

EXPERIMENTAL ANALYSIS OF NON-ISOTHERMAL TRANSFORMATIONS INVOLVING NUCLEATION AND GROWTH

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A critical examination is made of a recently suggested experimental technique which utilizes the Johnson-Mehl-Avrami transformation rate equation to describe non-isothermal transformations. It is shown that for transformations involving nucleation and growth the technique has limited applicability.

The general theory of transformation kinetics is largely confined to the description of isothermal transformation conditions. In large measure this is due to the mathematical simplicity of the description at constant temperature. However, there are many instances where the kinetic behavior of a system which is heated or cooled through the transformation region is of greater practical importance. Examples of such non-isothermal situations are as diverse as the heat treatment of metallic alloys and the melt spinning of polymer textile fibers. Under the proper experimental conditions the techniques of differential scanning calorimetry (DSC), differential thermal analysis (DTA), thermogravimetry (TG), etc. can be used to measure the time evolution of phase transformations under non-isothermal conditions. Generally, the experimental results of such thermoanalytical techniques are analyzed in terms of the formalism developed theoretically for isothermal conditions. In many instances this can be done successfully. However, in the case of transformations involving nucleation and growth it has been incorrectly asserted that the isothermal Johnson-Mehl-Avrami transformation rate equation can be applied without qualification to experimental results obtained under non-isothermal conditions. This paper is an attempt to clarify the limitations of employing the isothermal formalism in treating non-isothermal transformations involving nucleation and growth.

Isothermal transformation conditions

The problem of describing non-isothermal transformation kinetics is perhaps best approached by first outlining the formalism used to describe isothermal reaction conditions. There are several reasons for this assertion. The mathematical description of the isothermal theory of nucleation and growth is tractable and well developed in the literature. Most of the literature dealing with non-isothermal transformation kinetics is based at least in part on the formalism of the description

of isothermal transformations. The errors in the literature indicate that the general framework of the classical theory of nucleation and growth is not well understood by those adapting it for analysis of non-isothermal transformations. For these reasons and for the purposes of further discussions, a brief outline of the salient elements of the formal theory of transformation kinetics follows.

The concepts which underlie the theoretical description of phase transformations involving nucleation and growth were originally set forth by Volmer and Weber [1], Becker and Doring [2], Johnson and Mehl [3] and Avrami [4]. A comprehensive overview of the literature in this area has been given by Christian [5]. For the purposes of this paper it will be sufficient to consider the simplest type of growth. In particular consider the transformation kinetics of a system which demonstrates homogeneous (random) nucleation, and which has the growth rate of the product phase controlled by processes at the interface between the parent and product phases. In this instance the fraction of the product phase, x , which has formed at some time, t , is given by the well known result [4, 5]:

$$x(t) = 1 - \exp \left[- \int_0^t v(t, \tau) I(\tau) d\tau \right] \quad (1)$$

where $I(\tau)$ is the nucleation rate at time τ , and is in general a rapidly varying function of temperature; $v(t, \tau)$ is the volume of a particle of the product phase at time t and which started growth (by nucleation) at time τ .

Equation (1) holds for non-isothermal as well as isothermal transformation conditions. If it is assumed that the growth of the product phase is confined to m dimensions with identical growth rates in each of the m dimensions, then Eq. (1) can be rewritten as:

$$x(t) = 1 - \exp \left[- \int_0^t g [R(t) - R(\tau)]^m I(\tau) d\tau \right] \quad (2)$$

where g is a constant geometrical growth factor and $R(t) = \int_0^t Y(\theta) d\theta$ and where $Y(\theta)$ is the growth rate (velocity) along any one of the m growth directions at time θ and is in general a function of temperature.

Under isothermal conditions it can be assumed that the growth rate, Y [5, 6], and the homogeneous nucleation rate, I [5], will be constant. Equation (2) then reduces to:

$$x(t) = 1 - \exp \left[- \frac{Y^m I t^{m+1}}{4} \right] \quad (3)$$

Equation (3) is known as the Johnson-Mehl-Avrami equation, and is usually written in the form:

$$x(t) = 1 - \exp [-kt^n] \quad (4)$$

where k and n represent constants with respect to time at constant temperature.

Table 1

A summary of the values of n found under various transformation conditions after Christian [5]

Values of n in kinetic law $x(t) = 1 - \exp(-kt^n)$

(I) Polymorphic changes, discontinuous precipitation, eutectoid reactions, interface controlled growth, etc.

