a mathematical expression for the experimentally obtained DTA curve.

Equation (18) is valid only when $f(T) = 0$ with $f_G(T) > 0$ and $f_N(T) > 0$ for $T < T_o$. If these conditions are not satisfied the $k_{ng} \neq 1/K_{NG}$ and $a_G \neq a_N$, which means that two independent processes are superimposed. In this case, eqn. (20) does not represent a mathematical expression for the experimental DTA curve; this problem is addressed separately.

Determination of parameters a, b$_G$, k$_{ng}$ *and* K$_G$

The determination of a, b_G, k_{ng} and K_G parameters proceeds in three steps:

(i) the determination of initial values;
(ii) the refinement of parameters by using the integral equation;
(iii) the refinement of parameters by using the differential equation.

The determination of initial values of parameters

From eqns. (7) and (8) it can also be shown that

$$1 - \alpha = K_G(1 - \alpha_G) - K_N(1 - \alpha_N) \tag{21}$$

or

$$K_G = [(1 - \alpha) + K_N(1 - \alpha_N)]/(1 - \alpha_G) \tag{22}$$

Assuming negligible influence of nucleation after the maximum of the experimentally obtained DTA curve (Fig. 1) (i.e. $\alpha_N \rightarrow 1$ for temperature interval $T > T_P$) we have

$$K_G \geqslant (1 - \alpha)/(1 - \alpha_G) \tag{23}$$

Further, if the difference in the positions of the experimentally determined DTA maximum and the maximum of crystal growth is not significant the relation

$$K_G \geqslant (1 - \alpha_P)/(1 - 0.63) \tag{24}$$

is satisfied. Then for initial values K_G and K_N

$$K_G = (1 - \alpha_P)/0.37 \tag{25}$$

$$K_N = K_G - 1 = (0.63 - \alpha_P)/0.37 \tag{26}$$

and for k_{ng}

$$k_{ng} = K_G/K_N = (1 - \alpha_P)/(0.63 - \alpha_P) \tag{27}$$

Another set of initial values (i.e. values of a and b_G) can be obtained from the same assumptions. In this case, for $T > T_P$ and from eqns. (1) and (23), we obtain

$$-\ln[(1 - \alpha)/K_G] = g_G(T) = \exp[(a/T) + b_G] \tag{28}$$

corresponding to the linear relationship

$$\ln\{-\ln[(1 - \alpha)/K_G]\} = (a/T) + b_G \tag{29}$$

which serves for the determination of the initial values of parameters a and b_G.

The refinement of the initial values of parameters a, b_G, K_G *and* k_{ng}

It can be assumed that the interrelationship between $F(T)$ ($F(T) = f(T)$ or $1 - \alpha$) and k_{ng}, a, b_G, is

$$F(T) = \phi(k_{ng}, a, b_G) \tag{30}$$

according to which any change in a, k_{ng} or b_G is reflected in the $F(T)$

function and thus the total differential of eqn. (30) reads

$$dF = \sum_i (\partial F/\partial p_i)\, dp_i \tag{31}$$

where $p = k_{ng}, a, b_G$.

After substitution of

$$\Delta F = F - F_c \qquad \text{(for } dF\text{)} \tag{32}$$

$$\Delta p_i = p_i - p_{ic} \qquad \text{(for } dp_i\text{)} \tag{33}$$

we obtain

$$\Delta F = \sum_i (\partial F/\partial p_i)\, \Delta p_i \tag{34}$$

where p_i is the most probable value and p_{ic} the initially calculated value or a value obtained from a lower refinement cycle. F denotes the experimentally determined value and F_c is the calculated value.

The application of eqn. (34) to n experimental items of data gives a system of n equations with i unknowns. This system can be presented in a matrix form as

$$\boldsymbol{S}\boldsymbol{P} = \boldsymbol{R} \tag{35}$$

where $\boldsymbol{S}$ is the sensitivity function matrix

$$\boldsymbol{S} = \begin{pmatrix} \partial F(1)/\partial p_1 & \partial F(1)/\partial p_2 & \cdots & \partial F(1)/\partial p_i \\ \partial F(2)/\partial p_1 & \partial F(2)/\partial p_2 & \cdots & \partial F(2)/\partial p_i \\ \vdots & \vdots & & \vdots \\ \partial F(n)/\partial p_1 & \partial F(n)/\partial p_2 & \cdots & \partial F(n)/\partial p_i \end{pmatrix} \tag{36}$$

