THE INFLUENCE OF GRAIN SIZE ON THE OVERALL KINETICS OF SURFACE-INDUCED GLASS CRYSTALLIZATION

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A simple kinetic model of surface-induced glass crystallization is proposed. The grain size of glass powders, a constant density of surface nuclei and a steadily increasing temperature throughout the reaction are taken into account. The crystal growth rate and the density of surface nuclei can be estimated easily from overall kinetic curves (e.g. DTA curves) of powder of different grain size.

The usefulness of the model is demonstrated in the case of the primary surface-induced crystallization of cordierite glass powders.

Surface-induced glass crystallization is of increasing interest as a limiting effect in the manufacturing of glass ceramic materials by sinter crystallization technologies. Since glass powders are used in a broad range of particle size, it is necessary to take into consideration the influence of particle size on a surface-induced crystallization process and its overall description.

Especially the relation between the particle size and the mean nearest neighbour distance of surface nucleation sites determines the topokinetic character of the reaction. This character may change due to decreasing grain size.

Basically, the kinetics of surface-induced glass crystallization should be treated in terms of the topokinetic model given by Mampel[1] and Todes[2]. Unfortunately, it is difficult to apply this kinetic method, because no explicit formulae were given. Considering special limitations to the rates of surface nucleation and crystal growth (which is equivalent to special topokinetic assumptions), Mampel could derive previously known kinetic equations [3, 4, see also 5]. These topokinetic equations and a great number of other topokinetic formulae [6] are consequently limited to those reaction stages in which the simplifying topokinetic assumptions are valid.

On the other hand, the Avrami–Erofeev equation [7–9] has also been widely used as a formal kinetic method in the study of surface-induced glass crystallization [10].

A generalized form of this equation (similar to a Weillbull distribution law) was introduced, making it possible to describe the coalescence and impingement process by means of a specially chosen (or fitted) function of the reacted fraction $f(x)$ [10, 11, 16].

However, in this case too simplifying topokinetic assumptions must be adopted in order to interpret the fitted formal kinetic parameters. Hence, if the topokinetic character of the reaction does not remain unchanged, the kinetic parameters may appear to depend on time or grain size [10, 12, 13]. A physical interpretation becomes questionable in this case. In this sense, the use of modified Avrami–Erofeev equations is also limited to special topokinetic conditions still remaining to be satisfied. Even under unchanged topokinetic conditions, it is difficult to discuss the influence of grain size on the overall kinetics of surface-induced glass crystallization by means of the Avrami–Erofeev equation [6].

The aim of the present paper is to focus attention on the influence of grain size on the overall kinetics of surface-induced glass crystallization.

The simultaneous growth of surface-nucleated crystals into the bulk of cubic glass grains is described with regard to a possible change of the topokinetic character depending on time, grain size and the density of surface nuclei, as well as to a steadily increasing temperature throughout the reaction. Kinetic equations and theoretical DTA curves are given.

The primary crystallization of cordierite glass powders on a large scale of particle size was studied by DTA. The curves obtained are discussed in terms of the given model. Direct microscopic measurements are compared to prove the calculated kinetic parameters.

Theory

Assumptions

The adopted topokinetic simplifications are shown in Fig. 1. The glass powders are regarded as consisting of uniform cubic (edge length $= 2R_0$) glass particles (assumption $a1$). The growing crystallites are cuboids, differently characterized by $r(t)$ depending on the position of their surface nucleation sites ($a2$). Additionally, $r(t)$ denotes the thickness of the crystalline surface layer after the impingement of the single crystallites. t is the reaction time.

