Kinetic Study on Non-Isothermal Crystallization of Glass by Thermal Analysis

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For the purpose of analyzing the crystallization of glass by thermal analysis, a modified Ozawa-type equation and a modified Kissinger-type equation were derived on the basis of the nucleation and growth equations, and the validity of these equations was ascertained by applying to $Li_2O \cdot 2SiO_2$ glass whose kinetic data of crystallization were available. The modified Kissinger-type equation was identical with the so-called Kissinger equation only when the crystallization started at the surface, proceeding towards the inside of glass one-dimensionally. The modified Ozawa-type equation was identical with the so-called Ozawa equation when the number of crystal particles was constant irrespective of heating rate. The conditions under which these equations could be applied were discussed. It was concluded that the crystallization mechanism should be known in order to obtain the meaningful activation energy for crystallization by applying these equations.

I. INTRODUCTION

Thermal analysis has been used for studying the kinetics of chemical reactions[1~13] and the crystallization of glasses.[14~39] Many methods have been proposed and successfully applied to analyze the kinetics of n-th order chemical reactions.[1~13] These methods, however, can not be directly applied to the crystallization of glass because the crystallization is advanced not by the n-th order reaction but by the nucleation and growth process.[40] Although the activation energies for crystallization were determined in many reports by assuming first-order reactions,[15~20,22~25,31~37,40] the physical meaning of the activation energies thus obtained were obscure.

The Johnson-Mehl-Avrami equation was applied to the non-isothermal crystallization process.[17~20,31~32] This is not generally appropriate because the JMA equation was derived under isothermal crystallization.

We have proposed the methods for analyzing crystallization kinetics on the basis of nucleation and growth process, emphasizing that whether crystallization occurs as bulk crystallization or surface crystallization should be taken into account for obtaining the meaningful activation energy.[26~30] In the present study, crystallization kinetics in non-isothermal process was discussed on the basis of the nucleation and growth

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equations, and two simple methods, that is, the modified Ozawa-type and modified Kissinger-type equations, were proposed for analyzing the crystallization kinetics by DSC or DTA. The validity of these methods was discussed by comparing the results of calculation with experiments.

II. THEORY OF CRYSTALLIZATION KINETICS

(1) *Nucleation and crystal growth in glass*

It is known that, usually, the rate of crystal nucleation in glass reaches its maximum at a temperature somewhat higher than the glass transition temperature and then decreases rapidly with increasing temperature, while the rate of crystal growth reaches its maximum at a temperature much higher than the temperature at which the nucleation rate is hgihest.[42~45] Therefore, when a glass is heated at a constant rate, crystal nuclei are formed at lower temperature and grow in size at higher temperatures without any increase in number.[41] Variations of the nucleation rate, the growth rate, the number of nuclei formed per unit volume and the radius of crystal particle with temperature are shown schematically in Fig. 1.[46]
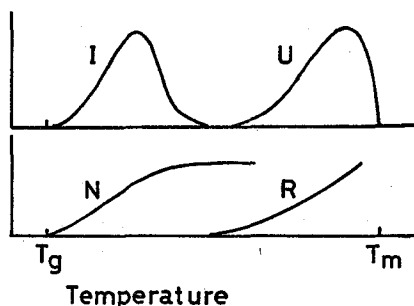

Fig. 1. Schematic representation of variations of the nucleation rate, the growth rate, the number of crystal nuclei per unit volume and the radius of crystal particle with temperature.

I: Rate of crystal nucleation. *U*: Rate of crystal growth. *N*: Number of crystal nuclei formed per unit volume heated at a constant heating rate. *R*: Radius of crystal particle heated at a constant heating rate. T_g: Glass transition temperature. T_m: Melting temperature.

The number of nuclei, N, formed per unit volume in the course of heating from room temperature, T_r, to a temperature, T, is expressed as[26~29]

$$N = \int_0^t I(T)dt = \frac{1}{\alpha}\int_{T_r}^T I(T)dT = \frac{N_0}{\alpha}, \tag{1}$$

where $\alpha = dT/dt$ is the heating rate and $I(T)$ is the rate of nucleation. N_0 does not depend on temperature if T is much higher than the temperature at which the nucleation rate is highest.

