

## **KINETIC MODELING OF ADVANCED INORGANIC GLASS-CERAMICS FORMATION BY CRYSTAL GROWTH FROM PRE-EXISTING NUCLEI**

*N. Koga<sup>1</sup> and J. Šesták<sup>2</sup>*

<sup>1</sup>Chemistry Laboratory, Faculty of School Education, Hiroshima University 1-1-1 Kagamiyama Higashi-Hiroshima 739–8524, Japan

<sup>2</sup>Division of Solid-State Physics, Institute of Physics, Czech Academy of Sciences, Cukrovarnicka 10 CZ-162 00, Praha 6, Czech Republic

### **Abstract**

Kinetic modeling of the crystal growth from pre-existing nuclei was reexamined to obtain a fundamental information about the controlled crystallization of glasses during formation of advanced inorganic glass-ceramics. Methods of kinetic analysis were reviewed by taking account of thermal history of the sample within the temperature range of nucleation. An accommodation function depending on the thermal history was introduced in the kinetic equation. The role of the accommodation function was reinvestigated when determining the activation energy from a series of kinetic curves. The kinetic description of the crystal growth in the samples with different thermal history was generalized by extrapolating the rate behavior to infinite temperature.

**Keywords:** accommodation function, crystal growth, glass-ceramics, kinetics, number of nuclei, thermal history

### **Introduction**

Crystallization process of glasses is of technological importance in the manufacture of glass-ceramics [1]. The physico-chemical properties of the glass-ceramics largely depend on the microstructure, the content of the crystalline and residual glass phases, etc. Controlled crystallization of the as-prepared glass with a specific composition makes it possible to obtain the glass-ceramic materials with desired properties. Detailed kinetic understanding on the crystallization process is therefore fundamental to design the conditions for the controlled crystallization and to regulate the morphology and microstructure of the product, ensuring the physico-chemical properties desired.

The crystallization of glasses is a complex process that may proceed in several stages. As often cited, these stages can consist of nucleation and crystal growth which are controlled by short-range diffusion or chemical reaction interface or by phase separation, structural relaxation and delocalization, long-range diffusion and viscous flow, heat transfer, etc. In a strict sense, the real kinetics of these processes can be fully described only on the basis of the fundamental understanding of the respective

elemental processes. It is usually difficult, however, to describe such simultaneous and/or consecutive processes separately.

Conventionally, an approach based on the physico-geometry of the advance of the reaction interfaces has been used to characterize the overall kinetics of the crystallization process. For a simple rate process of crystallization, kinetic equation is generally expressed by

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) f(\alpha) a(\alpha, t, T, P, \dots) \quad (1)$$

where  $\alpha$ ,  $f(\alpha)$  and  $a(\alpha, t, T, P, \dots)$  are the fractional reaction, kinetic model function derived on the basis of a simple physico-geometric characteristics of the reaction [2–5] and accommodation function [6, 7], respectively. The function  $a$  is understood as is accommodating the actual reaction kinetics in the fundamental kinetic equation of the Arrhenius type [8, 9]. In the conventional kinetic analysis, the  $a$  function is usually setting equal to unity, when assuming the highly idealized reaction behavior under strictly controlled conditions.

In this paper, an accommodation function is introduced for the kinetic analysis of the crystal growth from pre-existing nuclei where the number of pre-existing nuclei changes depending on the thermal history within the temperature range of nucleation. It has already been suggested by other authors [10–12] that change in the number of pre-existing nuclei has to be taken into account when determining the activation energy by the Kissinger method and isoconversion methods. More generalized kinetic modeling of such a process seems to be possible by introducing the accommodation function.

### Model of the crystallization process

Following behavior of a glass forming system is assumed in the present study.

1. The glass sample can be prepared by cooling of the glass forming melt even at a slow cooling rate.
2. Temperature ranges of nucleation and growth of the nuclei are separated sufficiently in a time scale of thermal treatment, where the formation of nuclei takes place in a lower temperature range and the subsequent growth of the nuclei proceeds independently in the higher temperature range.
3. The rate behaviors of nucleation during cooling of the glass forming melt and during heating of the as-prepared glass are identical, supposing of a relatively slow rate of the nucleation.
4. No secondary nucleation takes place in the temperature range of crystal growth.

### Number of pre-existing nuclei for subsequent growth

When a glass forming melt is cooled below glass transition temperature at a rate of  $\Phi_1$  and subsequently the formed glass is heated at a rate of  $\Phi_2$  up to a temperature between the higher limit of nucleation range and the lower limit of growth range, the system passes through the temperature range of nucleation twice. The number of

pre-existing nuclei,  $N$ , for the subsequent growth is expressed generally by the following equation [11, 12].

$$N = \int_0^t I(T) dt = a(\Phi) N_0 \quad \text{with} \quad N_0 = \int_{T_1}^{T_2} I(T) dT = \text{const.} \quad (2)$$

where  $I(T)$  and  $a(\Phi)$  are the rate of nucleation per unit volume and a function of  $\Phi_1$  and  $\Phi_2$ , respectively. Considering the relationship between the rate of nucleation and the rate of temperature change of the sample within the temperature range of nucleation, the  $a(\Phi)$  can be formalized for the following three different cases.