The nucleation is assumed to be so fast that all possible surface nuclei come into existence at $t=0$, giving a constant density of surface nuclei at detectable transformation rates ($a3$). The distribution of nuclei is spatially homogeneous, characterized by the nearest neighbour distance $2l$ ($a4$).
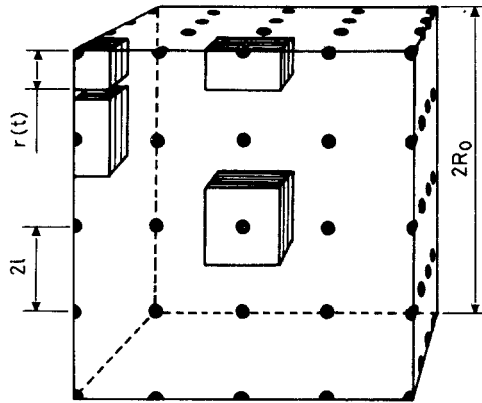
Fig. 1 Topokinetic assumptions used in the present paper. Surface nuclei (black points) are regularly distributed (nearest neighbour distance $2l$) at the surface of cubic glass particles (edge length $2R_0$), causing a simultaneous growth of crystallites (cuboids characterized by $r(t)$) into the bulk

Every nucleus located at the cubic faces and corners is surrounded by an area of $4l^2$ and $3l^2$, respectively. The temperature is equal at every point of the sample volume, remaining constant or increasing due to the heating rate α ($a5$). The crystal growth rate $r'(t) = dr(t)/dt$ only depends on the temperature $T = \alpha t$ ($a6$), following an Arrhenius law ($a7$):

$$r'(t) = u \exp\left(-E/R\alpha t\right) \qquad (1)$$

u and E are the pre-exponential factor and the apparent energy of activation, respectively. R is the gas constant.

Taking all these assumptions into account, the transformed (or reacted) fraction $x(t)$ and the transformation rate $x'(t) = dx(t)/dt$, which can be interpreted as a theoretical DTA signal ΔT [15, 16], depend only on the grain size (R_0), the nearest neighbour distance of surface nucleation sites ($2l$) and the crystal "radius", $r(t)$.

Calculation of $r(t)$

In order to calculate $r(t)$, the crystal growth rate $r'(t)$ has to be integrated with respect to time under non-isothermal conditions. If a starting temperature far below the softening point is chosen, the lower limit of the time integral can be set to zero. According to the assumptions ($a5$–7), we have

$$r(t) = \int_0^t u \exp\left(-E/R\alpha t'\right) dt' \qquad (2)$$

In the course of the calculations, it is necessary to solve the logarithmic integral $Ei(-E/R\alpha t)$ numerically [17–19]. In the present paper, a formula published by Lanczos [20] with high accuracy for $y = (-E/R\alpha t) < -2$ was applied:

$$Ei(y) \approx (1/y)\exp{(y)} \sum_{j=0}^{7} \frac{C_j}{y^j} \qquad (3)$$

where C_j are definite constants ($C_0 = 0.9999965$, $C_1 = 0.9989971$, $C_2 = 1.9487646$, $C_3 = 4.9482092$, $C_4 = 11.7850792$, $C_5 = 20.452384$, $C_6 = 21.1491469$, and $C_7 = 9.524041$). Taking only $n < 7$ terms into consideration in Eq. (3), several approximations $r_n(t)$ of $r(t)$ are given:

$$r_n(t) = tr'(t)\left\{1 - \sum_{j=0}^{n} \frac{C_j}{(-E/R\alpha t)^j}\right\} \qquad (4)$$

Setting $n = 1$ and $C_0 \approx C_1 \approx 1$, the well-known Doyle [17] approximation results. The relative error $f_n = |r_n(t) - r_7(t)|/r_7(t)$ of different approximations is shown in Fig. 2. If $r(t)$ is only taken as $tr'(t)$ (which is frequently used in the literature, e.g. [10]), a serious error is caused, characterized in its magnitude by the factor $R\alpha t/E$.
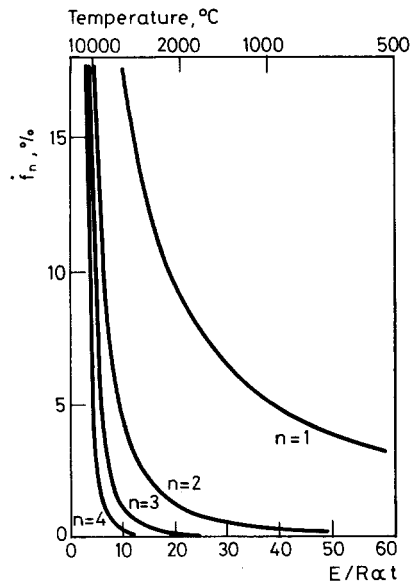
Fig. 2 The relative error f_n caused by the approach of $r(t)$ with $r_n(t)$ according to Eq. (4) is plotted against $E/R\alpha t$. For $E = 420$ kJ/mol and $\alpha = 10$ deg/min, the corresponding temperature $T = \alpha t$ is shown on the upper abscissa

