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Nonisothermal Kinetics of Crystal Growth from Preexisting Nuclei

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Fundamental kinetic equations for nonisothermal crystal growth from preexisting nuclei are derived, by introducing a concept of reduced time. A method of kinetic analysis of thermoanalytical data of these processes is proposed, and all kinetic parameters can be estimated by the method, so that the process proceeding under various temperature changes can also be predicted.

It is well known that crystalline nuclei form first in supercooled liquids and amorphous solids, and then they grow to crystallites. Some solid reactions also proceed in a similar way to this nucleation-and-growth process. When they occur isothermally, these processes follow Avrami's equation;

$$-\ln(1-C) = Zt^{n}, \tag{1}$$

where C, Z, t, and n are respectively the conversion, a constant, the time, and an integer dependent on the mechanism of the process.[1-3] Evans[4] derived this equation in an ingenious way, in which the nuclei are compared to rain-drops falling down on a pond and the fronts of the crystal growth are compared to the traversing wave fronts caused by the rain drops. He calculated expectancy of the number of the wave fronts passing over a particular point, and the unconverted fraction can be calculated by using the expectancy thus calculated and Poisson's distribution.

In 1971 the present author set forth theoretical considerations of nonisothermal kinetics of the processes by extending Evans' way to nonisothermal conditions. A method for kinetic analysis of thermoanalytical data of the processes proceeding at a linear rate of heating or cooling was also derived, and the method was applied to crystallization of poly(ethylene terephthalate) observed at linear cooling rates by differential scanning calorimetry (DSC).[5]

Recently various amorphous materials, such as amorphous magnetic materials and amorphous silicon for solar photovoltaic cells, are under extensive research and development, and to evaluate their thermal stability, crystallization behaviors of these materials are investigated by differential thermal analysis and DSC. To estimate the kinetic parameters for predicting the crystallization behavior is also important in research of latent heat thermal energy storage materials, especially of the materials containing nucleating agent. The kinetic analysis is also useful for inorganic glasses. For analyzing thermoanalytical data of crystallization of inorganic glasses and amorphous materials, mainly Kissinger plot[6] proposed for usual chemical reactions has been applied to the data. Therefore, it is erroneous to apply the plot to the crystallization processes for estimating the activation energy, as was already pointed out by Matusita and Sakka,[7] though the plot is rigorously applicable to first order reactions and approximately applicable to reactions of the other orders.[8]

Matusita and Sakka[7] derived a theory and an analytical method of the processes, in which the random nucleation occurs in lower temperature range and prior to the growth, which proceeds separately after the nucleation. They applied their method to crystallization of inorganic oxide glasses. However, they derived the theory roughly, neglecting the rigorous theoretical derivations of nonisothermal relations for crystallization[5] and chemical reactions,[8] so that "modified Ozawa plot" proposed by them should be corrected by rigorous theoretical considerations. To derive rigorous nonisothermal equations, isothermal equations for each unit process should be expanded separately to nonisothermal equations, because the expansion of isothermal kinetic equations as a whole may lead to erronous results.[5]

Moreover, their method does not have any means to check the applicability of the method in itself. In other words, there is no means to confirm certain applicability of the method by observing consistency between the observed process and the model on which the theory and method are based. Therefore, we can not deny possibility that the method may be applied outside of its applicability. A method to estimate the kinetic parameter, n, is also not included in their method, so that n may be determined inaccurately. By the method, the activation energy can only be estimated, and the other kinetic parameters can not be obtained. Therefore, the crystallization behavior of the materials under various conditions can not be predicted for assessing thermal stability of the materials, though Matusita and Sakka clearly and exactly criticized the arbitrary and unsupported application of the Kissinger plot.

The present author's theory and the method for kinetic analysis of the thermoanalytical data cover more general cases, in which the random nucleation and the growth occur either concurrently or separately.[5] However, the applicability of these theory and method is limited in the cases of linear heating or cooling. For the cases, in which the nucleation occurs separately in the lower temperature range prior to the growth, a simple, but rigorous, theory and method can be derived, and they are applicable to more general cases of temperature change. One can overcome the above-mentioned drawbacks by the present author's method for kinetic analysis based on this rigorous theory, and one can also predict the process proceeding under various types of temperature changes using the kinetic parameters thus obtained. In this paper, the theory and the method are reported.