The rate of crystal growth, U, is expressed by the following equation in the temperature range much lower than the temperature of maximum growth rate.[26]

$$U = U_0 \exp\left(-\frac{E}{RT}\right);$$ (2)

where E is the activation energy for crystal growth. The radius of the crystal particle, r, is expressed as[26~29]

$$r = \int_0^t U(T)\mathrm{d}t = \frac{U_0}{\alpha} \int_{T_r}^T \exp\left(-\frac{E}{RT}\right)\mathrm{d}T.$$ (3)

This integral can not be expressed by an elementary function. According to numerical evaluation,[47~48] this integral can be approximated as follows;

$$r = \frac{r_0}{\alpha} \exp\left(-\frac{E}{RT}\right).$$ (4)

(2) *Volume fraction of crystal.*

When a glass is heated at a constant rate, the volume fraction of crystal increases with time (or temperature). It should be noted here that the rate of increase in volume depends on the crystallization mechanism even if the linear rate is the same.

In the case of bulk crystallization in which each crystal particle grows three-dimensionally, variation of the volume fraction of crystals, x, is expressed by[26]

$$\frac{\mathrm{d}x}{\mathrm{d}t} = 4\pi N r^2 (1-x)\frac{\mathrm{d}r}{\mathrm{d}t}.$$ (5)

In this equation, $(1-x)$ is the correction factor for the impingement of crystal particles and reduction of glass phase.[49] Substituting Eqs. (1), (2) and (4) for N, $\mathrm{d}r/\mathrm{d}t$ $(=U)$ and r respectively, the following equation is derived;

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{A}{\alpha^3}(1-x)\exp\left(-\frac{3E}{RT}\right).$$ (6)

This is converted to

$$\frac{\mathrm{d}x}{1-x} = \frac{A}{\alpha^4}\exp\left(-\frac{3E}{RT}\right)\mathrm{d}T.$$ (7)

Integration of Eq. (7) leads to

$$-\ln(1-x) = \frac{B}{\alpha^4}\exp\left(-\frac{3E}{RT}\right).$$ (8)

In the case of surface crystallization, nuclei are formed only on the surface and crystals grow from the surface towards the inside of the glass one-dimensionally. Assuming a glass sphere of radius R_0 in which the surface layer of thickness r is crystallized as shown in Fig. 2, the volume fraction of crystal, x, is expressed as
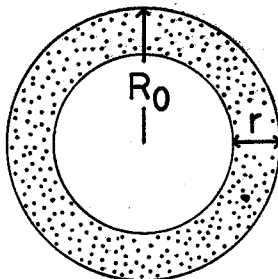
$$1-(1-x)^{1/3} = \frac{r}{R_0}.$$ (9)

Fig. 2. A glass sphere of radius R_0 having the surface crystalline
layer of thickness r.

Using Eq. (2) and differentiating, eq (9) becomes

$$\frac{dx}{dt} = \frac{3U_0}{R_0}(1-x)^{2/3}\exp\left(-\frac{E}{RT}\right).$$
(10)

Except in the region where x is close to one, the following approximation can be used;

$$1-(1-x)^{1/3} = -\frac{1}{3}\ln(1-x).$$
(11)

Then, equation (9) can be approximated as

$$-\ln(1-x) = \frac{3r}{R_0} = \frac{3r_0}{\alpha}\exp\left(-\frac{E}{RT}\right).$$
(12)

Combining Eqs. (6), (8), (10) and (12), the following simplified expressions are derived;

$$\frac{dx}{dt} = K_1\alpha^{-(n-1)}(1-x)^k\exp\left(-\frac{mE}{RT}\right)$$
(13)

and

$$-\ln(1-x) = K_2\alpha^{-n}\exp\left(-\frac{mE}{RT}\right),$$
(14)