A) When the values of  $\Phi_1$  and/or  $\Phi_2$  are small enough as compared to the rate of nucleation, the number of nuclei in the glass sample is saturated. In this case, the value of  $N$  is constant irrespective of  $\Phi_1$  and  $\Phi_2$  applied.

$$a(\Phi) = \text{const.} \quad (3)$$

The similar situation is expected when a suitable nucleus-forming agent is added or annealing within the temperature range of nucleation is performed for a sufficiently long time.

B) If the glass forming melt was rapidly quenched, the number of nuclei in the quenched glass can be practically ignored. On heating the glass sample at  $\Phi_2$ , the value of  $N$  is inversely proportional to  $\Phi_2$  [11, 12]. Therefore, we can write

$$a(\Phi) = \frac{1}{\Phi_2} \quad (4)$$

C) If the number of nuclei is not saturated when cooling the glass-forming melt at a slow  $\Phi_1$  and heating the prepared glass at  $\Phi_2$ , the value of  $N$  is influenced both by  $\Phi_1$  and  $\Phi_2$  [12]

$$a(\Phi) = \frac{1}{\Phi_1} + \frac{1}{\Phi_2} \quad (5)$$

This model was recently tested on the system of  $\text{Li}_2\text{B}_4\text{O}_7$ , which, exhibits similar behavior of glass formation, nucleation and crystal growth as assumed in the present study [13, 14].

### Kinetic equation for crystal growth

By assuming the Arrhenius relationship, the rate of linear advance of the crystallization interface,  $v(T)$ , can be expressed as [11, 12]

$$v(T) = v_0 \exp\left(-\frac{E}{RT}\right) \quad (6)$$

where  $v_0$  and  $E$  are the pre-exponential factor and activation energy for the linear growth, respectively. By taking account of the growth dimension and impingement of crystal particles, the following kinetic equation is derived for the overall crystal growth.

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (7)$$

with  $A = [gN_0 a(\Phi)]^{1/m} v_0$  and  $f(\alpha) = m(1-\alpha)[- \ln(1-\alpha)]^{1-1/m}$

where  $\alpha$ ,  $g$  and  $m$  are the fractional crystallization, a geometric factor depending on the growth dimension and the kinetic exponent depending on the growth dimension and rate law for the linear growth [2–5], e.g., linear law or parabolic law, respectively. The kinetic model function,  $f(\alpha)$ , is the Johnson-Mehl-Avrami-Erofeev-Kolgomorov(JMAEK) equation [2–5], which is utilized usually for the solid-state reactions of nucleation-growth type.

## Determination of activation energy for crystal growth

### *Isothermal method*

The sample, thermally treated within the temperature range of nucleation at various rates of temperature change of  $\Phi_1$  and  $\Phi_2$ , is then heated rapidly to a temperature within the temperature range of crystal growth and subsequently the temperature is kept constant to measure the isothermal kinetic curve for the growth. The rate equation at a constant temperature is

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (8)$$

where  $k$  is the apparent rate constant. When an appropriate value of  $m$  is assumed, a linear plot of  $d\alpha/dt$  vs.  $f(\alpha)$  is obtained, where the slope corresponds to the value of  $k$ . Taking account of the influence of  $\Phi_1$  and  $\Phi_2$  on the apparent value of  $k$ , the temperature dependence of  $k$  is expressed by

$$k = A' [a(\Phi)]^{1/m} \exp\left(-\frac{E}{RT}\right) \quad \text{with } A' = (gN_0)^{1/m} v_0 \quad (9)$$

The value of  $E$  is determined by the following Arrhenius plot taken account of  $a(\Phi)$  and the most appropriate value of  $m$  determined previously through plotting  $d\alpha/dt$  vs. various  $f(\alpha)$ .

$$\ln \frac{k}{[a(\Phi)]^{1/m}} = \ln A' - \frac{E}{RT} \quad (10)$$

### *Kissinger method*

The sample, thermally treated within the temperature range of nucleation at various rates of temperature change of  $\Phi_1$  and  $\Phi_2$ , is then heated linearly at various rates of

$\Phi_3$  to measure the non-isothermal kinetic curves for the growth. The Kissinger method [15] has been widely used for determining approximately the activation energy of the solid-state reaction from the temperature at maximum transformation rate at various heating rates.