Models

There are two models for the case of crystal growth from preexisting nuclei with negligible concurrent random nucleation. The first model is the crystal growth from impurity or nucleating agent, as is the case for latent heat thermal energy storage materials containing nucleating agent, and the number of the nuclei is independent on the thermal history of the materials. The second case is that the temperature range for random nucleation is much lower than that for the crystal growth, and the two temperature ranges are separated clearly, so that the number of the nuclei existing in the beginning of the growth is constant during the growth but dependent on the thermal history in the nucleation temperature range. For the crystal growth there are three cases, *i.e.*, one-dimensional growth, two-dimensional growth and three-dimensional growth.

Method for Deriving the Kinetic Equation

As mentioned before, the excellent and elegant way of Evans[4] is adopted and extended in this paper. First, let us consider the case in which many stones fall on the pond at the same time t_1. The stones are compared to the nuclei, and the wave fronts caused by the stones are compared to the front of the crystal growth. The expectancy, E, of the number of the wave fronts passing over a particular point until the time t_2 is equal to the number of the stones falling in a circle, the radius of which is the distance the wave fronts traversed from t_1 to t_2. It is given as follows:

$$E = \pi N R^2, \tag{2}$$

where N and R are the number of stones falling in a unit area and the distance which the wave fronts traversed from t_1 to t_2, respectively, and R is given below.

$$R = \int_{t_1}^{t_2} v \mathrm{d}t, \tag{3}$$

where v is the linear velocity of the wave fronts.

Because the fronts of crystal growth pass over a particular point only once in contrast with the wave fronts on the pond, the part of the pond, over which the wave fronts have not yet passed, has real physical meaning in crystallization, and it is the fraction of unconverted portion. The conversion of the crystallization can thus be expressed by applying Poisson's distribution as follows:

$$1 - C = \exp(-E), \tag{4}$$

or

$$-\ln(1-C) = E. \tag{5}$$

By applying this derivation to the nonisothermal conditions, we can obtain the fundamental equation for nonisothermal crystallization from preexisting nuclei.

Fundamental Equation for Nonisothermal Crystallization from Preexisting Nuclei

The number of preexisting nuclei per unit volume is dependent on the above-mentioned models. For the first model, the number of the nuclei, N, is a constant.

$$N = \text{constant} \tag{6}$$

On the other hand, N is given below for random nucleation for the second model as follows:

$$N = \int_0^{t_1} \nu(T) \mathrm{d}t, \tag{7}$$

where $\nu(T)$ is a nucleation rate per unit volume as a function of the temperature, T, and as is assumed in the model, the nucleation does not occur after the time t_1.

The expectancy, E, can be derived, taking into accounts of the dimension of the growth. For the one-dimensional growth,

$$E = dNR, \tag{8}$$

where d is the cross section of the needle-like crystallites. For the two-dimensional growth,

$$E = \pi d N R^2, \tag{9}$$

where d is the thickness of the disk-like crystallites. For the three-dimensional growth,

$$E = \frac{4\pi}{3} N R^3. \tag{10}$$

Taking account of the temperature dependence of the linear growth velocity, *i.e.*,

$$v(T) = v_0 f(T), \tag{11}$$

let us introduce a concept, reduced time, θ, namely[8,9]

$$\theta = \int f(T) \mathrm{d}t, \tag{12}$$

and

$$R = v_0 \theta. \tag{13}$$

Thus, the fundamental equation is given as follows:

$$-\ln(1-C) = Z_0 \theta^m, \tag{14}$$

where Z_0 equals to gNv_0^m and g and m are a constant and the number of the growth dimension, respectively. The constant, g, is equal to d, πd and $4\pi/3$ respectively for the one-dimensional growth, the two-dimensional growth and the three-dimensional growth. The integer, n, in Eq. 1 is equal to the number of growth dimension, m, for the isothermal crystallization from the preexisting nuclei without the concurrent random nucleation, while n is equal to $(m+1)$ for the isothermal crystallization with the concurrent random nucleation. The constant, Z, in Eq. 1 is equal to $gN\{v(T)\}^m$. We also get the next equation for the crystallization rate per unit reduced time,