$\boldsymbol{P}$ is the vector of corrections to the parameters

$$\boldsymbol{P} = \begin{pmatrix} \Delta p_1 \\ \Delta p_2 \\ \vdots \\ \Delta p_i \end{pmatrix} \tag{37}$$

and $\boldsymbol{R}$ is the vector of residuals in the $F(T)$

$$\boldsymbol{R} = \begin{pmatrix} \Delta F(1) \\ \Delta F(2) \\ \vdots \\ \Delta F(n) \end{pmatrix} \tag{38}$$

The best values for Δp_i are obtained by the least squares method and most reliable values for p_i from eqn. (34)

$$p_i = p_{\mathrm{ic}} + \Delta p_i \tag{39}$$

The refinement of parameters by using the integral equation

The basis for the first step of the refinement is eqn. (21) in its transformed form

$$F(T) = 1 - \alpha = K_{\mathrm{G}} \exp[-g_{\mathrm{G}}(T)] - K_{\mathrm{N}} \exp[-k_{\mathrm{ng}} g_{\mathrm{G}}(T)] \tag{40}$$

or

$$F(T) = 1 - \alpha = K_{\mathrm{G}}\{\exp[-g_{\mathrm{G}}(T)] - \exp[-k_{\mathrm{ng}} G_{\mathrm{G}}(T)]\} + \exp[-k_{\mathrm{ng}} g_{\mathrm{G}}(T)] \tag{41}$$

The parameters a, b_{G} and k_{ng} can be refined, and for this purpose the relations

$$\partial F/\partial b_{\mathrm{G}} = K_{\mathrm{G}}\{-g_{\mathrm{G}}(T) \exp[-g_{\mathrm{G}}(T)] + k_{\mathrm{ng}} g_{\mathrm{G}}(T) \exp[-k_{\mathrm{ng}} g_{\mathrm{G}}(T)]\} - k_{\mathrm{ng}} g_{\mathrm{G}}(T) \exp[-k_{\mathrm{ng}} g_{\mathrm{G}}(T)] \tag{42}$$

$$\partial F/\partial a = (\partial F/\partial b_{\mathrm{G}})/T \tag{43}$$

and

$$\partial F/\partial k_{\mathrm{ng}} = (K_{\mathrm{G}} - 1) g_{\mathrm{G}}(T) \exp[-k_{\mathrm{ng}} g_{\mathrm{G}}(T)] \tag{44}$$

must be included; and because $k_{\mathrm{ng}} = K_{\mathrm{G}}/(K_{\mathrm{G}} - 1)$ we also have

$$K_{\mathrm{G}} = k_{\mathrm{ng}}/(k_{\mathrm{ng}} - 1) \tag{45}$$

The refinement procedure can be repeated by using partial derivatives according to eqns. (42)–(44) and with F_{c}, which is obtained by including a, b_{G} and k_{ng} values calculated in a previous cycle from eqn. (41).

The refinement of parameters by using the differential equation

In the second step of the refinement the values obtained in the last cycle of previous refinement serve as initial values. The basic equation for this second step is eqn. (20) ($F(T) = \mathrm{d}\alpha/\mathrm{d}T$), and therefore

$$\partial F/\partial b_{\mathrm{G}} = f_{\mathrm{G}}(T)[1 - g_{\mathrm{g}}(T)] - f_{\mathrm{N}}(T)[1 - k_{\mathrm{ng}} g_{\mathrm{G}}(T)] \tag{46}$$

$$\partial F/\partial a = (\partial F/\partial b_{\mathrm{G}})/T \tag{47}$$

and

$$\partial F/\partial k_{\mathrm{ng}} = f_{\mathrm{N}}(T) g_{\mathrm{G}}(T) \tag{48}$$

with

$$f_{\mathrm{G}}(T) = -aK_{\mathrm{G}} g_{\mathrm{G}}(T) \exp[-g_{\mathrm{G}}(T)]/T^2 \tag{49}$$

$$f_{\mathrm{N}}(T) = -aK_{\mathrm{G}} g_{\mathrm{G}}(T) \exp[-k_{\mathrm{ng}} g_{\mathrm{G}}(T)]/T^2 \tag{50}$$

TESTING OF THE WORKED-OUT PROCEDURE

The model system and experimental data

The procedure for the determination of kinetic parameters from the DTA curve with overlapped exotherm and endotherm maxima (which are superimposed because of simultaneous nucleation and growth) has been demonstrated on a model system and applied in the determination of the kinetic parameters of mullite ($3Al_2O_3 \cdot SiO_2$) formation from diphasic gel.