Calculation of $x(t)$ and $x'(t)$

The calculations of the transformed fraction $x(t)$ and the transformation rate $x'(t)$ are reduced to simple geometric treatments if $r(t)$ is known. They are restricted, however, to definite topokinetic conditions according to different possible relations between R_0, l and $r(t)$.

(I) If the nearest neighbour distance of surface nucleation sites is less than the particle size $(l < R_0)$, the number of nuclei present at the surface of one glass cube $A(l, R_0)$ is (according to Fig. 1):

$$A = 6(R_0/l)^2 + 2$$

1. During the induction period $(r(t) < l < R_0)$, $A(R, l)$ denotes the number of single surface crystallites which are simultaneously growing into the bulk. At a given moment t, the volume of the crystal phase per glass cube is $Br(t)^3$, with:

$$B = 24\{(R_0/l) - 1/2\}^2 + 2$$

B differs from A because of the different size of the crystallites located at the corners, the edges or the faces of the glass cubes (see Fig. 1). The volume of the glass grain is $8R_0^3$ and we get:

$$x(t) = \frac{B}{8}\left(\frac{r(t)}{R_0}\right)^3 \tag{5}$$

The glass-crystal interface progressively increases throughout this reaction stage. Subsequently, the maximum of the reaction rate is not reached before the crystallites impinge on each other to form a compact surface layer. The glass-crystal interface is abruptly reduced at this moment t_{M1} when

$$r(t_{M1}) = l \tag{6}$$

causing a sharp "impingement" DTA peak at $T_{M1} = \alpha t_{M1}$.

2. During the subsequent growth of the compact crystalline surface layer $(l < r(t) < R_0)$ into the bulk, $x(t)$ is given by the well-known equation [1, 4, 5, 10]:

$$x(t) = 1 - \{1 - r(t)/R_0\}^3 \tag{7}$$

The glass-crystal interface gradually decreases throughout this reaction stage. However, due to the increasing temperature, during a DTA run the crystal growth rate $r'(t)$ increases. Thus, the transformation rate $x'(t)$ passes through a maximum at medium temperatures, causing an additional broad "layer growth" DTA peak at $T_{M2} = \alpha t_{M2}$. At this moment, $x''(t) = \mathrm{d}x'(t)/\mathrm{d}t$ can be set to zero. From Eqs (1) and

(4) with $n = 1$, we get:

$$r(t_{M2}) = R_0/3 \qquad (8)$$

3. Finally, all glass cubes are completely crystallized $(l < R_0 < r(t))$ and $x(t)$ remains at 1.

Thus, both the impingement of surface crystallites and the subsequent growth of the crystalline surface layer may cause a DTA peak as shown in Fig. 3. However, if
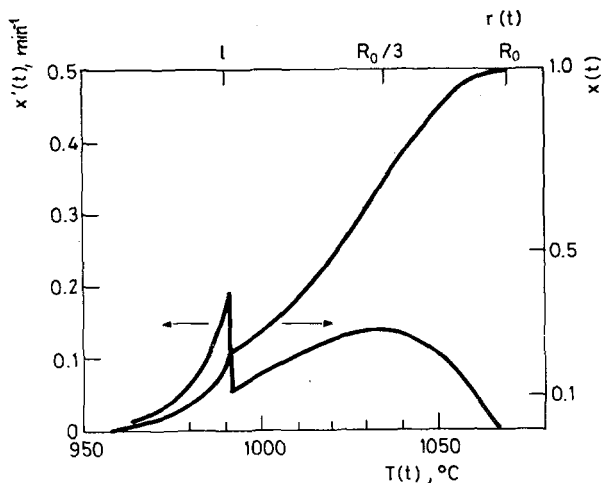

Fig. 3 The transformed fraction $x(t)$ and the transformation rate $x'(t)$ (interpreted as a theoretical DTA signal) are plotted against the temperature $T(t)$ and the corresponding "crystallite radius" $r(t)$. $R_0 = 65$ μm, $l = 5$ μm, $\alpha = 10$ deg/min, $u = 10^{18}$ μm/min and $E = 430$ kJ/mol were used in the calculations as an example

R_0 is less than $3l$, the compact surface layer is built when $r(t) > R_0/3$. Thus, the subsequent layer growth can not cause a second DTA peak, but a smooth shoulder.