$$\frac{\mathrm{d}C}{\mathrm{d}\theta} = m Z_0 (1-C) \theta^{m-1}, \tag{15}$$

and the crystallization rate per unit real time is given below:

$$\frac{\mathrm{d}C}{\mathrm{d}t} = \frac{\mathrm{d}C}{\mathrm{d}\theta}\frac{\mathrm{d}\theta}{\mathrm{d}t} = m Z_1 (1-C) \theta^{m-1}, \tag{16}$$

where Z_1 is $gNv_0^{m-1}v(T)$.

Equations for Linear Heating and Cooling

First, we will consider N for the second model. When the melt is cooled at a linear rate, ϕ_1, to the temperature where the nucleation does not occur and heated again at a linear rate, ϕ_2, to the temperature at which the crystal growth begins, N is given according to Eq. 7 as follows:

$$N=\left\{\frac{1}{\phi_1}+\frac{1}{\phi_2}\right\}\int_{T_1}^{T_2}v(T)\mathrm{d}T, \tag{17}$$

where T_1 and T_2 are the minimum and maximum temperatures of the nucleation, and the integral in Eq. 17 is a constant. Expressing this constant to be N_0 we get

$$N=N_0\left\{\frac{1}{\phi_1}+\frac{1}{\phi_2}\right\}. \tag{18}$$

When the materials are, then, heated up at a linear heating rate, ϕ_3, in the temperature range of the crystal growth, R is given as follows:

$$R(T)=\frac{1}{\phi_3}\int_{T_3}^{T}v(T)\mathrm{d}T, \tag{19}$$

where T_3 is the minimum temperature for the crystal growth.

Combining these relations, we get the equation for the first model:

$$-\ln(1-C)=\frac{Z_0}{\phi_3{}^m}\{F(T)\}^m, \tag{20}$$

where

$$F(T)=\int_{T_3}^{T}f(T)\mathrm{d}T. \tag{21}$$

For the second model, we get

$$-\ln(1-C)=\frac{Z_0'}{\phi_3{}^m}\{F(T)\}^m\left\{\frac{1}{\phi_1}+\frac{1}{\phi_2}\right\}, \tag{22}$$

where Z_0' is $gN_0v_0{}^m$.

For the crstallization rate per unit real time, we get following two equations for the first and second models:

$$\frac{\mathrm{d}C}{\mathrm{d}t}=\frac{mZ_1}{\phi_3{}^{m-1}}(1-C)\{F(T)\}^{m-1}, \tag{23}$$

$$\frac{\mathrm{d}C}{\mathrm{d}t}=\frac{mZ_1'}{\phi_3{}^{m-1}}(1-C)\{F(T)\}^{m-1}\left\{\frac{1}{\phi_1}+\frac{1}{\phi_2}\right\}, \tag{24}$$

where Z_1' is $gN_0v_0{}^{m-1}v(T)$.

If the temperature dependence of the linear crystal growth rate follows Arrhenius law, namely

$$f(T)=\exp\left(-\frac{\Delta E}{\mathbf{R}T}\right), \tag{25}$$

where ΔE and $\mathbf{R}$ are the activation energy and the gas constant, respectively, we obtain the next equation for the reduced time:

$$\theta=\frac{\Delta E}{\phi_3\mathbf{R}}\mathrm{p}\left(\frac{\Delta E}{\mathbf{R}T}\right), \tag{26}$$

where p is the p function proposed by Doyle[10] and $v(T)$ is assumed to be negligibly small at T_3. The p function is given as follows:

$$\mathrm{p}(y)=\frac{\exp(-y)}{y}-\mathrm{Ei}(-y), \tag{27}$$

where Ei is the exponential integral function. Therefore,

$$E(T)=\frac{\Delta E}{\mathbf{R}}\mathrm{p}\left(\frac{\Delta E}{\mathbf{R}T}\right). \tag{28}$$