A simulated DTA curve of the model system (Fig. 2) has been obtained according to eqn. (20) with the following assumed parameters: $a = -50\,000$ K; $mE = 390$ kJ mol^{-1}; $K_{\mathrm{G}} = 1.76$; $b_{\mathrm{G}} = 45.45$; $k_{\mathrm{ng}} = 2.32$; $T_{\mathrm{pg}} = 1100$ K; $T_{\mathrm{pn}} = 1080$ K.

Gel with stoichiometric mullite composition Al:Si = 3:1 was prepared by a method similar to that described by Hoffmann et al. [11]. Aluminium nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$) was dissolved in absolute ethanol with weight ratio of nitrate to alcohol of 1:9. The solution was kept in a

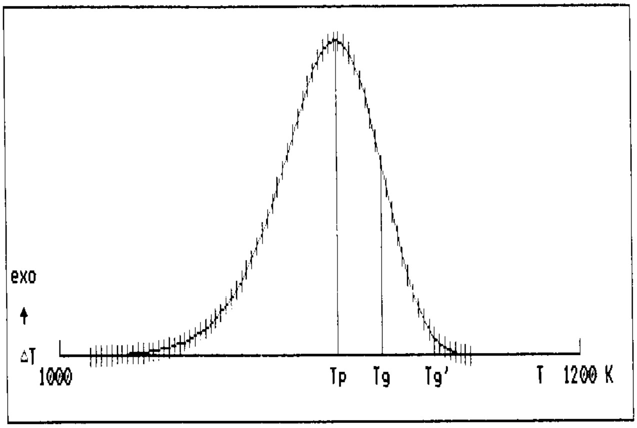

Fig. 2. A segment of the simulated DTA curve of the model system. T_g–T_g' is the temperature interval for which it is assumed that $f_{\mathrm{N}}(T) \approx 0$.

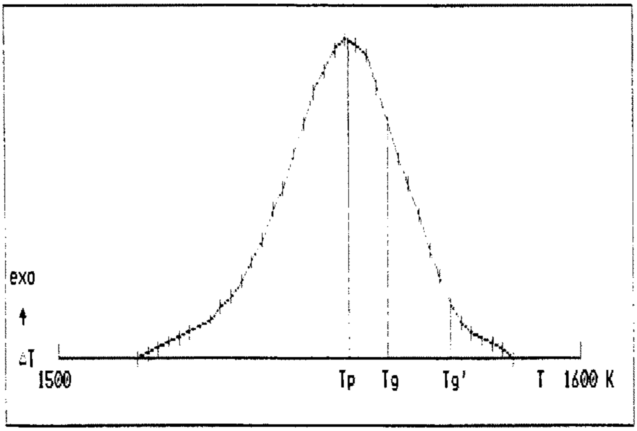

Fig. 3. The segment of the DTA curve of mullite in the range 1500–1600 K at a heating rate $\beta = 15\ \text{K min}^{-1}$. T_g–T_g' is the temperature interval for which it is assumed that $f_N(T) \approx 0$.

water bath overnight at 60°C. Tetraethyl orthosilicate (TEOS) previously mixed with ethanol in the same weight ratio was added dropwise to the nitrate solution. After 24 h of mixing, a 2 M aqueous NH_4OH solution was added dropwise over 2 h up to pH = 8. The TEOS and Al^{3+} of the starting solutions hydrolyzed and formed a colloidal suspension. The colloidal suspension obtained was aged for 24 h and filtered on a Buchner funnel. The dried gel was powdered, calcinated at 600°C for 2 h and subjected to DTA at heating rates β of 5, 7, 10, 15 and 20 K min^{-1} up to 1550°C.

The DTA curve of the precipitated mullite precursor displays two exothermic peaks. The first peak at 1011°C ($\beta = 15\ \text{K min}^{-1}$) is attributed (on the basis of X-ray diffraction) to the formation of Al–Si-spinel; the second peak at 1283°C is attributed to the formation of mullite. In Fig. 3 the second exothermic peak at 1283°C of mullite formation is shown.