Table I. Values of n, m and k for various crystallization mechanisms

Crystallization mechanism	n	m	k
Bulk nucleation with varying number of nuclei[*1]			
Three-dimensional growth	4	3	1
Two-dimensional growth	3	2	1
One-dimensional growth	2	1	1
Bulk nucleation with constant number of nuclei[*2]			
Three-dimensional growth	3	3	1
Two-dimensional growth	2	2	1
One-dimensional growth	1	1	1
Surface nucleation	1	1	2/3

[*1] The number of nuclei is inversely proportional to the heating rate.
[*2] The number of nuclei does not change with the heating rate.

where K_1 and K_2 are constants and n, k and m are the numerical factors depending on crystallization mechanism. The values of n, k and m for various crystallization mechanisms are summarized in Table I.

(3) *Ozawa-type plot.*

When a glass is heated at a constant heating rate, the volume fraction of crystal increases as expressed by Eq. (14). Equation (14) can be rewritten as

$$\ln \alpha = -\frac{mE}{nRT} - \frac{1}{n} \ln \left[-\ln \left(1-x \right) \right] + \text{Const.} \tag{15}$$

Thus, the plot of $\ln \alpha$ aginst $1/T$, where T is the temperature at which the crystal volume fraction reaches a specific value, gives a straight line and the slope gives the value of $(m/n)E$. For the crystallization mechanism of $n=m$, the activation energy for crystal growth can be directly obtained from this plot. Only in the case of $n=m$, equation (15) is identical with the so-called Ozawa plot which was derived for chemical reactions.[11~13] It should be noted here that for crystallization of glass, the meaningful activation energy can be obtained only when the crystallization mechanism is known precisely, namely, n and m are known, and it does not change with the heating rate.

(4) *Kissinger-type plot.*

When a glass is heated at a constant heating rate, the rate of increase of the crystal volume fraction is expressed by Eq. (13). The rate of increase of x reaches its maximum at a temperature T_0. Solving Eq. (13) for

$$\frac{d}{dt} \left(\frac{dx}{dt} \right) = 0,$$

the following equation is derived[30];

$$\frac{\alpha^n}{T_0{}^2} = \frac{K_1 kR}{mE} (1-x_0)^{k-1} \exp \left(-\frac{mE}{RT_0} \right), \tag{16}$$

where x_0 is the volume fraction at T_0. As is shown in Table I, k and, accordingly, the term $(1-x_0)^{k-1}$ are always equal to one except for surface crystallization. For surface crystallization, k is equal to $2/3$ and the term $(1-x_0)^{k-1}$ can be regarded as constant, comparing with the change of the exponential term. Therefore, equation (16) can be written as

$$\ln \left(\frac{\alpha^n}{T_0{}^2} \right) = -\frac{mE}{RT_0} + \text{Const.} \tag{17}$$

It the crystallization mechanism is known precisely and does not change with the heating rate, the plot of $\ln(\alpha^n/T_0{}^2)$ against $1/T_0$ gives the value of mE. Dividing mE by m, the activation energy for crystal growth can be obtained. It should be noted here that only when the surface crystallization is dominant, in other words, $n=m=1$ for all the heating rates, equation (17) is identical with the so-called Kissinger equation:

$$\ln\left(\frac{\alpha}{T_0{}^2}\right) = -\frac{E}{RT_0} + \text{Const}, \tag{18}$$

which was derived from the rate equation of n-th order chemical reactions.[9,10]

III. COMPARISON WITH EXPERIMENTS

(1) *Glasses used.*

In order to ascertain the validity of the modified Ozawa-type Eq. (15) and the modified Kissinger-type Eq. (17), DSC and DTA measurements were made on $Li_2O \cdot 2SiO_2$ glass. It is known that bulk crystallization and surface crystallization occur simultaneously in $Li_2O \cdot 2SiO_2$ glass.[26,50] At low heating rates, bulk nucleation is dominant and each particle grows three-dimensionally. As the heating rate increases, the contribution of surface crystallization increases.[26~30] It has been reported that the activation energy for crystal growth in this glass is equal to that for viscous flow.[43,46] The viscosity, η (poise), of $Li_2O \cdot 2SiO_2$ glass is expressed by the Fulcher equation;[43]

$$\log \eta = -1.44 + \frac{3.37 \times 10^3}{T - 460}. \tag{19}$$

The activation energy for viscous flow, $E\eta$, can be calculated as a function of temperature.

