ELSEVIER

Thermochimica Acta 291 (1997) 81–84

thermochimica acta

Application of thermal analysis methods to nucleation and growth transformation kinetics

J. Baram*, V. Erukhimovitch

Department of Materials Engineering , Ben-Gurion University, Beer-Sheva, 84105, Israel

Received 23 May 1996; received in revised form 30 September 1996; accepted 8 October 1996

Abstract

The applicability of popular thermal analysis methods like the one proposed by Ozawa and Kissinger, or the one derived from the Avrami kinetic formalism, to non-isothermal nucleation and growth transformation kinetics, is reassessed. Restrictions and limitations of both techniques are reevaluated, in order to clarify when and under which transformation conditions is each method justified. © 1997 Elsevier Science B.V.

Keywords: Activation energy; Avrami formalism; Nucleation and growth phase transformation; Ozawa and Kissinger techniques; Thermal analysis

1. Introduction

Differential scanning calorimetry (DSC) is a widely used experimental technique for the study of the kinetics of non-isothermal nucleation and growth transformations. The analysis of DSC results is performed by popular thermal analysis methods, as proposed by Ozawa [1], primarily for the kinetic analysis of polymer crystallization, and by Kissinger [2], originally developed for solid $\Rightarrow$ solid + gas type solid-state reactions. Derived relationships between the logarithm of the heating rate and the (inverse) temperature at the maximum of the reaction, as interpreted from a DSC trace, enables the evaluation of kinetic parameters, such as activation energy, transformation enthalpy and reaction order.

The applicability of these methods to nucleation and growth transformations such as crystallization of glassy metals, for example, has however been questioned in the past [3–5].

For isothermal transformations, kinetic analyses are performed for years by applying the Kolmogorov–Johnson–Mehl–Avrami (KJMA, or Avrami) formalism [6–9]. This method is based on an integral expression for the fraction transformed, which is then differentiated twice with respect to time for the derivation of the kinetic parameters [10–12].

The validity of applying the Avrami rate equation to non-isothermal transformation kinetics has been examined by Henderson [13]. He has shown that such a procedure can be used only under some specific restrictions, namely:

1. The growth rate of the new phase depends only on temperature, not explicitly on time.

---

*Corresponding author. Tel.: 972 7 6461 474; fax: 972 7 6101714 or 461474; e-mail: jbaram@bgumail.bgu.ac.il.

PII S0040-6031(96)03095-X

2. The transformation rate does not depend on thermal history.
3. Nucleation occurs at randomly dispersed second-phase particles.

These restrictions limit the applicability of the KJMA formalism to so-called 'site saturation' transformations [14] only, where nucleation takes place at the very start of the transformation, and the nucleation rate is zero thereafter. Under these restrictions, Henderson [13] has shown that the Kissinger method and the Avrami rate equation are equivalent, thus justifying the use of the thermal analysis methods to the study of non-isothermal nucleation and growth transformation kinetics, including derivation of activation energies and reaction orders.

Despite the abundant literature on the subject, it seems that there is still some confusion on the proper use of thermal analysis techniques in transformation kinetics studies. The purpose of this paper is to start with the basic non-isothermal kinetic equation, and then derive the appropriate relationship to be used for the estimation of the thermodynamic parameters.

2. Theoretical

Under isothermal conditions, the nucleation and growth transformation kinetics are described by the well-known Avrami (KJMA) equation [6–8]:

$$\xi(T,t) = 1 - \exp[-K(T)t^n] \tag{1}$$

Eq. (1) is a true kinetic equation. The rate of evolution of the product phase can be expressed at a product of two functions, namely temperature and fraction transformed:

$$\begin{aligned}\frac{d\xi(T,t)}{\mathrm{d}t} &= nK(T)[1-\xi(T,t)] \\ &\quad\times\left\{\ln\left[\frac{1}{1-\xi(T,t)}\right]\right\}^{\frac{n-1}{n}} \\ &\equiv K(T)f[\xi(T,t)]\end{aligned} \tag{2}$$