Thus, we get the fundamental equations for the first and second models:

$$-\ln(1-C)=\frac{Z_0\Delta E^m}{\phi_3{}^{\mathrm{m}}\mathbf{R}^m}\left\{\mathrm{p}\left(\frac{\Delta E}{\mathbf{R}T}\right)\right\}^m, \tag{29}$$

$$-\ln(1-C)=\frac{Z_0'\Delta E^m}{\phi_3{}^m\mathbf{R}^m}\left\{\mathrm{p}\left(\frac{\Delta E}{\mathbf{R}T}\right)\right\}^m\left\{\frac{1}{\phi_1}+\frac{1}{\phi_2}\right\}, \tag{30}$$

and the crystallization rate is given as follows:

$$\frac{\mathrm{d}C}{\mathrm{d}t}=\frac{mZ_1\Delta E^{m-1}}{\phi_3{}^{m-1}\mathbf{R}^{m-1}}(1-C)\left\{\mathrm{p}\left(\frac{\Delta E}{\mathbf{R}T}\right)\right\}^{m-1}, \tag{31}$$

$$\frac{\mathrm{d}C}{\mathrm{d}t}=\frac{mZ_1'\Delta E^{m-1}}{\phi_3{}^{m-1}\mathbf{R}^{m-1}}(1-C)\left\{\mathrm{p}\left(\frac{\Delta E}{\mathbf{R}T}\right)\right\}^{m-1}\left\{\frac{1}{\phi_1}+\frac{1}{\phi_2}\right\}. \tag{32}$$

At the maximum rate of crystallization,

$$\frac{\mathrm{d}^2C}{\mathrm{d}t^2}=0. \tag{33}$$

On the other hand, we have the next two relations;

$$\frac{\mathrm{d}C}{\mathrm{d}t}=\frac{\mathrm{d}C}{\mathrm{d}\theta}\frac{\mathrm{d}\theta}{\mathrm{d}t}=\exp\left(-\frac{\Delta E}{\mathbf{R}T}\right)\frac{\mathrm{d}C}{\mathrm{d}\theta}, \tag{34}$$

and

$$\frac{\mathrm{d}^2C}{\mathrm{d}t^2}=\exp\left(-\frac{2\Delta E}{\mathbf{R}T}\right)\frac{\mathrm{d}^2C}{\mathrm{d}\theta^2}+\frac{\phi_3\Delta E}{\mathbf{R}T^2}\exp\left(-\frac{\Delta E}{\mathbf{R}T}\right)\frac{\mathrm{d}C}{\mathrm{d}\theta}. \tag{35}$$

The above-mentioned p function can also be approximated as follows:

$$\mathrm{p}(y)\approx\frac{\exp(-y)}{y^2}\qquad(20\leqq y\leqq 50). \tag{36}$$

By applying this approximation and combining Eqs. 33 and 35, we get

$$\frac{\mathrm{d}C}{\mathrm{d}\theta}+\theta\frac{\mathrm{d}^2\mathrm{C}}{\mathrm{d}\theta^2}=0. \tag{37}$$

The same relation was also found previously for the usual chemical reactions.[8,9] By applying Eq. 5, the right hand side of Eq. 14 is found to be unity, so that the conversion at the maximum rate, C_m, is given as follows;

$$-\ln(1-C_m)=1, \tag{38}$$

then

$$C_m=1-\frac{1}{\mathrm{e}}. \tag{39}$$

Namely, the conversion at the maximum rate is about 63.2%, which is equal to that for the first order reaction.[11]

For nonisothermal crystallization in cooling mode, we drive the same equations as Eqs. 14, 16, 20 and 23, in which the lower limits of the integrals of $R(T)$, $F(T)$ and θ are the melting temperature or its time.