(II) If the particle size is less than the nearest neighbour distance of surface nucleation sites $(R_0 < l)$, only some of the glass grains carry a single surface nucleus located at a corner. Noting that every corner nucleus is surrounded by an area of $3l^2$, we have

$$A = 8(R_0/l)^2 \qquad (9)$$

In this case, $A(R_0, l)$ may be regarded as the mean number of nuclei present per glass cube.

1. During the simultaneous growth of crystallites $(r(t) < 2R_0)$ nucleated at different glass grains, we have:

$$x(t) = \frac{A}{8} \left(\frac{r(t)}{R_0} \right)^3 \qquad (10)$$

The maximum of the transformation rate occurs at $t = t_{M3}$ when the glass cubes have just been completely crystallized:

$$r(t_{M3}) = 2R_0 \tag{11}$$

Hence, a sharp "completion" peak corresponds to the end of the crystallization process, depending on R_0 again.

2. Afterwards, the transformed fraction $x(t)$ remains at A, which is the fraction that was able to crystallize at all.

Influence of grain size

If all parameters (l, u, E and α) are constant, $x(t)$ and $x'(t)$ only depend on R_0. For several fixed reaction times t_n, the value of the transformed fraction $x(R_0)$ is shown in Fig. 4. Both $x(t)$ and $x'(t)$ attain their greatest values at medium grain sizes, which is in good agreement with [1]. The overall crystallization process is too sluggish if $R_0 \gg l$ is given, and it is too incomplete in the case of $R_0 \ll l$.

In the early reaction stages, when $r(t)$ is much less than both l and R_0, the reacted fraction follows a $1/R_0$ law according to Eqs (5), (7) and (10). For $l \ll R_0$ and $r(t) \ll R_0$, this behaviour has already been shown by Filipowitch [5].

Generally, $x(R_0)$ follows that rule until $R_0 \gtrsim r(t)$ and $R_0 \gtrsim l$ if a moment t_n with $r(t) > l$ and $r(t) < l$ has been considered, respectively.

Calculated DTA curves are shown in Fig. 5(a). For $R_0 \gg l$, the broad "layer growth" DTA peak predominates, showing a strong grain size-induced shift of its
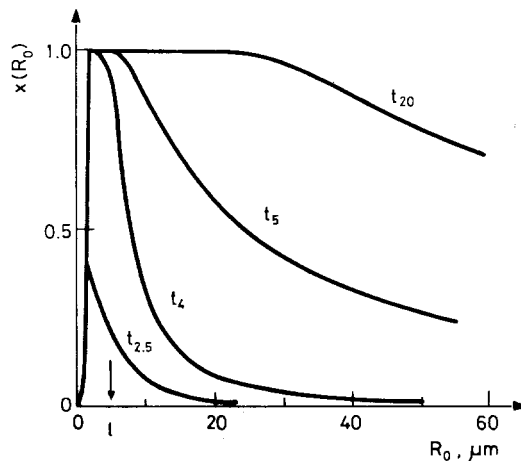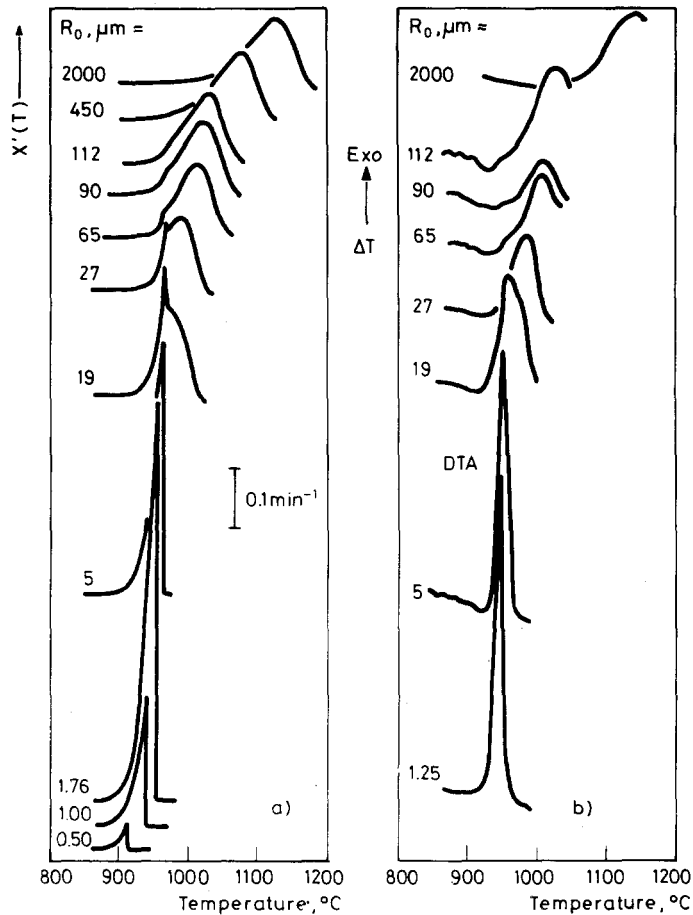

