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Letter to the Editor

Comments on "The non-isothermal devitrification of glasses in the CaO $4GeO_2$–SrO $4GeO_2$ composition range" by M. Catauro and A. Marotta (Thermochimica Acta 371 (2001) 121–126)

Crystallization is a complicated process, so that sometimes we found it was not well understood. One of the examples is seen in a recent paper [1] in this journal. It seems worthy to take this opportunity to make sure the non-isothermal kinetics of crystallization.

The essential points to be considered on this theme are the following two points [2–4]:

1. In general, crystallization proceeds by two elementary processes, i.e., nucleation and growth. The temperature dependences of these processes are different from each other. Therefore, in non-isothermal kinetics we must consider two different accelerating effects of these processes in heating modes and two different decelerating effects in cooling modes. If the rate constants follow Arrhenius law, we have, thus, two activation energies; one for the nucleation and the other for the growth.
2. Generally, Arrhenius law does not hold for these processes, except for special cases. For both the processes, the temperature dependences are so complicated that the rate constants decrease beneath the melting temperature with increase of the temperature, and they increase in a lower temperature range with increase of the temperature. Approximated relations for constant rate heating or cooling hitherto used for non-isothermal kinetics of chemical reactions are based on Arrhenius law. Therefore, these relations cannot generally be applied for non-isothermal kinetics of crystallization.

Kinetics equation of crystallization by constant rate heating or cooling was derived by the present author based on the above two points and it is described in a paper [5], which Catauro and Marotta referred [1]. However, in the paper by Catauro and Marotta [1], a different equation is cited. The correct equation in the original paper [5] is as follows:

$$\log\{-\ln(1-C)\} = \log\chi(T) - n\log\beta \qquad (1)$$

where C, T, $\chi(T)$, n and β are the crystallized fraction, the temperature, a function of the temperature based on integral of the temperature dependences of the above two rate constants, the Avrami exponent and the heating or cooling rate, respectively. This relation hold in general for non-isothermal crystallization by constant rate heating or cooling, where nuclei are assumed to be pre-existing or to form at random concurrently with the growth, and nuclei are assumed to be homogeneously distributed in the sample.

What we can do by using this equation is only to estimate the Avrami exponent, n, from the slope by plotting the left side against the logarithm of the heating or cooling rate at a given temperature, where $\chi(T)$ is a constant. First of all, we should make this plot to learn the Avrami exponent and also to confirm whether the Avrami model [2–4] holds in the crystallization we are investigating. Further kinetic analysis cannot be done, because the two elementary processes, nucleation and growth, have different temperature dependence, and only one exception is the case that n equals unity [6].

For special cases that Arrhenius law holds in the growth process and that the nuclei do not form concurrently with the growth, much more simple equations were derived, and they are described in another paper [7] by the present author. These equations are

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different from that cited by Catauro and Marotta [1], as follows:

$$\log \beta = -0.4567\left(\frac{E}{RT}\right) + \text{const.} \tag{2}$$

and

$$\log \beta = -0.4567\left\{\frac{(n-1)E}{nRT}\right\} + \text{const.} \tag{3}$$

where E and R are the activation energy and the gas constant, respectively, and they hold at a given crystallized fraction and at the temperature for the maximum crystallization rate. As is clearly discussed [7], the equations are both for the above special cases, and the former equation holds for the cases of pre-existing nuclei, while the latter equation holds for the case that the nucleation temperature range is separated from that for the growth, so that the nucleation proceeds independently from the growth.

The equation cited by Catauro and Marotta [1] is somewhat different from Eqs. (2) and (3), and it is as follows:

$$\ln \beta = -\frac{E}{RT_{\mathrm{p}}} + \text{const.} \tag{4}$$

where T_{p} is the temperature at the maximum crystallization rate. This equation was first derived by Matusita and Sakka [8,9] together with an equation similar to Eq. (3), and they named the plots by the equations as modified Ozawa plot, but it is not modification but approximation [7].

First of all, we should notice that these equations were derived on different models, so that their applicabilities are different from each other.

In order to apply these equations and to get correct results, we should apply Eq. (1) to the observed process first, because of its widest applicability. Thus we can examine the linearity of the plot and also we can get the Avrami exponent. When we do not get linear plots, the process we are observing is not the process such as described above, and at the moment we do not have any means to analyze the process furthermore. When we get the linear plot, we can estimate the activation energy by using Eqs. (2), (3) or (4), provided that Arrhenius law holds for the growth rate constant and we get linear plots by applying Eqs. (2), (3) or (4) [7]. By using the estimated activation energy and the estimated Avrami exponent, we can get a linear plot of $-\ln(1-C)$ versus θ^n or θ^{n-1} for Eqs. (2) or (3) [7], if the observed process is in accordance with the model for which Eqs. (2)–(4) were derived. In this plot θ is the reduced time [10] and it is equal to $\int \exp(-E/RT)\,\mathrm{d}t$, t being the time. This plot is similar to the plot for isothermal crystallization, and t is replaced by θ in the non-isothermal run, but the slope is different [7].

It should also be mentioned that T_{p} is not the peak temperature in the DTA curve as is defined in the paper [1], but the temperature at the maximum crystallization rate. In a power compensation DSC curve obtained with a DSC of high response, T_{p} may approximately coincide with the temperature at the maximum crystallization rate, but it is not commonly real for high temperature DTA, because its response is not so high [11].

Finally, surface nucleation should be mentioned. As far as the present author learned, non-isothermal kinetics of crystallization by surface nucleation has not yet been derived. It is keenly needed, because it is sometimes observed [1].

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