The determination of initial values of kinetics parameters and the refinement procedure

In order to compare the experimentally obtained DTA curve and the curve calculated according to eqn. (20), values of k_G, a, b_G and k_{ng} should be determined first. For this purpose the temperature interval 1014–1156 K in the case of the model system has been divided into 71 parts, in steps of 2 K. The corresponding $f(T)$ values were used in a further treatment. In this case the $f(T)$ maximum is at 1106 K, and the corresponding α_P value is 0.567. The initial value for K_g of 1.17 was determined according to eqn. (25) and the initial value for k_{ng} of 6.88 according to eqn. (27). The calculated value $K_G = 1.17$ has been used for the determination of the initial values of

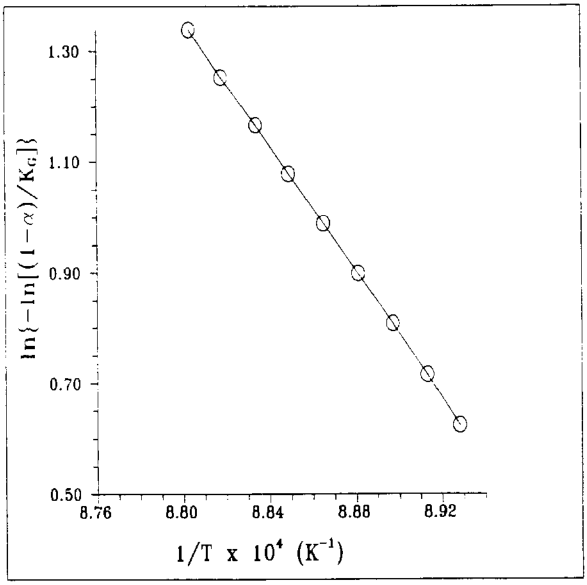

Fig. 4. $\ln\{-\ln[(1-\alpha)/K_G]\}$ vs. $1/T$ for the model system; α values in the temperature interval 1124–1144 K are taken into account.

a and b_G according to eqn. (29). Figure 4 shows the linear relationship of $\ln\{-\ln[(1-\alpha)/K_G]\}$ and $1/T$. Nine items of data for α have been used for the determination of this linear interdependence in the temperature interval 1124–1144 K (Fig. 2). Parameter values $a = -56\,891$ (which corresponds to $E = 443$ kJ mol^{-1}) and $b_G = 51.4$ were obtained by the least squares method. This set of initial values for a, b_G, K_G and k_{ng} (Table 1, column 2) has been used for the first refinement according to eqns. (40)–(45). After 10 cycles the first set of refined values was obtained (Table 1, column 3). The number of cycles for the second refinement is determined by the difference between two consecutive k_{ng} values ($k_{ng}(j)$ and $k_{ng}(j-1)$). This difference should be less than ε, i.e.

$$\varepsilon < |k_{ng}(j) - k_{ng}(j-1)| \qquad (51)$$

TABLE 1

Calculated values of parameters a, mE, b_G and k_{ng} for the model system, in the initial determination and after the first and second refinements

Parameter	Before refinement	After first refinement	After second refinement	True value
a/K	−56891	−51806	−51549	−50000
mE/(kJ mol^{-1})	443.5	403.8	401.8	390.0
b_G	51.4	47.0	46.8	49.45
k_{ng}	6.88	2.91	2.89	2.32

TABLE 2

Initially determined values of parameters K_G, k_{ng}, a, mE and b_G parameters for crystallization of mullite at various heating rates β

DTA no.	β/(K min^{-1})	α_P	K_G	k_{ng}	a/K	mE/(kJ mol^{-1})	b_G
1	5	0.487	1.386	3.59	−209305	1631	136.42
2	7	0.497	1.360	3.78	−203148	1583	132.04
3	10	0.540	1.242	5.12	−158958	1239	102.85
4	15	0.531	1.267	4.74	−164934	1285	106.08
5	20	0.498	1.357	3.80	−154800	1206	100.50

with

$$\varepsilon = 0.01 \times k_{ng}(j) \tag{52}$$

where j denotes the number of cycles.

For the analysis of the model system only two cycles ($j = 2$) were necessary in the second refinement in order to meet the conditions given by eqns. (51) and (52). The results of this second refinement are listed in Table 1, column 4.