$K(T)$ is therefore legitimately interpreted as a function of an activation energy E, and is represented by an exponential, Arrhenius-type, function of temperature [15]:

$$K(T) = K_0\exp\left[-\frac{E}{RT}\right] \tag{3}$$

where R is the gas constant and K_0 a pre-exponential factor. The value of $n(0.5 < n < 4)$ in the kinetic law is an indication of the nature of the transformation [9]. The activation energy E includes the contribution of the energies needed to activate both the nucleation (E_n) and growth (E_g).

Eq. (1) is the kinetic law that is commonly used to interpret experimental results obtained by non-isothermal analysis techniques, such as DSC, and to calculate the activation energy of the rate controlling transformation. Relationships have been derived for the determination of activation energies from non-isothermal data by Ozawa [1] and Kissinger [2] from DSC traces. Both methods are based on the fundamental requirement (a), namely the rate of fraction transformed per unit time, $(\mathrm{d}\xi(T,t))/\mathrm{d}t$ is the product of 2 separable functions of temperature T and of fraction transformed $\xi(T,t)$:

$$\frac{\mathrm{d}\xi(T,t)}{\mathrm{d}t} = g(T)f(\xi) \tag{4}$$

Two other requirements are: (b) $f(\xi)$ is independent of the heating rate, and (c) the temperature dependence of the rate of transformation $g(T)$ is exponential, i.e. Arrhenius-type (or Vogel–Fulcher) [16].

Henderson [13] has shown that Eq. (1) can be applied to non-isothermal kinetics *only in the case of site saturation*, and even then is restricted to linear growth kinetics, i.e. to a temperature (and not time) dependent growth rate. However, in a non-isothermal nucleation and growth solid-state transformation, the evolution of the volume fraction $\xi(T,t)$ of the new phase with time t and temperature $T(t)$ is:

$$\xi(T,t) = 1 - \exp\left[-g\int_0^t I(T(t'))\left\{\int_{t'}^t G(T(\tau))\mathrm{d}\tau\right\}^n \mathrm{d}t'\right] \tag{5}$$

$I(T(t))$ and $G(T(t))$ are the nucleation and the growth rates, respectively, and g is a geometrical factor that depends on the dimensionality of growth [6–8]. For an interface-controlled growth, n is an integer; for a diffusion-controlled growth n may also take half-integer values [9].

In the particular so-called 'site saturation' [14] case, when heterogeneous nucleation takes place at randomly distributed pre-existing nucleation sites N_0, the nucleation rate being therefore zero, Eq. (5) is reduced to:

$$\xi(T,t) = 1 - \exp\left[-gN_0\left\{\int_0^t G(T(\tau))\mathrm{d}\tau\right\}^n\right] \tag{6}$$

Under the restrictions mentioned by Henderson [13] and assuming and Arrhenius-type growth rate, Eq. (6) can be written as:

$$\xi(T,t) = 1 - \exp\left[-gN_0\left\{\bar{\beta}\int_{T_{\text{initial}}}^{T_{\text{final}}} \exp\left[-\frac{E}{RT(t)}\mathrm{d}T\right]\right\}^n\right] \tag{7}$$

In that specific case, E may be written as E_g, the activation energy for growth solely. Eq. (7) is the kinetic law which shall be used now, instead of Eq. (1), for the interpretation of the thermal analysis methods.

The use of the non-isothermal Eq. (7) in the Ozawa or Kissinger thermal analyses methods, and the consecutive derivation of activation energies, is allowed if and only if it is a true kinetic equation with exponential temperature dependence of the rate [16]. This is however *not* the case, as shown below.