The first derivation of Eq. (1) with respect to time gives [16]

$$\frac{d^2\alpha}{dt^2} = A \exp\left(-\frac{E}{RT}\right) f(\alpha) \left[ \frac{df(\alpha)}{d\alpha} A \exp\left(-\frac{E}{RT}\right) + \frac{\Phi_3 E}{RT^2} \right] \quad (11)$$

At the peak maximum

$$\left( \frac{d^2\alpha}{dt^2} \right)_p = 0 \quad (12)$$

where subscript  $p$  denotes the value at the peak maximum. The general kinetic equation of the Kissinger method is obtained by combining Eqs (11) and (12) [16].

$$f'(\alpha_p) A \exp\left(-\frac{E}{RT_p}\right) + \frac{\Phi_3 E}{RT_p^2} = 0 \quad \text{with} \quad f'(\alpha) = \frac{df(\alpha)}{d\alpha} \quad (13)$$

By assuming the value of  $m$ , the apparent value of  $E$  is estimated using the following equation taken account of  $a(\Phi)$  [10, 12].

$$\ln \left\{ \frac{\Phi_3}{T_p^2} \left[ \frac{1}{a(\Phi)} \right]^{1/m} \right\} = -\frac{E}{RT_p} + \ln \left[ f'(\alpha_p) \frac{A'R}{E} \right] \quad (14)$$

Because, in many cases, the plots of  $\ln[(\Phi_3/T_p^2)/a(\Phi)^{1/m}]$  vs.  $T_p^{-1}$  show fairly linearity irrespective of  $m$  assumed, the correct value of  $E$  can not be selected without previous knowledge of  $m$ .

#### *Isoconversion method*

The isoconversion methods [17] can be applied to obtain the value of  $E$ , where kinetic relationship among the kinetic data of a series of kinetic curves at a selected  $\alpha$  is used. Taking logarithms of Eq. (7) by considering  $a(\Phi)$  [12],

$$\ln \left\{ \frac{d\alpha}{dt} \left[ \frac{1}{a(\Phi)} \right]^{1/m} \right\} = \ln[A'f(\alpha)] - \frac{E}{RT} \quad (15)$$

It follows from Eq. (15) that a correction of vertical axis by taking account of  $a(\Phi)$  and  $m$  is required for applying the Friedman method [18] in order to determine the value of  $E$  for the process assumed.

Similarly, the isoconversion method in integral form is also formalized for the present process. Integral kinetic equation is given as [3, 4]

$\Phi_3$

$$g(\alpha) = \frac{AE}{\Phi_3 R} \frac{\exp(-y)}{y} \pi(y) \text{ with } g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} \text{ and } y = \frac{E}{RT} \quad (16)$$

where  $\pi(y)$  is an approximate function of exponential integral. Using the simplest function of  $\pi(y)$ , i.e.,  $\pi(y) = 1/y$ , the equation of the integral isoconversion method is given by [12]

$$\ln \left\{ \frac{\Phi_3}{T^2} \left[ \frac{1}{a(\Phi)} \right]^{1/m} \right\} = \ln \frac{A'R}{g(\alpha)E} - \frac{E}{RT} \quad (17)$$

As is the case with the Kissinger method, the apparent values of  $E$  for the value of  $m$  assumed are obtained from the isoconversion methods. Previous knowledge of the  $m$  value of further analytical procedure is required to select the correct value of  $E$ .

### Kinetic model and pre-exponential factor

In order to generalize the kinetic description for the crystal growth of the sample with different thermal history, i.e.,  $\Phi_1$  and  $\Phi_2$ , it is convenient to extrapolate the rate behavior in real time to that in generalized time  $\theta$  at infinite temperature [19]. For example, the kinetic curves of crystal growth obtained under a linear heating at  $\Phi_3$  can be extrapolated to infinite temperature by the following equations using the  $E$  value determined by assuming  $m$ .

$$\theta \approx \frac{E}{\Phi_3 R} \frac{\exp(-y)}{y} \pi(y) \text{ with } \pi(y) = \frac{y^3 + 18y^2 + 88y + 96}{y^4 + 20y^3 + 120y^2 + 240y + 120} \quad (18)$$

and

$$\frac{d\alpha}{d\theta} = \frac{d\alpha}{dt} \exp\left(\frac{E}{RT}\right) \quad (19)$$

where  $\pi(y)$  is an approximate function proposed by Senum and Yang [20]. By taking account of  $a(\Phi)$ , the kinetic equations at infinite temperature are written as

$$g(\alpha) = A'\theta_n \text{ with } \theta_n = \theta[a(\Phi)]^{1/m} \quad (20)$$

and

$$\left(\frac{d\alpha}{d\theta}\right)_n = A'f(\alpha) \text{ with } \left(\frac{d\alpha}{d\theta}\right)_n = \left(\frac{d\alpha}{d\theta}\right) \left[\frac{1}{a(\Phi)}\right]^{1/m} \quad (21)$$

According to Eqs (20) and (21), linear plots of  $g(\alpha)$  vs.  $\theta_n$  and  $(d\alpha/d\theta)_n$  vs.  $f(\alpha)$  can be obtained when utilizing an appropriate value of  $m$  throughout the kinetic analysis. The value of  $A'$ , determined from the slope of these linear plots, is the constant value obtained by reducing the value of  $N$  in the respective measurements to  $N_0$ .

