

KINETICS OF GROWTH FROM PRE-EXISTING SURFACE NUCLEI

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Isothermal and non-isothermal kinetics of three dimensional growth processes from nuclei pre-existing on surface of infinite plate specimen have been derived. Some useful and interesting relations have been found, and methods for kinetic analysis of experimental data are proposed.

Keywords: growth processes, isothermal growth, non-isothermal kinetics

Introduction

It is well known that growth processes from nuclei are observed in some solid reactions and crystallizations. For these processes, isothermal kinetics of growth from nuclei occurring randomly in bulk, for both of pre-existing nuclei and nuclei forming concurrently with growth, were investigated, and the isothermal kinetics had been established long time ago [1]. This kinetics theory was expanded to non-isothermal conditions by the present author [2–4], and the method has been applied to data obtained by constant rate cooling [2, 5, 6]. For solid reactions of inorganic substances the kinetics of this type was also applied and discussed [7, 8].

Growth processes from surface nuclei have also been often observed [7], but kinetics of surface nucleation for powdered sample was only dealt with theoretically [7] and rigorous theoretical considerations on kinetics of these processes have not been made. There are also two cases for surface nuclei; pre-existing nuclei and nuclei forming concurrently with growth, and geometries of the specimen have also influence on kinetics as well as dimension of the growth. In this paper three-dimensional growth processes from randomly pre-existing surface nuclei in an infinite plate specimen are theoretically considered, and fundamental relations are elucidated. The kinetic analysis methods for these processes are also considered by using the fundamental relations and described in this paper.

Theoretical considerations

Logics

For isothermal bulk nucleation and growth processes, useful and elegant theoretical considerations were made by Evans [9] by using Poisson's statistical dis-

tribution. In this theory an analogy was used between the processes under consideration and wave propagation on pond surface caused by rain. Random rain drops are compared to random nucleation, and wave propagation is compared to growth from the nuclei. However, difference is between them, because the wave propagation front can pass a particular point at multiple times but the growth front passes a particular point only once. Therefore, what we can do is as follows. Expectancy of number of waves passing over a particular point is first calculated, and then unconverted fraction, which is not passed over by the growth front, is obtained by applying Poisson's statistical distribution. This mathematical method is very useful and elegant, as it was used in non-isothermal crystallizations before [2], so that this method is also applied to the present problem, i.e., three-dimensional growth from randomly pre-existing surface nuclei in an infinite plate specimen.

Isothermal growth from nuclei on upper surface

Let us consider isothermal change first for convenience, and for the sake of simplicity nuclei are assumed pre-existing on the upper surface only (not on the lower surface). First let us consider expectancy of number of the fronts passing over a particular point, P , locating at depth of x from the surface. The expectancy and hence the conversion are dependent on the depth, x , so that distribution of unconverted fraction along the depth should be considered and then it is integrated to get the total average conversion of the specimen, $C(t)$, t being the time. Hereafter, the linear growth rate constant is expressed by G .

In order to get the above-mentioned distribution of the unconverted fraction, the specimen was divided into two layers comparing x with Gt . For x larger than

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Gt , the expectancy, $E(x, t)$ at the time, t , is zero, because the growth front has not yet reached the point. Namely,

$$E(x, t) = 0 \text{ for } x \geq Gt \quad (1)$$

The unconverted fraction at the point, P (or at the depth of x), $U(x, t)$, is also the unity.

$$U(x, t) = 1 \text{ for } x \geq Gt \quad (2)$$

For Gt larger than x , the growth front from nuclei can reach the particular point, P . The farthest point, Q , from which the front can reach the point, is located at Gt distance far from the particular point, P , and the point, Q , is on the surface. Thus, these nuclei, which can send the front to P by the time, t , occur within a circle; and its center, O , is the crossing point at which the perpendicular line from the point, P , crosses the surface, while the radius, r , is equal to the square root of $(G^2t^2 - x^2)$, because a triangle OPQ is a right-angled triangle. Then

$$E(x, t) = N\pi(G^2t^2 - x^2) \text{ for } x \leq Gt \quad (3)$$

where N is density of nuclei on the surface. The unconverted fraction, $U(x, t)$ can be calculated by applying Poisson's statistical distribution.

$$U(x, t) = \exp\{-E(x, t)\} \text{ for } x \leq Gt \quad (4)$$

Namely,

$$U(x, t) = \exp\{-\pi N(G^2t^2 - x^2)\} \text{ for } x \leq Gt \quad (5)$$

By integrating $U(x, t)$ from $x = 0$ to d , d being the thickness of the specimen, we can get total average unconverted fraction of the specimen.