(2) *Differential scanning calorimetry (DSC).*

The DSC measurements were made as reported previously.[27,29] Bulk glass, instead of powder, was used as samples to avoid the effect of particle radius distribution. To fill the sample holder (4 mm in inner diameter and 2 mm in depth) with glass, a glass melt of 100 mg was poured into it, remelted in an electric furnace at 1400°C for 20 min, and allowed to cool in air. The volume fraction of precipitated crystals can be obtained from the DSC curve by using

$$x = \frac{S}{S_0}, \tag{20}$$

where S_0 is the area under the DSC curve between T_1 (the temperature at which crystallization starts) and T_2 (the temperature at which crystallization is completed) and S is the area between T_1 and T as shown in Fig. 3.

Figure 4 shows the example of the modified Ozawa-type plot in which $\ln\alpha$ is plotted against reciprocal of absolute temperature at which the volume fraction of crystal reaches 0.3 and 0.7. According to Eq. (15), the values of $(m/n)E$ can be obtained from these slopes. Figure 5 shows the relation between $\ln\alpha$ and $1/T_0$, where T_0 is the peak temperature in the DSC curve. Since the volume fraction of crystal at peak temperature, x_0, is almost the same irrespective of α as shown in Table II, equation (15) should hold for the peak temperatures. The values of the $(m/n)E$ are shown in Table III together with the activation energy for viscous flow, E_η, in the temperature range of exothermic peaks in the DSC curves. Since the bulk
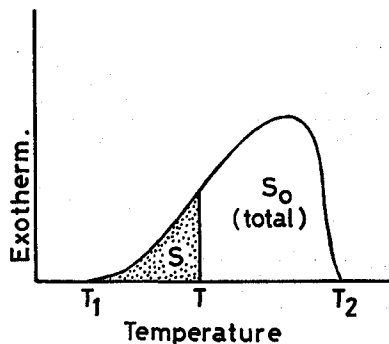
Fig. 3. A typical DSC curve. T_1: Temperature at which crystallization starts. T_2: Temperature at which crystallization is completed.
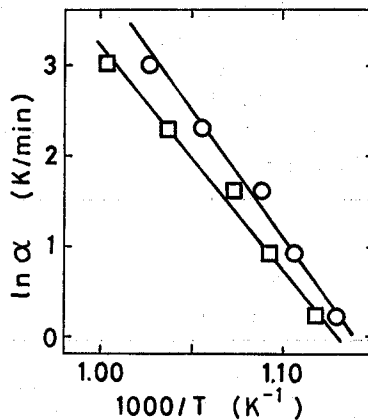

Fig. 4. Modified Ozawa-type plot of $Li_2O \cdot 2SiO_2$ glass.
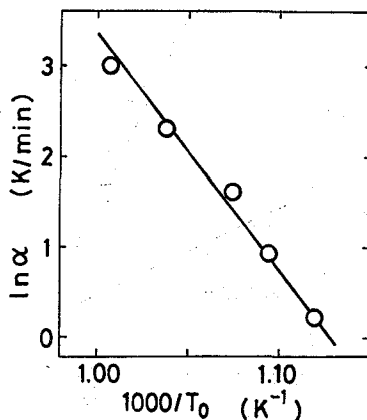
    $\bigcirc$: $x=0.3$ $\square$: $x=0.7$

Fig. 5. Relation between natural logarithm of heating rate and reciprocal of peak temperature in DSC curve of $Li_2O \cdot 2SiO_2$ glass.

