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THE APPLICABILITY OF DTA TO THE STUDY OF THE CRYSTALLISATION PROCESS OF CERAMIC FIBRES

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ABSTRACT

Šesták's method for the determination of the activation energy of the crystallisation of mullite in ceramic fibres has been applied. The investigations performed proved that the mechanism of the crystallisation of mullite is far from the classical theories describing the devitrification process of glass. The determination of the kinetic parameters by Šesták's method requires the verification of the introduced simplification every single time.

INTRODUCTION

Ceramic fibres are the attractive heat-insulating materials with low thermal conductivity. They are intermediate products for the production of heat-insulating materials both in the elastic form (blankets) and stiff form (blocks, plates), with a low apparent density. Ceramic fibres with the chemical composition of kaolin (approximately 45% Al_2O_3 and 53% SiO_2) have a glassy structure. Examination of the behaviour of fibres at high temperature [1—3] proved that, beginning at about 1170 K, the effect of devitrification of the glassy phase may be observed. As a result the crystallisation of mullite begins, followed by the crystallisation of crystobalite. It is well known that the crystallisation of glass is an unfavourable process, influencing its mechanical properties. The effects of devitrification are still more visible when it occurs in separate fibres having diameters of a few μm.

The fibres are especially sensitive to the size of the crystallising crystals, growing in a lateral direction to the fibre axis. This kind of crystallisation leads to cracking of separate fibres. It restricts the maximum working temperature to about 1500 K while the melting temperature of this kind of material reaches 2000 K. Therefore, it is beneficial to be acquainted with the phenomena occurring in fibres at high temperatures in order to develop a method of counteraction against these unfavourable processes.

The crystallisation of glass is an exothermal process connected with the emission of a definite amount of heat. It enables the application of differential thermal analysis for the study of the crystallisation processes of glass. Values determined by DTA can be used for the estimation of kinetic data of a definite reaction [4—6].

Application of differential thermal analysis to the examination of the crystallisation of glass is a comparatively new phenomenon, and is closely connected with the development of studies on the controlled crystallisation of glass [7,8]. The work of Šesták [9] makes possible the determination of the activation energy of the crystallisation of the defined phase as detected by DTA.

The nucleation of crystal growth can be described by Avrami's equation

$$-\ln(1-\alpha) = k \cdot t^m = A \cdot t^m \cdot \exp(-E/RT) \quad (1)$$

where, α = the extent of crystallisation [10]; k = the overall rate constant; T = temperature; t = time; exponential factor m = a function of the reaction mechanism as well as the geometry of the crystallising phase; and E = the complex activation energy composed of the activation energy of the individual processes, nucleation, crystal growth and diffusion.

Equation (1) can be differentiated to yield

$$\frac{d\alpha}{dt} = (1-\alpha) \cdot A'[-\ln(1-\alpha)]^n \exp -E/mRT \quad (2)$$

where $n = (m-1)/m$.

Based on Borchard and Piloyan's assumption that the reaction rate $d\alpha/dt$ is proportional to the temperature deflection, ΔT, as detected by DTA, Šesták arrives at

$$\log \Delta T = E'/4.57\ T + \log [A'\ f(\alpha)] \quad (3)$$

Šesták further assumes that $\log A'[f(\alpha)]$ = const. when the increasing temperature has a much larger effect on the change in ΔT compared with the change A' f(α). Šesták verified this assumption by testing the crystallisation of B_2O_3-based glass, and obtained data supporting this assumption in the area of advancing values: ΔT. Thus from eqn. (3)

$$\log \Delta T = E'/4.57\ T + \text{const.} \quad (4)$$

Based on eqn. (4) log ΔT vs. $1/T$ may be plotted with the slope $E'/4.57$, where $E' = E/m$.

EXPERIMENTAL

The method proposed by Šesták was applied to the study of the crystallisation kinetics of ceramic fibres. The tests were carried out on samples of fibres in the form of fine grains <0.06 mm.

The DTA pattern was recorded on a MOM Budapest derivatograph operating up to 1770 K. The heating rate, which was constant in the temperature range 290—1770 K, was 7 K min^{-1}.

Moreover, the digital millivoltometer, with an accuracy of 0.001 mV, was adjusted in parallel to the differential system of the thermoelement, measuring the temperature of the tested specimen and standard (α-Al_2O_3).