Fig. 4 Considering several reaction times t_n and consequently several definite values of $r(t_n)$, the reacted fraction x only depends on R_0. The reacted fraction x is plotted against R_0 for $r(t_n) = 2.5, 4, 5$ and 20 μm ($l = 5$ μm)

Fig. 5(a) Calculated DTA curves for different values of R_0 are shown for $l = 5$ μm, $\alpha = 10$ deg/min, $u = 10^{18}$ μm/min and $E = 420$ kJ/mol

Fig. 5(b) Experimental DTA curves attributed to the surface-induced growth of μ-cordierite are shown for the sake of comparison. R_0 denotes the mean particle radii of the glass powders used. The arbitrary unit of ΔT was defined by fitting the experimental to the calculated DTA curve in the case of $R_0 = 2000$ μm

peak position. With decreasing grain size, the sharp "impingement" peak becomes more significant and the half-width of the whole DTA trace decreases.

This is caused by the grain size-independent peak position and the small half-width of the "impingement" peak.

For $R_0 < l$, the sharp "completion" peak predominates. The corresponding DTA peak position shifts to lower temperatures again. However, the peak gradually disappears due to the decreasing values of $A(R_0, l)$ if R_0 decreases.
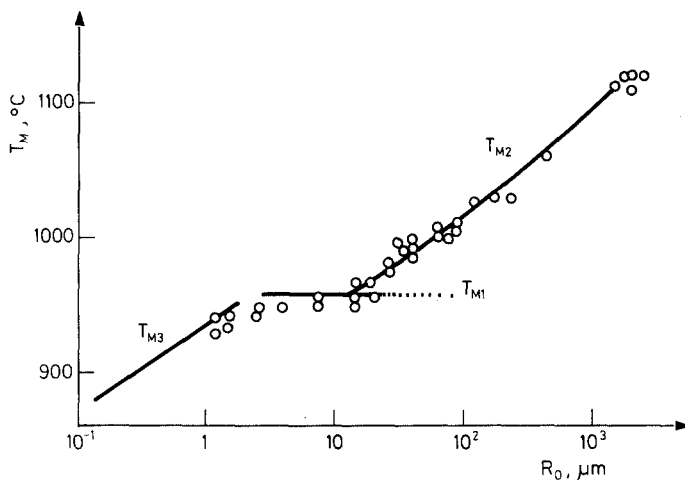
Fig. 6 The influence of grain size (R_0) on the different DTA peak positions T_{M1}, T_{M2} and T_{M3} according to Eqs (6), (8) and (11), respectively, is shown. Calculated values (lines) and experimental results (circles) according to Fig. 5 are given

In Fig. 6, the influence of particle size on the different DTA peak temperatures is shown, calculated after Eqs (6), (8), (11) and (4) with $n = 1$ for the parameters already used in fig. 5(a). Vice versa, these parameters can readily be determined from experimental DTA peak temperatures.