Table II. Volume percent of crystals at peak temperature in DSC for various heating rates

	Heating rate (K/min)				
	1.25	2.5	5	10	20
Vol%	65	68	66	69	65

glass was used as samples, bulk nucleation is dominant and each crystal particle grows three-dimensionally. Therefore, n and m should be 4 and 3 respectively. In Table III, the activation energy for crystal growth, E, thus obtained are also shown. It is seen that the activation energies, E, are very close to E_η, considering the uncertainty of the values of n and m.

Table III. Values of $(m/n)E$ obtained from DSC by using the modified Ozawa-type plot, the activation energy for crystal growth, E, assuming $n=4$ and $m=3$ and the activation energy for viscous flow, E_η in the temperature region of exothermic peaks

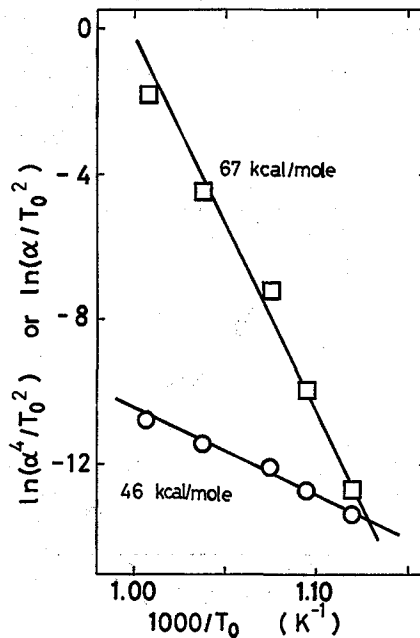| Volume fraction	$(m/n)E$ (kcal/mole)	E (kcal/mole)	Average E_η (kcal/mole)
0.3	56	70	63 (600–700°C)
0.5	51	68	62 (600–715°C)
0.7	49	66	61 (600–725°C)
Peak temperature	53	70	61 (600–725°C)

Fig. 6. Kissinger-type plot of data obtained from DSC curves of Li$_2$O·2SiO$_2$ glass.

○: $n=m=1$　□: $n=4$ and $m=3$

The peak temperature, T_0, may be regarded as the temperature of maximum crystallization rate, and therefore, the Kissinger-type plot also may be valid. Figure 6 shows the so-called Kissinger plot with $n=m=1$ in which $\ln(\alpha/T_0^2)$ is plotted against $1/T_0$ and the modified Kissinger-type plot with $n=4$ and $m=3$ in which $\ln(\alpha^4/T_0^2)$ is plotted against $1/T_0$. The activation energy, E, obtained from the so-called Kissinger plot with $n=m=1$ (46 kcal/mole) is much less than E_η (61 kcal/mole). However, the E-values obtained from the modified Kissinger-type plot with $n=4$ and $m=3$ (67 kcal/mole) is very close to E_η (61 kcal/mole).

(3) *Differential thermal analysis (DTA)*.

DTA measurements were made as reported previously.[26,30] Three types of

samples were prepared; (1) glass particles passing through a sieve of 44 μm openings, (2) glass particles passing through a sieve of 149 μm openings and remaining on that of 74 μm openings and (3) bulk glass (disc of 5 mm in diameter and 2 mm thick) which was remelted in a sample holder at 1400°C for 20 min and cooled in air. As already mentioned, bulk crystallization and surface crystallization occur simultaneously in $Li_2O \cdot 2SiO_2$ glass. It is supposed that surface crystallization is dominant in sample (1) and (2) and bulk crystallization is dominant in sample (3), especially at low heating rates.