When the growth front does not reach the rear surface ($Gt \leq d$),

$$1 - C(t) = [d - Gt + \int_0^{Gt} \exp\{-\pi N(G^2t^2 - x^2)\} dx] / d \quad (6)$$

$$= \{\psi_1(Gt) \exp(-\pi N G^2 t^2) + d - Gt\} / d \text{ for } Gt \leq d \quad (6')$$

where

$$\psi_1(u) = \int_0^u \exp(\pi N x^2) dx \quad (7)$$

After the growth front reaches the rear surface ($Gt \geq d$),

$$1 - C(t) = \left[\int_0^d \exp\{-\pi N(G^2t^2 - x^2)\} dx \right] / d \quad (8)$$

$$= \psi_1(d) \exp(-\pi N G^2 t^2) / d \text{ for } Gt \geq d \quad (8')$$

Isothermal growth from nuclei on both surfaces

For this growth process we can get fundamental equations by modifying the above equations. We should take into accounts of growth from the rear surface together with the growth from the upper surface, so that the specimen is divided into two plates of the same thickness. The above equations need modification. When the growth fronts do not reach the central plane of the specimen ($Gt \leq d/2$), Eqs (1) and (2) hold for $Gt \leq x \leq (d - Gt)$ (central part), and Eqs (3), (4) and (5) also hold for $x \leq Gt$ and $(d - x) \leq Gt$.

Therefore,

$$1 - C(t) = 2[d/2 - Gt + \int_0^{Gt} \exp\{-\pi N(G^2t^2 - x^2)\} dx] / d \quad (9)$$

for $Gt \leq d/2$

$$= 2\{\psi_1(Gt) \exp(-\pi N G^2 t^2) + d/2 - Gt\} / d \text{ for } Gt \leq d/2 \quad (9')$$

$$1 - C(t) = 2 \left[\int_0^{d/2} \exp\{-\pi N(G^2t^2 - x^2)\} dx \right] / d \quad (10)$$

for $Gt = d/2$

$$= 2\psi_1(d/2) \exp(-\pi N d^2/4) / d \text{ for } Gt = d/2 \quad (10')$$

When the growth fronts pass over the central plane at $d/2$, we should take into accounts of the growth front from both of the surfaces.

For the case Gt is larger than $d/2$ but smaller than d ($d/2 \leq Gt \leq d$), we should consider three layers. For the layer where x and $(d - x)$ are smaller than Gt ($d - Gt \leq x \leq Gt$, the central part of the specimen), the growth fronts from the both surfaces pass over, so that the two expectancies are added. Therefore

$$E(x, t) = \pi N[(G^2t^2 - x^2) + \{(G^2t^2 - (d - x)^2)\}] \quad (11)$$

$$U(x, t) = \exp[-\pi N(2G^2t^2 - 2x^2 + 2xd - d^2)] \quad (11')$$

for $(d - Gt) \leq x \leq Gt$

But for the other two layers, in the other word for the other range of x , the growth front reaches from only one surface, either from the lower surface or from the upper surface, so that Eqs (3), (4) and (5) hold.

Thus by integrating these three layers we have

$$1 - C(t) = 2\{\psi_1(d - Gt) + \psi_2(d - Gt)\} \exp(-2\pi N G^2 t^2) / d \quad (12)$$

for $d/2 \leq Gt \leq d$

where

$$\psi_2(u) = \int_u^{d/2} \exp\{\pi N(2x^2 - 2dx - d^2)\} dx \quad (13)$$

After the both growth fronts reach the surfaces ($d \leq Gt$), we get the following equation by integrating Eq.(11) from 0 to d .

$$1 - C(t) = 2\{\psi_2(0)\} \exp(-2\pi N G^2 t^2) / d \text{ for } d \leq Gt \quad (14)$$

Expansion to non-isothermal conditions

The quantity of temperature dependence is only the growth rate constant, G , in the processes under consideration, and hence the temperature dependences of the all above kinetics equations are governed by this single quantity, so that expansion of these isothermal equations to the non-isothermal equations can be done by simply replacing Gt by $G_0\theta$. The symbol, θ , expresses the generalized time [3] defined by the following equations.