Supplementary equipment in the form of a scanner and printing machine made possible the printing of temperature data of a specimen and inert substance as well as the temperature difference ΔT every 5 sec.

RESULTS

The DTA pattern of ceramic fibres in the temperature range 290—1770 K is presented in Fig. 1. It shows the only sharp exothermic peak, with maximum temperature 1244 ± 2 K. On the basis of previous investigations [1—3], it can be assumed that this peak corresponds to the crystallisation of mullite. However, no exothermic peak corresponding to the crystallisation of crystobalite is observed, although the authors stated the crystallisation of this phase in the temperature range 1420—1720 K.

X-Ray investigations of the sample after the DTA analysis proved merely the presence of the mullite phase. The results of these tests show that on heating ceramic fibres at a rate of 7 K min^{-1} to 1770 K only mullite undergoes crystallisation. The results for the peak corresponding to the crystallisation of this phase were calculated using the method of regression analysis on a Hewlett—Packard computer. A linear relationship for the first 13 measuring points was obtained by plotting log ΔT vs. $1/T$ from the available data. The slope of a straight line was 240 which gives $E' = 240 \times 4.57 = 1097$ kcal mole^{-1}. Since the E' value obtained could not be accepted, the measuring apparatus was calibrated. For this purpose one of the glasses was prepared, the crystallisation of which was tested by Šesták (glass No. 4-30 MnO, Fe_2O_3 and 70% B_2O_3).

DTA analysis was performed and the results described as mentioned above (Fig. 2). A linear relationship of log ΔT vs. $1/T$ for the initial 60 measuring

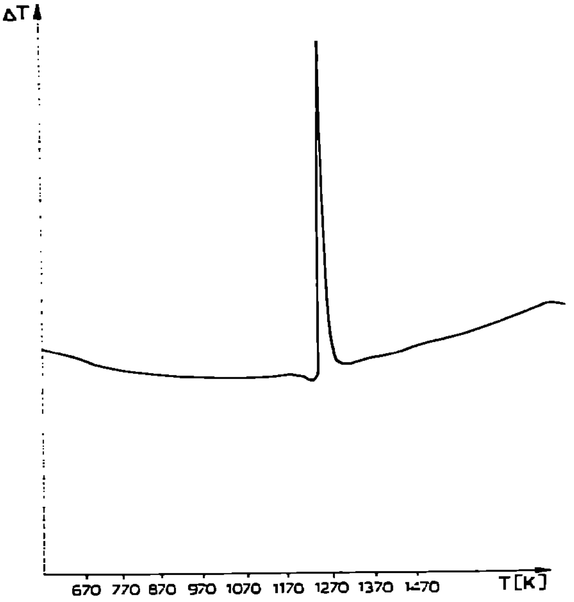

Fig. 1. DTA pattern of ceramic fibres.

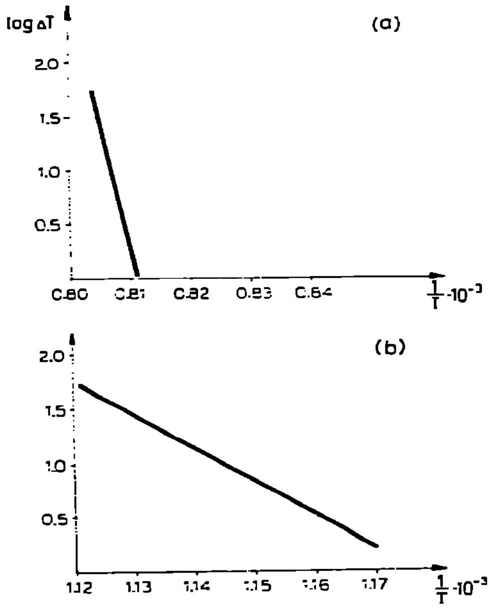

Fig. 2. The relation log ΔT vs. $1/T \cdot 10^{-3}$ for the crystallisation of mullite in aluminosilicate glass (a) and the spinel $Mn_xFe_{3-x}O_4$ in B_2O_3-based glass (b) derived from DTA data.