It may be probable that the volume fraction of crystal at the peak temperature is almost the same irrespective of the heating rate as is the case of DSC. Figure 7 is the plot of $\ln\alpha$ against reciprocal of the peak temperature. The values of $(m/n)E$ obtained by using Eq. (15) and the activation energies for crystal growth, E, determined assuming that $n=m=1$ for sample (1) and (2) and $n=4$ and $m=3$ for sample (3) are shown in Table IV together with the activation energies for viscous flow, E_η, in the
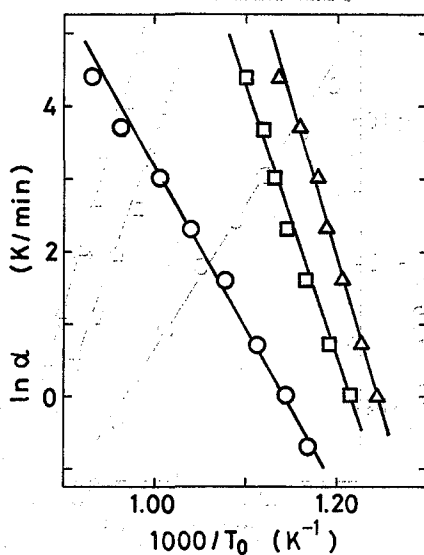

Fig. 7. Relation between heating rate and reciprocal of peak temperature in DTA curve of $Li_2O \cdot 2SiO_2$ glass.

$\triangle$: sample (1) $\square$: sample (2) $\bigcirc$: sample (3)

Table IV. Values of $(m/n)E$ obtained from DTA by using the modified Ozawa-type plot, the activation energy for crystal growth, E, and the activation energy for viscous flow, E_η, in the temperature region where exothermic peaks are found

Sample No.	Particle size (μm)	$(m/n)E$ (kcal/mole)	E (kcal/mole)	Average E_η (kcal/mole)
1	44	86	86 ($n=m=1$)	80 (530–600°C)
2	74–149	75	75 ($n=m=1$)	70 (560–640°C)
3	Bulk	44	60 ($n=4$ and $m=3$)	65 (590–700°C)

temperature range of exothermic peaks in DTA curves. The values of E are very close to E_η respectively, indicating that bulk crystallization is dominant in sample (3) and surface crystallization is dominant in sample (1) and (2).

It may also be probable that the crystallization rate reaches its maximum at the peak temperature, T_0, and, therefore, the Kissinger-type plot may be valid. Figure 8 shows the so-called Kissinger plot with $n=m=1$ in which $\ln(\alpha/T_0^2)$ is plotted against $1/T_0$. The activation energies, E_1, obtained by using Eq. (18) which is equivalent to $n=m=1$ in Eq. (17) are shown in Table V. It is seen that the values of E_1 of sample (1) and (2) are very close to E_η respectively, but that of sample (3) is much less than E_η. This unreasonably low value is caused by the assumption that $n=m=1$, that is, surface crystallization is dominant. Figure 9 shows the plot of $\ln(\alpha^4/T_0^2)$ against $1/T_0$ for sample (3). The activation energy, E_2, according to Eq. (17) with $n=4$ and $m=3$ is 64 kcal/mole, agreeing witn E_η very well. This agreement indicates that bulk crystallization is dominant in sample (3).
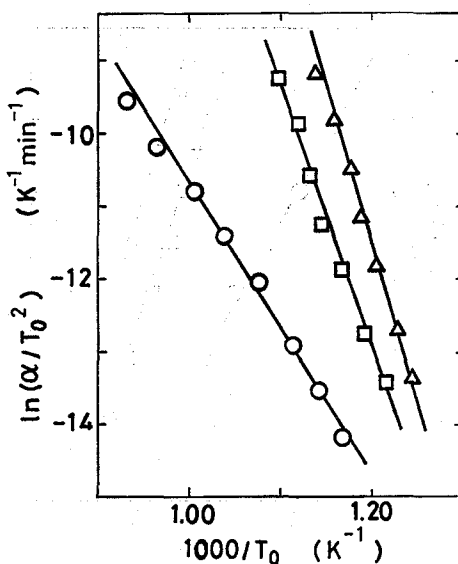

Fig. 8. Kissinger plot of data obtained from DTA curves of $Li_2O \cdot 2SiO_2$ glass $(n=m=1)$

△ : sample (1)   □ : sample (2)   ○ : sample (3)