Methods for Kinetic Analysis of Thermoanalytical Data

First of all, we should ascertain whether the process under measurement is the first model or the second one. It is useful for this purpose to observe the effect of the thermal history in the nucleation temperature range, for instance by changing ϕ_1 and/or ϕ_2 in wide range. Then, the value of m can be determined by using Eqs. 20 and 22, namely for the first model,

$$\log(-\ln(1-C)) = \log[Z_0\{F(T)\}^m] - m\log\phi_3, \quad (40)$$

and for the second model cooled and heated at the same rate ($\phi_1=\phi_2=\phi_3$),

$$\log(-\ln(1-C)) = \log[2Z_0'\{F(T)\}^m] - (m+1)\log\phi_3. \quad (41)$$

When we observe the process at different rates of heating and cooling and plot $\log(-\ln(1-C))$ against $\log\phi_3$ at the same temperature, we get linear plots, and the slopes of the plots are equal to $-m$ or $-(m+1)$, because the first term in the right hand side of the above equations is constant at the same temperature. When we use the specimens of the second model obtained by quenching and observed the crystal growth at different heating rates ($\phi_1 \gg \phi_2=\phi_3$), the slopes of the plots are also equal to $-(m+1)$, because $1/\phi_1$ is negligibly small and

$$\log\{-\ln(1-C)\} = \log[Z_0\{F(T)\}^m] - (m+1)\log\phi_3. \quad (42)$$

From the intercept of these plots, we get the first terms in Eqs. 40, 41, and 42, and they are the temperature integral of Z or $gN_0\{v(T)\}^m$. These plots are essentially the same as those proposed for more general cases by the present author previously.5) As pointed out previously, we can predict the crystallization behavior at linear rates by using the kinetic parameters thus obtained.

For the case that m equals to unity, *i.e.*, the one-dimensional growth, a simple relation can be applied to the data. From Eqs. 23 and 24, we get for the first model

$$\frac{\mathrm{d}C}{\mathrm{d}t} = Z(1-C), \quad (43)$$

where Z is $gNv(T)$.
and for the second model

$$\frac{\mathrm{d}C}{\mathrm{d}t} = Z'(1-C)\left\{\frac{1}{\phi_1}+\frac{1}{\phi_2}\right\}, \quad (44)$$

where Z' is $gN_0v(T)$. When both the conversion and the rate of conversion are obtained, we can directly estimate Z or Z' as a function of the temperature by using the above relation. The temperature dependence of the linear growth rate can also be obtained by comparing the rate of conversion observed at different heating rates at a given conversion, as is seen in Eqs. 23 and 24. However, the obtained values are somewhat complicated for the case that m is not equal to unity.

If the temperature dependence of the crystal growth rate follows the Arrhenius law, further kinetic analysis can be done by using the data obtained at different heating rates, because the p function can be approximated as follows, and this is much better approximation than Eq. 36;10)

$$\log \mathrm{p}(y) \approx 2.315 - 0.4567y \quad (20 \leqq y \leqq 60). \quad (45)$$

We get the next equations at a given conversion from Eqs. 29, 30, and 45; for the first model,

$$\log\phi_3 + 0.4567\frac{\Delta E}{\mathbf{R}T} = \text{constant}, \quad (46)$$

and for the second model ($\phi_1=\phi_2=\phi_3$, or common ϕ_1 but different $\phi_2=\phi_3$),

$$\log\phi_3 + 0.4567\frac{m\Delta E}{(m+1)\mathbf{R}T} = \text{constant}. \quad (47)$$

Thus, when we plot the logarithm of the heating rate against the reciprocal absolute temperature at a given conversion, we obtain linear plots and we can estimate the activation energy from the slope as is described in Eqs. 46 and 47. This relation is also applicable to the maximum rates, such as the peaks in DSC curves, because the conversions at the maximum rates are equal to each other, as is shown in Eq. 39. The above procedure to estimate the activation energy is similar to, but somewhat different in its coefficient from, so-called "modified Ozawa plot" proposed by Matusita and Sakka,7) and it is essentially the same as the procedure for usual chemical reactions.8)

By applying rougher approximation, *i.e.*, Eq. 36, we get the next equations at a given conversion and also at the maximum rate; for the first model

$$\frac{\Delta E^m}{\phi_3{}^m\mathbf{R}^m}\left\{\exp\left(-\frac{\Delta E}{\mathbf{R}T}\right)\Big/\frac{\Delta E^2}{\mathbf{R}^2T^2}\right\}^m = \text{constant}, \quad (48)$$

and for the second model

$$\frac{\Delta E^m}{\phi_3{}^{m+1}\mathbf{R}^m}\left\{\exp\left(-\frac{\Delta E}{\mathbf{R}T}\right)\Big/\frac{\Delta E^2}{\mathbf{R}^2T^2}\right\}^m = \text{constant}. \quad (49)$$