By multiplying Eqs (20) and (21), the following equation can be obtained [21].

$$\left(\frac{d\alpha}{d\theta}\right)_n \theta_n = \left(\frac{d\alpha}{d\theta}\right)_\theta = f(\alpha)g(\alpha) \quad (22)$$

Equation (22) shows that the multiplied value of  $(d\alpha/d\theta)\theta$  is only dependent on  $\alpha$ . For the JMAEK equation, the value of  $f(\alpha)g(\alpha)$  shows the maximum at  $\alpha=0.632$ , irrespective of  $m$  [21]. Validity of the above kinetic procedure based on the JMAEK equation can be evaluated from the position of the maximum of the value of  $(d\alpha/d\theta)\theta$ .

### Practical significance of the kinetic modeling

For the crystallization of glasses in which the temperature ranges of nucleation and crystal growth are separated sufficiently in a time scale of thermal treatment, the generalized kinetic equation, Eq. (7), can be derived by introducing the accommodation function. The function can be derived from the dependence of the number of pre-existing nuclei for the subsequent growth on the cooling rate during the glass-formation and heating rate during the crystallization treatment.

Thermoanalytical (TA) methods have widely been used for the kinetic characterization of the crystallization of glasses. As the glass sample passes through the temperature range of nucleation during the measurement, dependence of the number of nuclei on the heating rate during the TA measurement has to be taken into account when analyzing the kinetics of crystal growth [10–12]. In addition, changes in the crystallization kinetics due to the thermal history of the sample can be described more comprehensively by considering the dependence of the number of nuclei on the cooling rate during the glass-formation treatment [12–14].

In preparation of advanced glass-ceramic materials, the kinetic understanding accounting for the thermal history of the glass-sample can be used to control systematically the crystallization process and the characteristics of the product glass-ceramics. The practical applicability of the model described has already been tested for the crystallization process of  $\text{Li}_2\text{B}_4\text{O}_7$  [13, 14].

### References

- 1 Z. Strnad, *Glass-Ceramic Materials*, Elsevier, Amsterdam 1986.
- 2 S. F. Hulbert, *J. Brt. Ceram. Soc.*, 6 (1961) 11.
- 3 M. E. Brown, D. Dollimore and A. K. Galwey, *Reactions in the Solid State*, Elsevier, Amsterdam 1980.
- 4 J. Šesták, *Thermophysical Properties of Solids*, Elsevier, Amsterdam 1984.
- 5 H. Tanaka, N. Koga and A. K. Galwey, *J. Chem. Educ.*, 72 (1995) 251.
- 6 J. Šesták, *J. Thermal Anal.*, 33 (1988) 1263.
- 7 N. Koga, *J. Thermal Anal.*, 49 (1997) 45.
- 8 N. Koga and H. Tanaka, *J. Thermal Anal.*, 41 (1994) 455.
- 9 N. Koga and J. Málek, *Thermochim. Acta*, 282/283 (1996) 69.
- 10 K. Matusita and S. Sakka, *J. Non-Cryst. Solids*, 38/39 (1980) 741.
- 11 K. Matusita, T. Komatsu and R. Yokota, *J. Mater. Sci.*, 19 (1984) 291.

- 12 T. Ozawa, *Bull. Chem. Soc. Jpn*, 57 (1984) 639.
- 13 N. Koga, K. Yamaguchi and J. Šesták, *J. Therm. Anal. Cal.*, 56 (1999) 755.
- 14 N. Koga and J. Šesták, *J. Am. Ceram. Soc.*, in press.
- 15 H. E. Kissinger, *Anal. Chem.*, 29 (1957) 1702.
- 16 J. M. Criado and A. Ortega, *J. Non-Cryst. Solids*, 87 (1986) 302.
- 17 T. Ozawa, *Thermochim. Acta*, 203 (1992) 159.
- 18 H. L. Friedman, *J. Polym. Sci., Part C*, 6 (1964) 183.
- 19 T. Ozawa, *Bull. Chem. Soc. Jpn*, 38 (1965) 1881; *Thermochim. Acta*, 100 (1986) 109.
- 20 G. I. Senum and R. T. Yang, *J. Thermal Anal.*, 11 (1975) 445.
- 21 J. Malek, *Thermochim. Acta*, 200 (1992) 257.