Table V. Activation energies for crystal growth, E_1 and E_2, obtained from equation (17) assuming $n=m=1$ and $n=4$ and $m=3$ respectively, and the activation energy for viscous flow E_η, in the temperature region where exothermic peaks are found

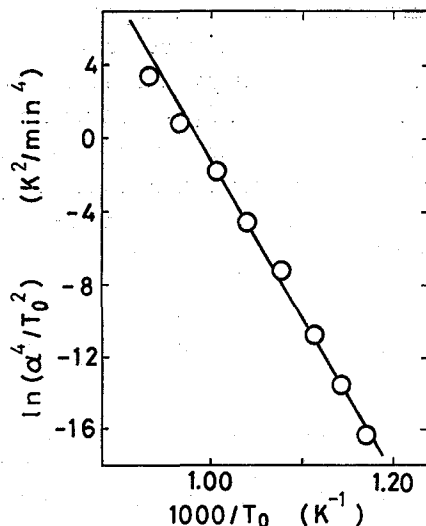| Sample No.	Particle size (μm)	E_1 ($n=m=1$) (kcal/mole)	E_2 ($n=4$ and $m=3$) (kcal/mole)	Average E_η (kcal/mole)
1	44	85		80 (530–600°C)
2	74–149	72		70 (560–640°C)
3	Bulk	38	64	65 (590–700°C)

Fig. 9. Modified Kissinger-type plot ($n=4$ and $m=3$) of data obtained
from DTA curves of sample (3).

IV. DISCUSSION

So far, a number of authors examined the kinetics of crystallization of glass by thermal analysis.[14~39]   Many of them used the so-called Kissinger plot,[22~25,33~37,40] assuming that the crystallization proceeds as a first order reaction.   The physical meaning of the activation energy thus obtained is obscure unless crystallization occurs by the surface crystallization mechanism.   Crystallization mechanism changes with the condition of crystallization.[26~30]   Even with the same glass, crystallization mechanism changes with sample size as shown in Figs. 7 and 8.   It is necessary to know the crystallization mechanism to obtain the meaningful activation energy by thermal analysis, and only when the mechanism is known precisely, the activation energy for crystal growth can be obtained.   If the crystallization advances with more than two kinds of mechanism, namely, if surface crystallization and bulk crystallization occurs simultaneously as shown in Fig. 10, it is difficult to find the physical meaning of the activation energy precisely.
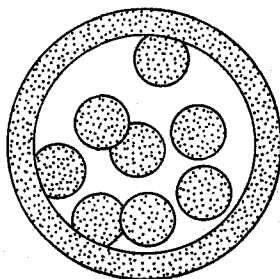

Fig. 10. Schematic representation of the mixed crystallization mechanism.

As a method for obtaining the activation energy for crystal growth, the modified Ozawa-type plot and the modified Kissinger-type plot are very useful and convenient. For the peak temperatures, T_0, both plots give the same activation energies as shown in Figs. 5~9. This is due to the facts that T_0 is the temperature at which the crystallization rate is maximum and the volume fraction of crystal at T_0 is almost the same irrespective of the heating rate. This indicates that the change of $\ln T_0$ with heating rate is negligibly small compared with that of $\ln \alpha$, namely, the change of $\ln(\alpha^n/T_0^2)$ in Eq. (17) with heating rate is almost equal to that of $\ln \alpha^n$.

V. SUMMARY

The equations correlating the thermal analysis curve with the heating rate were derived on the basis of the nucleation and growth theory. These equations, that is, the modified Ozawa-type and Kissinger-type equations, contain numerical factors which depend on the crystallization mechanism, and when the surface crystallization is dominant, the equations are identical with the so-called Ozawa equation and Kissinger equation respectively. In addition, when the number of crystal particles is fixed and does not change with heating rate, the modified Ozawa-type equation is identical with the so-called Ozawa equation. The validity of the equations was ascertained by applying to the crystallization of $Li_2O \cdot 2SiO_2$ glass. It was concluded that the crystallization mechanism should be taken into account for obtaining the meaningful activation energy for crystallization.

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