Transformation conditions	n
Increasing nucleation rate	> 4
Constant nucleation rate	4
Decreasing nucleation rate	3-4
Zero nucleation rate (saturation of point sites)	3
Grain edge nucleation after saturation	2
Grain boundary nucleation after saturation	1

(II) Diffusion controlled growth

Transformation conditions	n
All shapes growing from small dimensions, increasing nucleation rate	$> 2\frac{1}{2}$
All shapes growing from small dimensions, constant nucleation rate	$2\frac{1}{2}$
All shapes growing from small dimensions, decreasing nucleation rate	$1\frac{1}{2} - 2\frac{1}{2}$
All shapes growing from small dimensions, zero nucleation rate	$1\frac{1}{2}$
Growth of particles of appreciable initial volume	$1 - 1\frac{1}{2}$
Needles and plates of finite long dimensions, small in comparison with their separation	1
Thickening of long cylinders (needles) (e.g., after complete end impingement)	1
Thickening of very large plates (e.g., after complete edge impingement)	$\frac{1}{2}$
Precipitation on dislocations (very early stages)	$\sim 2/3$

Under isothermal conditions, an exponential growth law of the form of Eq. (4) can be used to describe the transformation kinetics of many transformations when the growth rate is constant and it can also be used as an approximation for the early stages of diffusion controlled growth [5]. This, of course, requires the proper choice of k and n . Table 1 summarizes the values of n found under various transformation conditions; but it must be emphasized that this tabulation is in no way complete or unique. Additional information (other than just the value of n) is necessary in order to delineate the physical processes which govern a particular transformation. This limitation has not been emphasized in some of the recent literature [7-9].

The isothermal transformation rate, $\frac{dx(t)}{dt}$, can be easily determined from Eq. (4) by differentiating with respect to time.

$$\frac{dx}{dt} = knt^{n-1} \exp[-kt^n]. \quad (5)$$

Because of the explicit relation between x and t given by Eq (4), Eq (5) can be rewritten equivalently as:

$$\frac{dx}{dt} = nk^{\frac{1}{n}}(1-x) \left[\ln \left(\frac{1}{1-x} \right) \right]^{\frac{n-1}{n}} \quad (6)$$

where k , it should be remembered, is a function of temperature.

Equation (6) is sometimes referred to as the Johnson–Mehl–Avrami transformation rate equation. Thus, it can be seen that Eq. (6) clearly indicates that under isothermal conditions there is a unique relationship between the fraction transformed, x , and the transformation rate, $\frac{dx(t)}{dt}$.

Non-isothermal transformation conditions

Recently Eq. (6) has been applied to the analysis of non-isothermal transformations [7–12]. In view of the preceding development its applicability should be questioned. Under non-isothermal conditions both Y , the growth rate, and I , the nucleation rate, are no longer constant during the transformation. In general Y and I are rapidly varying functions of temperature and in principle their functional dependence on temperature is quite different. Thus, Eq. (4) and therefore Eq. (6) will not follow from Eq. (2).

The fact that Eq. (6) cannot be correctly applied to non-isothermal transformations involving nucleation and growth can be seen from the following heuristic argument. The simplest non-isothermal treatment is one involving partial isothermal transformations at two different temperatures. Consider the crystallization of two identical pure liquid (one component) systems by homogeneous nucleation and growth. Under isothermal conditions such a system would comply with all the assumptions used in the development of Eqs (3) and (4) above. Let system 1 be severely undercooled below its melting point to temperature, T_1 , and crystallized isothermally until a fraction, x_0 , has transformed. Under these conditions one could expect a high nucleation rate and a slow growth rate [5]. Thus the transformed fraction, x_0 , could be characterized by relatively numerous crystals but small crystal size. Let system 2 be only slightly undercooled to temperature, T_2 , and crystallized isothermally until a fraction, x_0 , has transformed. In this case the nucleation rate could be expected to be low and the growth rate high [5]. The transformed fraction, x_0 , of system 2 would be characterized by relatively larger average crystal size and a smaller number of crystals than in system 1. If systems 1 and 2 with transformed fractions, x_0 are then brought to a common temperature, T , and allowed to continue transforming isothermally, it is obvious that system 1 will have the higher transformation rate because of the higher surface area to volume ratio in its transformed fraction, x_0 . Equation (6) would erroneously predict identical transformation rates. Clearly, the transformation rate for systems demonstrating nucleation and growth are dependent on thermal history as well as the state variables of fraction transformed, x , and temperature, T .