If β is the *constant* heating rate practiced in DSC, then Eq. (7) can be written as:

$$\xi(T) = 1 - \exp\left[-\frac{gN_0K_0^n}{\beta^n} \times \left\{\int_{T_{\text{initial}}}^{T_{\text{final}}} \exp\left[-\frac{E}{RT}\right]\mathrm{d}T\right\}^n\right] \tag{8}$$

A number of numerical approximations to the exponential integral have been proposed in the literature [14], the most widely used being Doyle's relationship [17]:

$$\ln\int_y^\infty \frac{\exp[-y]}{y^2}\mathrm{d}y = -5.33 - 1.052y \tag{9}$$

Rewriting the variable $y = E/RT$, and introducing the numerical constant C, Eq. (8) reads:

$$\xi(T) = 1 - \exp\left[-\frac{C}{\beta^n}\exp\left[-1.052\frac{nE}{RT}\right]\right] \tag{10}$$

The time derivative of Eq. (10) is:

$$\frac{\mathrm{d}\xi(T,t)}{\mathrm{d}t} = (1 - \xi(T(t)))\frac{C}{\beta^n} \times \exp\left[-1.052\frac{nE}{RT(t)}\right]\frac{1}{T^2(t)} \tag{11}$$

In the non-isothermal Eq. (11) the aforementioned requirements (a) and (b) are fulfilled. The temperature dependence of the rate of transformation is however not experimental, Arrhenius-type. Requirement (*c*) is not fulfilled.

The activation energy of a transformation E, can be evaluated by measuring the temperature T_m, at the point of maximum reaction rate, while heating at a constant rate β. In a DSC experiment, the maxima in reaction rate coincides with the exothermic peak associated with the transformation in the DSC trace. Measuring the peak temperatures at varying heating rates and determining the slope of a plot of either $\ln\beta$ (Ozawa method [1]), or β/T_m^2 Kissinger method [2]) against $1/T_m^2$ enables the evaluation of the activation energy [13]. The same procedure is now used. Taking an additional time derivative of Eq. (11), and equating it to zero to find the maximum, yields, after some algebraic manipulations Eq. (12), as follows:

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\mathrm{d}\xi(T,t)}{\mathrm{d}t}\right) &= \\ &\frac{C}{\beta^{n-1}}(1 - \xi(T(t))) \times \exp\left[-1.052\frac{nE}{RT(t)}\right]\frac{1}{T^3(t)} \\ &\times\left\{-\frac{C}{\beta^{n-1}}\exp\left[-1.052\frac{nE}{RT(t)}\right]\right. \\ &\left.\times\frac{1}{T(t)} + 1.052\frac{nE\beta}{RT(t)} - 2\beta\right\}\end{aligned} \tag{12}$$

Eq. (12) is zero, when $T = T_m$, thus resulting in the following relationship between the heating rate and the peak temperature:

$$\beta\left\{1.052\frac{nE}{RT_m} - 2\right\} = \frac{C}{\beta^{n-1}}\frac{1}{T_m} \times \exp\left[-1.052\frac{nE}{RT_m}\right] \tag{13}$$

If $1.052(nE/RT_m) \gg 2$, as it generally occurs [13], one finally gets the relationship between the heating rates and the peak temperatures for non-isothermal kinetics, for plotting the straight line, whose slope is the activation energy E divided by R:

$$\ln\beta + C' = -1.052\frac{E}{RT_m} \qquad (14)$$

which is analogue to the relationship obtained by Ozawa [1], *not* to the one proposed by Kissinger [2] and Henderson [13]. It should be reminded that the use of Eq. (14) for the estimation of activation energies is anyway applicable only to non-isothermal, site saturation, heterogeneously nucleated transformations.