$$G_0\theta = G_0 \int_0^t h(T) dt \quad (15)$$

where G_0 , T and $h(T)$ are constants, the temperature and a function expressing the temperature dependence of the growth rate constant, respectively. In other words, the growth distance of the front is Gt in the isothermal processes and it is $G_0\theta$ in the non-isothermal processes, as is seen in Eq. (15). The other quantities in the non-isothermal processes are all constant and quite the same as in the isothermal processes, and they are not influenced by the thermal history of the specimen under observation. This simple replacement is valid only for the pre-existing nuclei and not for the concurrently forming nuclei where the situation is quite different [4], because two temperature dependent quantities are involved, i.e., the growth rate constant and the nucleation rate constant.

Discussions

By insight into the above equations we can get some useful relations for kinetic analysis of thermo-analytical results of this type of processes. As easily seen, the thickness of the specimen has much influence on the process. This point should also be taken into accounts in application of the above results to the kinetic analysis.

Before the growth front reaches the rear surface (in the growth from the upper surface) or the central plane (in the growth from the both surfaces), the absolute value of the conversion is not dependent on the thickness (Eqs (6') and (10')). Therefore when we observe crystallization of this type for specimens of different thickness by differential scanning calorimetry, for instance, the heat evolution is the same irrespective of the difference in the thickness, if the area of the surfaces is equal to each other. The heat evolution for the thinner specimen deviates in the earlier stage from this same heat evolution, when the growth front reaches the rear surface or the central plane in this specimen. The thicker specimen deviates in the later stage. The situation is the same for mass loss in solid

reaction of this type. This is typical to the processes in which the processes start at the surface, and diffusion-controlling processes is another example. This behavior can be used for identification of the process and also for estimating the growth rate.

After the growth front reaches the rear surface or the central plane in the growth, this situation changes, and observed results are dependent on the thickness. Relations useful for kinetic analysis in this stage are Eqs (8') and (14). The following relation can be used for results of specimens of the same thickness. When $\ln\{1-C(t)\}$ is plotted vs. the square of the time, t^2 , we get a linear plot, but this linear plot has an intercept, so that the plots are similar to the Avrami plots but it is somewhat different because of the intercept. The following point is also another difference. The exponent 2 means the three-dimensional growth in this process, while the exponent 2 is the evidence for the two-dimensional growth for the growth by pre-existing bulk nuclei and for the one-dimensional growth by random bulk nucleation, as Avrami showed clearly [1].

For whole range of the process, Gt or $G_0\theta$ is a single quantity governing the rate of the process. Therefore, Friedman - Ozawa plot [10] (plot of logarithm of the rate of the process vs. the reciprocal absolute temperature at a given conversion) for results using the specimen of the same thickness gives a plot similarly to the Arrhenius plot, and the temperature dependence of the growth rate constant can be obtained. When the plot is linear, we can get the activation energy of the process.

Furthermore, Ozawa - Flynn - Wall plot [11, 12] (plot of logarithm of the heating rate vs. the reciprocal absolute temperature at a given conversion) and Kissinger - Sunose - Akahira plot [13, 14] (plot of logarithm of the heating rate by the square of the absolute temperature vs. the reciprocal absolute temperature at a given conversion) can also be applied, but only for results obtained by heating and for the process of Arrhenius type temperature dependence. If the plot is not linear or if the obtained activation energy is dependent on the conversion, the process under observation is not the process in which a single elementary process is involved and the temperature dependence of the rate constant is not the Arrhenius type.

If the temperature dependence, especially the activation energy, can be elucidated, we can get an experimental master curve by plotting the conversion vs. the generalized time [11]. See Eq. (15). Furthermore, when the generalized rate, i.e., $dC(t)/d\theta$, is plotted vs. the generalized time or $C(\theta)$, we can get another experimental master curve, where $dC(t)/d\theta$ is equal to $dC(t)/dt \exp(E_a/RT)$, E_a , R and T are the activation energy, the gas constant and the absolute temperature, respectively. If we could get a smooth mas-

ter curve with small scattering, it is an evidence for the facts that the model described in this paper is valid for the process under observation.

Because the above Evans' mathematical method is very elegant and useful, theoretical consideration for other types of growth process from surface nuclei can be made, similarly to the above-mentioned derivation.

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