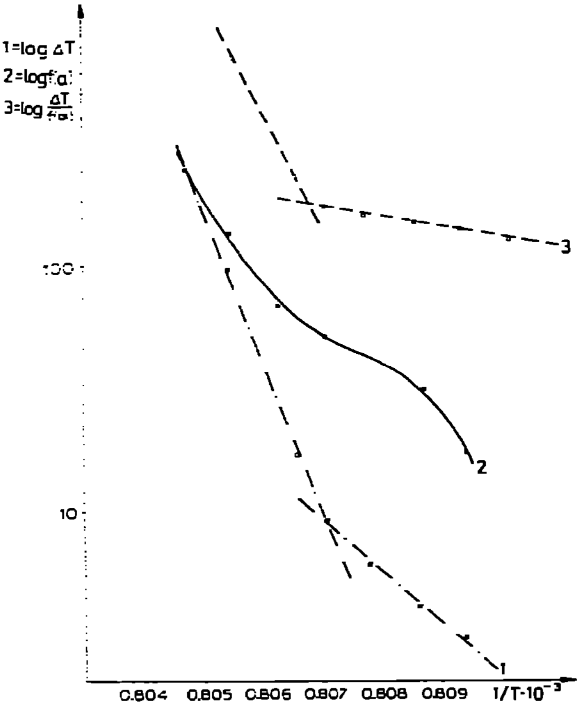

Fig. 3. The relation log ΔT, log f(α) and log ΔT/f(α) vs. $1/T \cdot 10^{-3}$ derived from DTA data for crystallisation of mullite. ——·——, log ΔT = f($1/T$); ————, log f(α) = f($1/T$); — — —, log [ΔT/f(α)] = f($1/T$).

points was obtained (correlation coefficient of a straight line 0.98). The slope of a straight line was 30 which gives $E' = 30 \times 4.57 = 137$ kcal mole^{-1}.

For a similar glass Šesták obtained the value of 125 kcal mole^{-1}, so the average error amounts to 10% which is the accepted value in kinetic calculations. Moreover, the difference in the obtained E'-value could also arise during the preparation of the glass itself and therefore the accuracy of the apparatus seems to be satisfactory.

In order to determine why the E'-value was so highly abnormal for the crystallisation of mullite in ceramic fibres, Šesták's simplifications were verified. Expression (3) can be written as follows

$$\log \frac{\Delta T}{\mathrm{f}(\alpha)} = \frac{E'}{4.57} + \log A' \tag{5}$$

where $\mathrm{f}(\alpha) = (1 - \alpha) \cdot [-\ln(1 - \alpha)]^n$

If Šesták's assumption is true then for log f(α) to be constant a plot of log ΔT/f(α) vs. $1/T$ and log ΔT vs. $1/T$ should give parallel lines with a slope of $E'/4.57$.

In order to determine the function f(α) it is necessary to assume the extent of crystallinity α to be proportional to the relevant area under the DTA peak; we also have to approximate the value of m. The extent of crystallinity α was determined from numerical integration by means of Simpson's algorithm [11] on the Hewlett—Packard computer. The value of m is assumed to be 2.5 for three-dimensional spherical nuclei, their constant growth being diffusion controlled.

f(α) for the first 13 measuring points was determined and log $\Delta T/\mathrm{f}(\alpha)$ vs. $1/T$ was plotted. A straight line with a slope of $E'/4.57 = 5$, which gives $E' = 23$ kcal mole^{-1}, was obtained.

Figure 3 presents diagrams of the dependence of log f(α), log ΔT and log $\Delta T/\mathrm{f}(\alpha)$ vs. $1/T$. According to Šesták the plot log $\mathrm{f}(\alpha) = \mathrm{f}(1/T)$ should be parallel to the $1/T$ axis or should have a negligibly small slope. The diagram obtained, log f(α), for the crystallisation of mullite shows a greater slope to the $1/T$ axis, especially for the initial points of measurement which served for the determination of a straight $\Delta T = \mathrm{f}''(1/T)$.

Significant change f(α) with the increasing temperature indicates the complex nucleation mechanism and nuclei growth in the tested glass. Moreover, the application of Avramy's equation

$$-\ln(1-\alpha) = k\cdot t^m$$

describing reactions in which nucleation is a stage controlling complex process rate for kinetic analysis of the crystallisation of ceramic fibres seems to be doubtful.

CONCLUSION

Summing up, it is necessary to say that the crystallistation of mullite in ceramic fibres depends on different factors, different from those accepted by classical theories of the crystallisation of glass. In order to desribe the mechanism of this process, further investigations should be carried out using different supplementary methods. It should be stressed that the method of determination of the activation energy of the crystallisation of glass given by Šesták is not universal. It is indispensible to verify the stability of the function f(α) against temperature every single time.

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