It seems that the confusion that has arisen during the years about the use of the Kissinger method, or the Avrami formalism, to non-isothermal nucleation and growth transformation kinetics lies in the way the basic Eq. (6) is differentiated against time for obtaining a rate equation. As there is an implicit time dependence of the growth function G, the differentiation of the integral on $G(T(t))$ is not straightforward. In fact, the often used relation:

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_0^t G(T(t))\mathrm{d}\tau = G(T(t)) \qquad (15)$$

is incorrect. If Eq. (15) is used, the time derivation of Eq. (3) results in an (incorrect) true kinetic equation, with an exponential dependence of the temperature [18]:

$$\frac{\mathrm{d}\xi(T,t)}{\mathrm{d}t} = (1-\xi(T(t)))n \times \{-\ln(1-\xi(T(t)))\}^{1-\frac{1}{n}}K_0 \exp\left[-\frac{E}{RT(t)}\right] \qquad (16)$$

Of course, if the mathematically incorrect Eq. (16) is used instead of Eq. (11), the derived thermodynamic parameters of the considered transformation, are not necessarily the same.

It has, however, already been judiciously mentioned [19] that "Two different phenomenological theories are widely (and apparently indiscriminately) used for the determination of ...kinetic parameters: the Kissinger [2] and the Avrami [7] theories. ... Although ... they lead to mathematically different expressions, the calculated effective activation energies for crystallization seem very similar." It is then concluded [19] that "it is not possible to discriminate between the two [Avrami and Kissinger] theories, ... as far as the results of the linear regression [practiced in both cases] are quite similar and the deduced activation energy [for the same transformation] differs only a few percent" [19].

The discrimination between the two theories can probably be made only through mathematical arguments, as has been done in the present paper. Anyway, the correct use of any thermal analysis method must conform to the nature of the phase transformation, which is itself not always known a priori. The relation between experimental and physical conditions and the applicability of a specific kinetic equation (or thermal analysis method) is currently under investigation [20].

References

[1] T. Ozawa, Bull. Chem. Soc. Japan, 38 (1965) 1881; J. Therm. Analysis, 2 (1970) 301.
[2] H.E. Kissinger, Analyt. Chem., 29 (1957) 1702; J. Res. Natn. Bur. Std., 57 (1957) 217.
[3] W.W. Wendlant, Thermal Methods of Analysis, 2nd edn., Wiley, New York (1974) ; J.H. Sharp, in R.C. Mackenzie (Ed.), Differential Thermal Analysis, Academic Press, New York, (1972) Vol. 2 .
[4] K. Matusita, T. Komatsu and R. Yokota, J. Mat. Sci. 19 (1984) 291.
[5] L.V. Meisel and P.J. Cote, Acta metall. 31 (1983) 1053.
[6] A.E. Kolmogorov, Akad. Nauk. SSSR, IZV, Ser. Mat. 1 (1937) 355.
[7] M. Avrami, J. Chem. Phys., 7 (1939) 1103; 8 (1940) 212; 9 (1941) 177.
[8] W.A. Johnson and R.F. Mehl, Trans. Am. Inst. Min. Engrs. 135 (1939) 416.
[9] J.W. Christian, "The Theory of Transformations in Metals and Alloys", 2nd edn., Pergamon, New York (1975).
[10] F. Skvara and V. Satava, J. Therm. Analysis 2 (1970) 325.
[11] J. Sestak, Thermochim. Acta 3 (1971) 1.
[12] J. Sestak, Phys. Chem. Glasses 6 (1974) 137.
[13] D.W. Henderson, J. Non-Crystalline Sol. 30 (1979) 301.
[14] J.W. Cahn, Acta Met., 4 (1956) 449; Acta Met., 4 (1956) 573.
[15] R.V. Muraleedharan, Journal of Thermal Analysis 37 (1991) 2729.
[16] J.W. Graydon, S.J. Thorpe and D.W. Kirk, Acta metall. mater. 42 (1994) 3163.
[17] C.D. Doyle, J. Appl. Polym. Sci. 6 (1962) 639.
[18] T. Kemeny and L. Granasy, J. Non-Crystalline Sol. 68 (1984) 193.
[19] P. Altuzar and R. Valenzuela, Materials Letters 11 (1991) 101.
[20] V. Erukhimovitch and J. Baram, work in progress..