An analogous treatment for the determination of parameters has also been carried out for five experimentally obtained DTA curves from the crystallization of mullite with $\beta = 5$, 7, 10, 15 and 20 K min^{-1}. For every

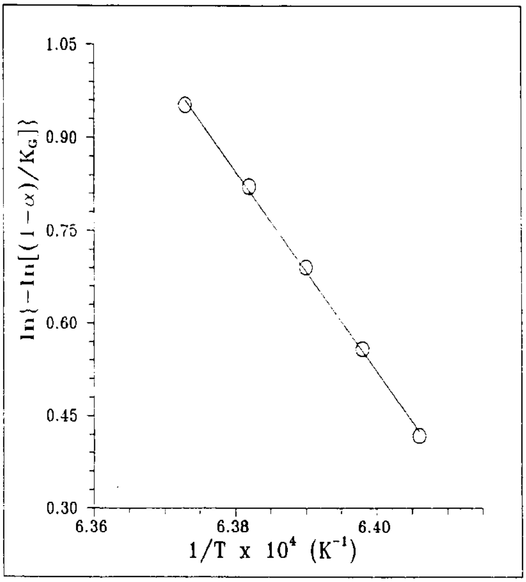

Fig. 5. ln{−ln[(1 − α)/K_G]} vs. 1/T for crystallization of mullite calculated from the DTA curve for which β = 15 K min^{-1}; α values for the temperature interval 1563–1575 K were used.

curve an interval has been selected in order to obtain the linear relationship of eqn. (29) by using previously determined initial values of K_G and k_{ng} calculated from corresponding α_P values. Table 2 gives the initial values obtained, and Fig. 3 shows the DTA curve for which $\beta = 15\ \mathrm{K\ min^{-1}}$ and the selected interval containing five experimentally determined α values. Figure 5 shows the linear relationship $\ln\{-\ln[(1-\alpha)/K_G]\}$ vs. $1/T$ for the same sample.

DISCUSSION

Table 1 illustrates the significant difference obtained between the initial and refined values of the parameters found in the analysis of the model system. Very good agreement has also been observed between the simulated and calculated DTA curves of the model system (Fig. 6). This agreement is especially significant because there is a big difference between the exothermic curve of growth ($f_G(T)$) and "experimental" (simulated) curve ($f(T)$) (Fig. 6). The difference appears because of the significant contribution of the endothermic nucleation curve ($f_N(T)$). Table 3 gives values for T_{pg} and T_{pn}. In the kinetic analysis of the crystallization of mullite

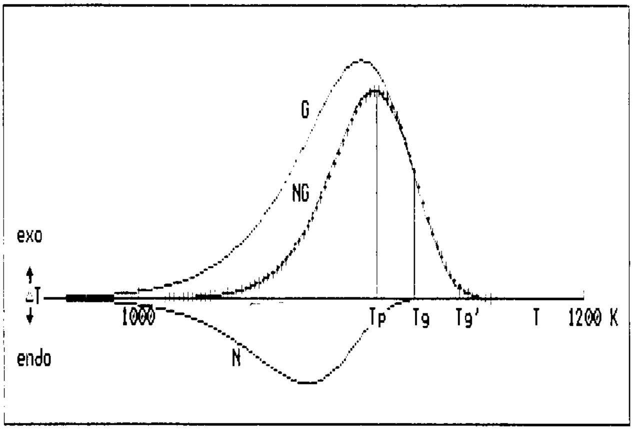

Fig. 6. Calculated "experimental" DTA curve of nucleation and growth (NG) for the model system with exothermic growth (G) and endothermic nucleation (N); † indicates the assumed starting values of $f(T)$.

TABLE 3

Assumed and calculated temperature of maximum for growth curve T_{pg} and nucleation curve T_{pn} of the model system parameters

	T_{pg}/K	T_{pn}/K
Assumed	1100	1080
Calculated	1102	1078

TABLE 4

Calculated values for mE and k_{ng} parameters in the course of mullite crystallization at various heating rates β

DTA no.	$\beta/(\mathrm{K\,min^{-1}})$	$mE/(\mathrm{kJ\,mol^{-1}})$			k_{ng}		
		Init.	After first ref.	After second ref.	Init.	After first ref.	After second ref.
1	5	1631	1643	1682	3.59	3.59	3.59
2	7	1583	1586	1580	3.78	3.78	3.77
3	10	1239	1488	1499	5.12	5.12	3.36
4	25	1285	1391	1391	4.74	4.74	3.67
5	20	1206	1298	1315	3.80	3.80	3.02

significant differences between the initial and refined values of parameters were also detected. This is illustrated in Table 4. The first refinement yielded significant changes in mE values, but was of no influence on the initial k_{ng} values. However, after the second refinement significant changes were also observed for k_{ng} in some cases, whereas the changes in mE values were insignificant.