Discussion

The primary crystallization of cordierite glass powders was studied by DTA. The experimental DTA curves attributed to the crystallization of μ-cordierite according to X-ray measurements on analogously heat-treated samples are given in Fig. 5(b).

Following the model given above, the characteristic grain size influence on the DTA curves indicates a surface-induced crystallization process. It should be noted, however, that it is necessary to take into account powders on a large scale of particle size, at least over a range of one order of magnitude. Otherwise, the sharp "impingement" peak (T_{m1}) or the "completion" peak (T_{m3}) might be attributed to a volume-nucleated growth of the crystalline phase, which causes a grain size-independent DTA peak position too. In the present paper, the grain size was varied over the range of three orders of magnitude (Fig. 6).

The calculated DTA curves could be fitted well to the experimental traces, as shown in Figs 5(a) and (b). The parameters used were $l = 5$ μm, $E = 420$ kJ/mol and $u = 10^{18}$ μm/min ($\alpha = 10$ deg/min).
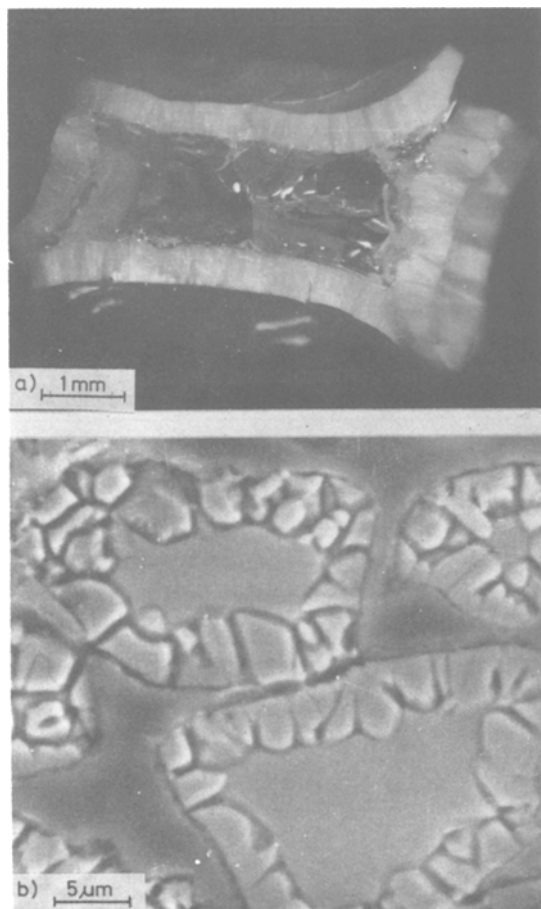
Fig. 7 The primary crystallization of μ-cordierite is nucleated at the surface of the glass particles in the case of bulk *(a)* and powdered glass samples *(b)*. In the case of coarse particles, the overall crystallization process is dominated by the growth of a compact surface layer. In the case of fine powders, the growth of single surface crystallites dominates. The crystallites are visible as bright points at the surface of several glass grains which are only smoothly, contrasted by the back ground in transmitting, partially polarized light

For the sake of comparison the primary crystallization of the cordierite glass powders used was studied by direct microscopic methods.

As illustrated in Fig. 7, the crystallization was really found to start at the surface of the glass particles in the case of bulk and fine-grained samples. The topokinetic character of the overall crystallization process is dominated by the growth of a compact crystalline surface layer in the case of bulk samples, and by the growth of

single surface crystallites in the case of fine powders. To approximate the glass grains as cubic (a1) seems to be justified at the very least in competition with a spherical model commonly used in the literature [1, 2, 5].

