Note

THE PILOYAN METHOD IN DTA STUDIES OF GLASS DEVITRIFICATION

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A kinetic analysis of the applicability of the Piloyan method to the process of glass devitrification for evaluation of the exponent n in the Johnson-Mehl-Avrami equation is carried out.

Criado's conclusions concerning the value of the slope of the Piloyan plot are criticized.

In a previous paper [1] the non-isothermal devitrification of glasses was studied. A method was described for evaluating the exponent n of the Johnson-Mehl-Avrami (JMA) equation by comparing the slope nE/R of the Piloyan [2] plot ($\ln \Delta T$ *vs.* $1/T$) with the slope E/R of the Ozawa [3] plot ($\ln \beta$ *vs.* $1/T_p$).

This method was criticized by Criado [4], whose kinetic analysis concludes that the Piloyan plot gives a straight line with a slope E/R and not nE/R.

This conclusion, which disagrees with the experimental results [5, 6] and with the numerical analysis carried out by Colmenero et al. [7], is based on some incorrect assumptions, as shown in the following kinetic analysis.

The isothermal devitrification of glasses is well described by a JMA equation

$$-\ln(1-\alpha) = (kt)^n \qquad (1)$$

where α is the crystallization degree at time t, n is a parameter related to the crystallization mechanism [5, 8] and the constant k is usually found to be of the Arrhenius type

$$k = A\exp(-E/RT) \qquad (2)$$

where E is the activation energy for crystal growth and A is a constant related to the number of nuclei [9].

When a glass devitrifies during a DTA run under non-isothermal conditions, as the temperature changes linearly with time, the JMA kinetic equation becomes:

$$-\ln(1-\alpha) = \int_{T_0}^{T} \frac{d(kt)^n}{dT}\, dT \qquad (3)$$

and the rate constant has to be expressed as

$$k = A \exp\left[-\frac{E^*}{R(T - T_0)}\right] \tag{4}$$

where T_0 is a constant.

During the crystal growth the time t and the temperature T are related by

$$T = T_0 + \beta t \tag{5}$$

where β is the DTA heating rate.

At each temperature T the rate of crystal growth is

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \beta \frac{\mathrm{d}\alpha}{\mathrm{d}T} = \beta(1 - \alpha)\frac{\mathrm{d}(kt)^{\mathrm{n}}}{\mathrm{d}T} \tag{6}$$

The temperature derivative of $(kt)^{\mathrm{n}}$ is

$$\frac{\mathrm{d}(kt)^{\mathrm{n}}}{\mathrm{d}T} = \frac{1}{T - T_0}(kt)^{\mathrm{n}} n \left(\frac{E^*}{R(T - T_0)} + 1\right) \tag{7}$$

As in most devitrification reactions

$$\frac{E^*}{R(T - T_0)} \gg 1 \tag{8}$$

Eqn. (7) can be approximated as

$$\frac{\mathrm{d}(kt)^{\mathrm{n}}}{\mathrm{d}T} = (kt)^{\mathrm{n}} \frac{nE^*}{R(T - T_0)^2} \tag{9}$$

and Eqn. (6) becomes

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \beta(1 - \alpha)(kt)^{\mathrm{n}} \frac{nE^*}{R(T - T_0)^2} \tag{10}$$

After Borchardt and Daniels [10] the deflection ΔT from the DTA baseline is proportional to the instantaneous reaction rate, and thus the slope of the plot ln ΔT *vs.* $1/T$ (Piloyan plot) is

$$\frac{\mathrm{d} \ln \Delta T}{\mathrm{d}\frac{1}{T}} = \left(\frac{T}{T - T_0}\right)^2 \frac{\mathrm{d} \ln \Delta T}{\mathrm{d}\frac{1}{T - T_0}} \tag{11}$$

and

$$\frac{\mathrm{d} \ln \Delta T}{\mathrm{d}\frac{1}{T - T_0}} = -\frac{nE^*}{R}\left[1 - (kt)^{\mathrm{n}} - 2\frac{R(T - T_0)}{nE^*}\right] \tag{12}$$

For low values of α (initial part of the DTA crystallization peak($(kt)^n \ll 1$; hence, taking into account relation (8), the term in brackets on the right side of equation (12) is very close to unity.

Hence

$$\frac{\mathrm{d}\ln \Delta T}{\mathrm{d}\frac{1}{T}} = -\frac{nE^*}{R}\left(\frac{T}{T-T_0}\right)^2 \tag{13}$$

In the narrow temperature range of the initial part of the DTA crystallization peak the terms $\frac{T}{T-T_0}$ can be regarded as constant and the kinetic equation is governed by an Arrhenius law.

So

$$\frac{\mathrm{d}\ln \Delta T}{\mathrm{d}\frac{1}{T}} = -\frac{nE}{R} \tag{14}$$

The kinetic analysis of Criado starts from the following rate equation

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(1-\alpha)\left[-\ln(1-\alpha)\right]^{\frac{n-1}{n}} \tag{15}$$

This equation can easily be derived from the more general Eqn. (6), assuming that

a) $$E^*/R(T-T_0) \ll 1 \tag{16}$$

b) $$(kt)^{n-1} = \left[-\ln(1-\alpha)\right]^{\frac{n-1}{n}} \tag{17}$$

For most solid-state reactions one typically observes [11] that $E^* \gg R(T-T_0)$. Accordingly, assumption a) is incorrect and assumption b) is not valid under non-isothermal conditions.

To summarize, we can conclude that the JMA parameter n can be evaluated by using the Piloyan method if the activation energy value is already known.

If the value of E is unknown, the value of n can be evaluated [1] from the ratio of the slopes of the Piloyan and the Ozawa plots [2, 3].

References

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