The differences in mE dependence on β were also observed in some other systems, but so far there is no adequate explanation for this phenomenon.

In spite of the mentioned differences in mE, every experimentally obtained DTA curve was in very good agreement with the corresponding calculated curve. One example is illustrated in Fig. 7. For the experimentally determined DTA curves ($f(T)$) a set of $f_G(T)$ (exo) and $f_N(T)$ (endo) curves was obtained, three independent linear functions ln β vs. $1/T_P$ were

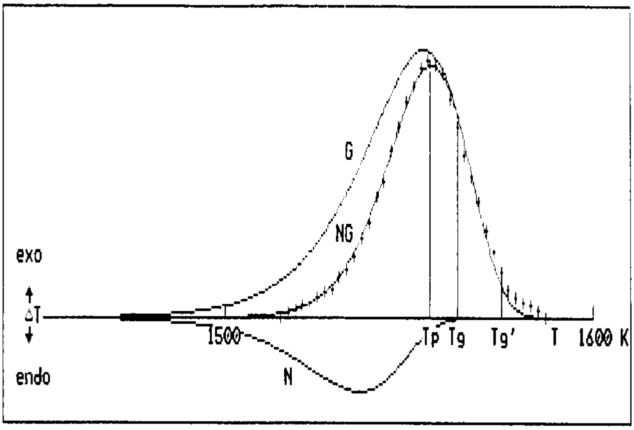

Fig. 7. Calculated $f(T)$ curve of nucleation and growth (NG) for crystallization of mullite with exothermic growth (G) and endothermic nucleation (N); † indicates the experimental values from the DTA curve.

TABLE 5

Experimentally determined (Exp.) and calculated (G and N) temperatures of maxima T_P

DTA no.	β/(K min^{-1})	T_P/K			m		
		Exp.	G	N	Exp.	G	N
1	5	1534	1534	1520	1.84	1.75	1.65
2	7	1538	1538	1523	1.73	1.64	1.55
3	10	1546	1545	1530	1.63	1.55	1.46
4	15	1555	1554	1537	1.52	1.45	1.37
5	20	1561	1560	1544	1.44	1.37	1.29
		$\bar{E}$[a]			$\bar{m}$[b]		
		Exp.	G	N	Exp.	G	N
		915	961	1019	1.63	1.55	1.46

[a] Values obtained according to ref. 4.

[b] Values obtained by dividing mE values (Table 4) by mean values for $\bar{E}$.

calculated [4] which gave $\bar{E}_{exp}$, $\bar{E}$(G) and $\bar{E}$(N) values. In Table 5, experimentally determined T_P values are compared with T_P values obtained from $f_G(T)$ and $f_N(T)$ curves, and in Fig. 8 linear relationships ln β vs. $1/T_P$ are presented. The differences between $\bar{E}$ values obtained from $f_G(T)$ and $f_N(T)$ are not large (961 and 1019 kJ mol^{-1} respectively) and we can take the

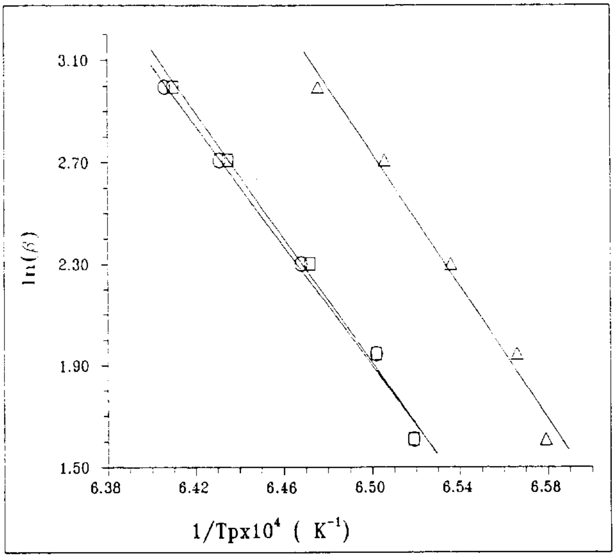

Fig. 8. ln β vs. $1/T_P$ according to Ozawa [4] from experimental T_P values (○) and calculated values for T_{pg} (□) and T_{pn} (△). β = 5, 7, 10, 15 and 20 K min^{-1}.