Therefore, for the first model

$$\ln\frac{\phi_2}{T^2} + \frac{\Delta E}{\mathbf{R}T} = \text{constant}, \quad (50)$$

and for the second model

$$\ln\frac{\phi_3{}^{m+1}}{T^{2m}} + \frac{\Delta E}{\mathbf{R}T} = \text{constant}. \quad (51)$$

The activation energy can also be estimated by the similar plots of $\ln \phi_3/T^2$ or $\ln \phi_3{}^{m+1}/T^{2m}$ against the reciprocal absolute temperature. Kissinger plot mentioned in the introduction is the same plot as Eq. 50 applied to the maximum rate, but modification such as shown in Eq. 51 should be made. Moreover, these plots are applicable to a given conversion. Matusita and Sakka7) derived an equation similar to, but different in its exponent from, Eq. 51. These plots are not preferable to the plots by Eqs. 46 and 47, because they are based on the rough approximation of Eq. 36 and the terms are complicated, so that much error may be involved in actual applications. Recently, it was pointed out from experimental evaluation for usual chemical reactions that Kissinger plot has no practical advantages over Ozawa plot and that the conversion at the peak of heat-flux DSC curve is not practically a constant due to instrumental effect and heat transfer within the sample, while uniform temperature within the sample is implicitly assumed in all theoretical considerations.12)

When the linear plots obtained at different conversions are not parallel to each other and the activation energies estimated vary along the conversion, the observed process is inconsistent with the model from which the theory and the method are derived, and we should abandon the kinetic analysis. When we get the constant activation energy, we can calculate the reduced time at different conversions by using the activation energy and Eq. 26, so that we can draw the curve of the conversion versus the reduced time, which is the experimental master curve. Because the reduced time is proportional to the real time in isothermal cases and also equal to the real time at infinite temperature, the methods for analyzing isothermal data can be applied to this experimental master curve. For example, when we plot $\log(-\ln(1-C))$ against $\log \theta$, we get a linear line with the slope of m and, when we plot $-\ln(1-C)$ against θ^m, we get also a linear line. In both plots for the second model, both ϕ_1 and ϕ_2 should be constant and common, otherwise they should be reduced taking into account of their effect in Eqs. 14 and 30.

The linearity of these master lines can be used to ascertain the consistency between the observed process and the model on which the theory and the method are based. We can also calculate the reduced time for various temperature changes by using the activation energy, and, thus, we can predict the crystallization behavior for the various types of temperature changes.

Concluding Remarks

The nonisothermal kinetic models in this paper are those of the special cases dealt with in the previous paper.[5] However, because the random nucleation does not occur concurrently with the crystal growth in the present cases, the more generally applicable equations are derived here than in the previous paper. The relations described previously for the general model[5] are limited for the case of the linear cooling and heating. On the other hand, the relations applicable to various types of temperature changes are presented in the present paper.

The concept of the reduced time can be introduced in the more complicated process than the usual chemical reactions[8] and diffusions,[9] and it is also clearly shown that the concept of the reduced time is very useful and effective in nonisothermal kinetics. As is seen in Eqs. 14 and 15, the real time, t, in the isothermal kinetic equations can be replaced by the generalized time, *i.e.*, the reduced time, and this generalized nonisothermal kinetic equations are applicable both to nonisothermal cases and to isothermal cases, where θ is equal to $tf(T)$ and Z is replaced by Z_0.

The conversion at the maximum rate for the linearly heated process in which Arrhenius law holds is revealed to be constant even in the complicated processes such as the crystal growth, and it is interesting to note that this constancy is also found in the usual chemical reactions and diffusion in which Arrhenius law holds,[11] so that it seems to be generally true that the conversion at the maximum rate for the linear heating is constant for the process in which only a single unit process proceeds and Arrhenius law holds for the rate constant.

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