The density of surface nucleation sites turned out to be only slightly increased throughout the applied heat treatments, as previously reported by Kalinina [22]. The nearest neighbour distance was found to be constant in the range $l = 1$–10 μm. This well confirms the value obtained by fitting the DTA curves. The assumption of a constant density (or nearest neighbour distance) of nucleation sites in overall kinetic models does not seem to be an essential limitation, as already suggested by Turnbull [25], even including volume nucleation sites. By means of direct measurements of the thickness of the compact crystalline surface layer grown under isothermal ($T = 950$–1100°; $t = 5$–420 min) and non-isothermal ($T = 920$–1200°; $\alpha = 10$ deg/min) conditions, the crystal growth rate could be proved to be explicitly independent of t at a given temperature (a5) and follows an Arrhenius law (a7). The fitted parameters obtained from the microscopic measurements under isothermal and non-isothermal conditions, $E = 418$ kJ/mol ($u = 3 \cdot 10^{17}$ μm/min) and $E = 415$ kJ/mol ($u = 10^{18}$ μm/min), respectively, confirm the results obtained from fitting the DTA curves as well as values published by Uei [23] ($E = 360$ kJ/mol) and Kalinina [24] ($E = 466$ kJ/mol).

It must be noted, however, that the calculated "impingement" peak (T_{M1}) and the grain size-induced disappearance of the "completion" peak (T_{M3}) are considerably overdrawn in contrast to the experimental DTA curves. This may be due to the fact that the given model (Fig. 1) represents a rather simplified view of a complex situation.

The main deviations may be caused by the assumption of the simultaneous impingement of all surface crystallites due to their simplified cuboid shape and their uniform nearest neighbour distance (assumptions a2 and a7). Thus, it had been necessary to correct the "impingement" peak height with $\sqrt{\{(R_0/l) + 1\}}$ in order to fit the shape of the calculated DTA curves shown in fig. 5(a). This correction term could be explained by assuming not randomly distributed nucleation sites. Notwithstanding several confirming microphotographs, the derivation of such conclusions out of the overall kinetic data seems to be exaggerated.

The application of the model given above should be restricted to the approximate calculation of mean values of the crystal growth rate or of the nearest neighbour distance of surface nucleation sites, and should be backed up by additional direct measurements.

Basically, it is possible to generalize the treatment by dropping several assumptions adopted here. This turns out, however, to cause progressively larger complications. Substituting some simplifications by others according to particular

topokinetic conditions, which may be regarded as a fitting process itself, seems to be preferable to the use of generalized kinetic models in the case of special nucleation sites.

Conclusion

In the case of surface-induced glass crystallization, a characteristic influence of the grain size on the shape of the corresponding overall kinetic curves (e.g. DTA curves), as shown in Fig. 5, can be expected.

If the density of surface nucleation sites does not depend on (or only slightly varies with) the grain size, and if the crystal growth rate obeys an Arrhenius law, the influence of the particle size can be used to estimate these parameters according to the given kinetic Eqs (5)–(11). It seems possible to apply the model analogously to other surface-induced solid-state reactions.

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Zusammenfassung — Es wird ein einfaches Modell zur umsatzkinetischen Beschreibung einer oberflächeninitiierten Kristallisation von Glaspulvern vorgestellt. Das Modell berücksichtigt die Korngröße der Glaspulver, eine konstante Verteilungsdichte von Oberflächenkristallkeimen sowie eine Temperaturerhöhung konstanter Heizrate während der Reaktion. Aus umsatzkinetischen Kurven (z. B. DTA-Kurven) von Glaspulvern unterschiedlicher Korngrößen lassen sich die Verteilungsdichte der Oberflächenkristallkeime sowie die Kristallwachstumsgeschwindigkeit abschätzen. Die Anwendungsmöglichkeiten des Modells werden am Beispiel der oberflächeninitiierten Kristallisation von Cordieritglaspulvern demonstriert.

Резюме — Предложена кинетическая модель поверхностно-наведенной кристаллизации стекол. На всем протяжении реакции учитывались размер зерен порошкообразных стекол, постоянная поверхностная плотность зерен и постоянное увеличение температуры. Скорость роста кристаллов и плотность поверхности центров кристаллизации могут легко установлены на основе полных кинетических кривых (напр. кривых ДТА) порошков с различным размером зерен. Показана неприменимость такой модели для случая первичной поверхностно-наведенной кристаллизации порошков стеклообразного кордерита.