mean value for $\bar{E}$ as 990 kJ mol^{-1}. Between this mean value and E value determined directly from experimental DTA curves ($\bar{E} = 915$ kJ mol^{-1}) the difference is bigger. This is not surprising because (as already explained) the experimental DTA curve is not suitable for kinetic analysis in the case of the system under consideration. The difference might be even larger, depending on the degree of overlapping of exothermic and endothermic effects.

With the increase of β values, m values decrease, in accordance with the change in mE values. The mean m value obtained from functions of nucleation and growth is 1.5. Because $m = n + q$, there are three possibilities for evaluating n and q: assuming one-dimensional growth at the interface or two-dimensional growth controlled by diffusion and retarded nucleation, $n = 1$ and $q = 0.5$; assuming one-dimensional growth controlled by diffusion with constant nucleation rate, $n = 0.5$ and $q = 1$.

Based on a detailed study of the isothermal reaction kinetics, microstructure and phase-transformation mechanism, Wei and Halloran [12] were the first to illustrate that mullite formation from diphasic gels occurs by a nucleation and growth mechanism with an apparent activation energy of 1070 ± 200 kJ mol^{-1}. The transformation is preceded by a temperature-dependent incubation period with a similarly high apparent activation energy of 987 ± 63 kJ mol^{-1}. They concluded that this transformation is either interface-controlled or short-range-diffusion-controlled, near the alumina–mullite–silica interfaces. However, with this model, Wei and Halloran could not explain the experimentally observed time-dependence of mullite crystal growth. According to Sundaresan and Aksay [13], only the dissolution of alumina in the amorphous gel can provide an explanation for the time-dependent growth of mullite, and this is the rate-limiting step in the process.

Huling and Messing [14, 15] synthesized hybrid gels containing a mixture of polymeric (molecular scale homogeneous) mullite precursors and colloidal gel, and examined their phase-transformation kinetics and resulting microstructures. Their results suggest that the rate limiting step may not be diffusion controlled, but instead may be associated with the presence of alumina (spinel-type) in the matrix.

The obtained value of the apparent activation energy of nucleation and crystal growth (990 ± 29 kJ mol^{-1}) is in good agreement with the values obtained by Wei and Halloran ($E_N = 987$, $E_G = 1070$ kJ mol^{-1}). Besides, the decrease of the mE values with the decrease of the heating rate of the DTA scan is also in accordance with the time-dependence of mullite crystal growth as experimentally observed under isothermal kinetics.

The isothermal kinetic studies of the present authors (to be published elsewhere), reveal the activation energy of mullite growth $E = 999$ kJ mol^{-1} and the Avrami exponent $n = 1$, up to $\alpha = 0.70$, for the same sample investigated. From these observations it is reasonable to conclude that the rate-limiting step in the formation of mullite is not diffusion-controlled, and the first assumption that the growth rate is limited by the interface reaction is more probable.

The same method was used to determine the apparent activation energy of nucleation and crystal growth, and the mechanism of the processes for various diphasic and colloidal gels with pseudoboehmite and amorphous SiO_2, or for the completely non-crystalline diphasic precursors [16].

CONCLUSION

Kinetic parameters of a non-isothermal reaction have been determined by using a newly derived equation (eqn. (20)) for the case of overlapped exothermic and endothermic DTA effects occurring due to simultaneous nucleation and growth processes. Specifically, by applying DTA with different β values for the crystallization of mullite, a value for the activation energy has been obtained which is in agreement with the literature. Not only the activation energy of the nucleation and crystalization of mullite, but also the Avrami exponent evaluated by proposed method is in good agreement with the isothermal kinetics data.

The determination of the kinetic parameters mentioned was enabled by refining the initial values. This refinement can be successful only if the proposed mathematical model corresponds fully to the kinetic process in the course of the DTA. Accordingly, every mechanism of non-isothermal kinetics calls for specifically modified equations in the initial determination and in the refinement of parameters.

All calculations were carried out by applying the computer program NOIZOKIN.

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