Phrased somewhat differently, Eq. (1) is dependent on the path of integration in temperature-time space. The reason for this dependence is the independent variation of the rate at which particles are created (nucleated) and the rate at which they grow.

There are, however, certain special cases when the transformation rate equation (Eq. 6) does correctly describe transformations involving nucleation and growth. In a different context such transformations were termed isokinetic by Avrami. Avrami [4] noted that when the nucleation rate, I , was proportional to the growth rate, Y , the transformation would take the same course, except for time scale, regardless of the transformation path. While this is true, it does not represent a condition that one would expect to find in light of the current models used to describe nucleation and growth. Cahn [13] identified a special case of greater physical significance. When all nucleation takes place early in the course of a transformation, it is said to have undergone site saturation. There are a variety of important situations where one might expect this condition to be obtained [5]. In this case, provided that the growth rate is dependent only on temperature, the transformation will be identical at all temperatures; the temperature will control only the rate at which the transformation evolves. In the two cases cited above the transformation rate will be a unique function of x , and T . Cahn [13] has shown that in general when $\frac{dx}{dt}$ is given by a unique function of x and T , the transformation will be isokinetic. It should be emphasized that if such a function exists, it must be the same for isothermal and non-isothermal transformation conditions, and therefore, the Johnson–Mehl–Avrami transformation rate equation Eq. (6) will hold.

Conclusion

Thus, the technique of non-isothermal analysis outlined by Sestak [7, 10, 11] and others [8, 9, 12] using the Johnson–Mehl–Avrami transformation rate equation can only be rigorously applied to transformations involving nucleation and growth in a limited number of special cases. The special case of site saturation is one of considerable importance for which this method of analysis is correct. Following the methods used to develop Eq. (4), it is possible to show that only the functional dependence of growth rate on temperature and the value of n can be determined. In this case the temperature dependence of the nucleation rate cannot be elucidated.

Ozawa [14] has outlined another method of non-isothermal analysis which holds for any type of transformation involving nucleation and growth. Using Ozawa's method, it is possible to directly determine the value of n by measuring the transformation behavior as a function of constant cooling or heating rates. In the general case of simultaneous nucleation and growth, however, this method likewise cannot be used to determine the functional dependencies of nucleation rate or growth rate on temperature.

Experimentally, the time evolution of a phase transformation is usually determined by measuring $x(t)$, $\frac{dx(t)}{dt}$ or some other physical quantity which is proportional to $x(t)$ or $\frac{dx(t)}{dt}$. In terms of the theoretical model discussed above, this amounts to a direct measurement of Eq. (1) or its first time derivative. Interpretation of such measurements under non-isothermal conditions is difficult if the integration involves the product of two non-constant terms. Their behaviour cannot in principle be separated. Of course, if for some reason the probable functional dependence of I and Y are known, their validity may be tested by integrating Eq. (1) and comparing the result to the experimentally observed behaviour. For instance, this analysis technique might be used to test the validity of isothermally determined parameters in temperature ranges not accessible to isothermal analysis. However, there appears to be no systematic way by which the measurement of x or $\frac{dx}{dt}$ under non-isothermal conditions can lead to the direct determination of the nucleation rate and the growth rate as functions of temperature.

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RÉSUMÉ — On examine d'une manière critique une technique expérimentale récemment proposée qui utilise l'équation des vitesses de transformation proposée par Johnson-Mehl-Avrami pour décrire les transformations non-isothermes. On montre que la technique n'a qu'une applicabilité limitée pour les transformations qui s'effectuent par nucléation et croissance.

ZUSAMMENFASSUNG — Eine kritische Prüfung der neulich vorgeschlagenen Versuchstechnik, welche die Johnson-Mehl-Avrami Transformations-Geschwindigkeitsgleichung zur Beschreibung nichtisothermer Umwandlungen einsetzt, wird vorgenommen. Es wird gezeigt, daß die Methode für Umwandlungen mit Kernbildung und Wachstum nur eine geringe Einsatzfähigkeit besitzt.

Резюме — Проведено критическое исследование недавно предложенного экспериментального метода, в котором для описания неизотермических превращений используется уравнение скорости превращения Джонсона—Мехл—Аврами. Показано, что этот метод имеет ограниченное применение для превращений, включающих образование центров кристаллизации и их роста.