

should read instead:

$$\frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) + \ln \frac{T_2 - T_0}{T_1 - T_0} = 1.59 \text{ or } 0.64; \quad (13)$$

where T_0 is the temperature at zero time. Large errors may result if the second term on the left has been omitted; more often than not it amounts to a significant proportion of 0.64 or 1.59, especially when the data have been obtained at a high heating rate.

Thirdly, and most crucially, it is debatable whether Equations 1 and 2 are applicable to the situation in hand. In a dynamic experiment, when T is a function of t , α cannot simply depend on the instantaneous value of $u(t) \equiv k[T(t)]t$. Rather, the way in which T has been changing with t must also affect α . This effect is taken into account in the equations:

$$1 - (1 - \alpha)^{1/n} = \int_0^t k \, dt \quad (14)$$

and

$$-\ln(1 - \alpha) = \left(\int_0^t k \, dt \right)^n. \quad (15)$$

The equations used in [1] are valid only in the isothermal case, when k is constant and can be taken out of the integral. The formulae for E proposed there may therefore need more drastic revisions.

References

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Reply to 'Comments on "Activation energy for the crystallization of glass from DDTA curves"'

The method of obtaining the value of the activation energy for the crystallization of glass from a single derivative differential thermal analysis (DDTA) curve recently proposed by the authors [1] is criticized by [2].

As the main remark concerns the use under non-isothermal conditions of the two kinetic equations:

$$1 - (1 - \alpha)^{1/3} = kt \quad (1)$$

and

$$-\ln(1 - \alpha) = (kt)^3 \quad (2)$$

where α is the volume fraction of the crystals, k is a constant and t is time, some elucidations are required.

We assumed that under non-isothermal conditions t in Equation 2 represents the time of heating at each temperature T [3] and therefore it has to be considered constant and proportional to the reciprocal of the differential thermal analysis (DTA) heating rate, β , i.e.

$$kt = \frac{k'}{\beta}. \quad (3)$$

Substituting Equation 3 into Equations 1 and 2 we obtained the two kinetic equations proposed by Matusita and Sakka [4, 5] for surface and bulk crystallization of glass from a fixed number of nuclei under non-isothermal conditions.

From the roots of each of the two equations:

$$9(kt)^3 - 8(kt) + 1 = 0 \quad (4)$$

and

$$(kt)^6 - 3(kt)^3 + 1 = 0 \quad (5)$$

that satisfy the condition that at the inflection-point temperatures, T_f , on the DDTA curve (see Fig. 2 [1])

$$\frac{d^2 \Delta T}{dT^2} = \frac{d^3 \alpha}{dT^3} = 0 \quad (6)$$

we obtain

$$\frac{(kt)_{T_{f_2}}}{(kt)_{T_{f_1}}} = \frac{(k')_{T_{f_2}}}{(k')_{T_{f_1}}} = \frac{8 + 28^{1/2}}{8 - 28^{1/2}} \quad (7)$$

and

$$\frac{(kt)_{T_{f_2}}}{(kt)_{T_{f_1}}} = \frac{(k')_{T_{f_2}}}{(k')_{T_{f_1}}} = \left(\frac{3 + 5^{1/2}}{3 - 5^{1/2}} \right)^{1/3} \quad (8)$$

respectively, where ΔT is the height of a point on the DTA curve (see Fig. 1 [1]).

Taking the logarithms of Equations 7 and 8 the proposed relations [1] can be derived:

$$\frac{E}{R} \left(\frac{1}{T_{f_1}} - \frac{1}{T_{f_2}} \right) = 1.59 \quad (9)$$

and

$$\frac{E}{R} \left(\frac{1}{T_{f_1}} - \frac{1}{T_{f_2}} \right) = 0.64 \quad (10)$$

where E is the activation energy for crystal growth and R is the gas constant.

It is evident that no terms, as suggested by Tang [2], were omitted. Finally, concerning the approximation of the m th temperature derivative of (kt) ,

$$\frac{d^m (kt)}{dT^m} \approx \left(\frac{E}{RT^2} \right)^m (kt) \quad (11)$$

it is assumed that in deriving Equations 4 and 5 from Equations 1 and 2, its validity is based, as properly remarked by Tang, on the assumption

that $E/RT \gg 4$. This assumption represents a limit to the general applicability of the method to solid state reactions, but Equation 11 can be considered adequate in glass devitrification owing to the high activation energy values.

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Comments on "The influence of Mg contents on the formation and reversion of Guinier–Preston zones in Al–4.5 at% Zn–xMg alloys

The aim of this communication is to present calorimetric studies which provide some comments on the recent publication of Honyek *et al.* [1].

We shall first report some measurements on binary Al–Zn alloys (total impurity content < 0.01%). Fig. 1 shows thermal curves obtained on heating alloys containing 5.8–11.9 wt% (2.5–5.3 at%) Zn at a rate of $\frac{1}{3}^\circ\text{C min}^{-1}$; these alloys have been homogenized at 400°C over 6 h, quenched in iced water and aged for 1 day at room temperature. One or two endothermic peaks accompany the dissolution of the metastable GP-zones formed during ageing. In the case of the 10.1% (4.4 at%) Zn alloy, the dissolution is complete at around 145°C , whereas in equilibrium

studies, zones may not exist above 110°C [2] or 120°C [3]. This retardation of the dissolution process is quite normal under dynamic conditions; it increases with increasing scanning rate and attains a value of $70\text{--}80^\circ\text{C}$ at a rate of $20^\circ\text{C min}^{-1}$, as seen from Fig. 2. Moreover, the proportion of the peaks changes with heating rate. It is preferable to use small rates as far as possible, if conclusions on the equilibrium behaviour are to be drawn.

Fig. 2 is taken from [4] which describes the influence of homogenization temperature before water-quenching and ageing on the mean sizes of metastable phases in the Al–10.1% Zn alloy. Two endothermic peaks are observed with alloys quenched from 400 to 525°C and aged for 4 days at room temperature, three on alloys cooled from 275°C followed by ageing. Electron microscopic observations [5] have allowed these peaks to be attributed to the dissolution of spherical GP-zones, of ellipsoidal GP-zones and of the rhombohedral