Thermochimica Acta, 114 (1987) 201–208
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

ON THE KINETIC PARAMETERS FROM NON-ISOTHERMAL DATA: MATHEMATICAL CONSIDERATIONS

J.A. CUSIDÓ *, J. PUIGDOMÈNECH * and C. BONET **

* *Departament de Física, E.T.S.A.Vs., Universitat Politècnica de Catalunya, Apartat de Correus 508, Terrassa, Barcelona (Spain);* ** *Departament de Matemàtiques, E.T.S.E.I.B., Universitat Politècnica de Catalunya, Diagonal 647, 08028 Barcelona (Spain)*

(Received 29 July 1986)

ABSTRACT

The kinetic parameters determination of the crystallization of a disordered solid solution subjected to non-isothermal treatments is often considered using a large variety of physical models. Some authors propose the use of Johnson–Mehl–Avrami's classic expression which corresponds to both isothermal and non-isothermal kinetic parameters, according to experimental results.

In this paper we carry out research, starting from the generalized model most widely used by the non-isothermal problem, in which we prove the validity of Johnson–Mehl–Avrami's expression.

1. INTRODUCTION

Amorphous solid solutions can be considered as a state chemically and topologically homogeneous from which it is possible to study the different crystalline phases, the morphologies and the distributions which can be obtained from controlled kinetics of crystallization (e.g. phase apparition and grain size). It is for this reason that it is interesting to study the kinetics of crystallization in non-isothermal processes.

There is a substantial number of expressions which have been generated lately to determine the kinetic parameters which characterize such types of processes, and which we are going to summarize now.

The essential equation used to analyse the kinetics of crystallization is based on the relation [1]:

$$\frac{d\alpha}{dt} = f(\alpha)K[T(t)] \tag{1}$$

where α is the fraction of crystallized volume, and $f(\alpha)$ is the characteristic function of the reaction mechanism, taking the following values when nucleation and growing processes are considered [1]:

$$f(\alpha) = (1-\alpha)^n \tag{2}$$

where n is the order of the dimensionality of the reaction, which varies between 1 and 3. When the reaction is due to a diffusion process, the function becomes [1]:

$$f(\alpha) = \frac{1}{2\alpha} \tag{3}$$

The term $K[T(t)]$ in most of the proposed models is the well-known Arrhenius expression:

$$K[T(t)] = A \exp(-E/\mathrm{R}T(t)) \tag{4}$$

where A is the so-called pre-exponential term, E is the activation energy of the process, T the absolute temperature and R the ideal gas constant.

Expression (4), as it takes non-isothermal conditions into account, becomes a function as temperature is time dependent: $T(t)$. In order to solve this difficulty, which, in general, represents the mathematical resolution of expressions of this type, it has been proposed to consider alternatively [2]:

$$K[T(t)] = AT^m \exp(-E/\mathrm{R}T) \tag{5}$$

where m = integer or semi-integer values. This expression is a generalization of the temperature dependence of the rate constant.

On the other hand, the fact that the crystallization rate is only important when the temperature is near the glass temperature, T_g, makes some authors propose the use of alternative expressions, such as [3,4]:

$$K[T(t)] = A \exp\left(-E/k'(T - T_g)\right) \tag{6}$$

which is called Fulcher's law.

The solution to equation (1) in isothermal conditions, by means of equations (2) and (4), takes us to the well-known Johnson–Mehl–Avrami expression [5]:

$$\alpha = 1 - \exp\left[-(kt)^n\right] \tag{7}$$

With the same expressions, and for the non-isothermal treatment cases of linear type, $T = T_0 + \beta t$, De Bruijn et al. [6] have published a correct mathematical treatment, since there are a substantial number of papers [1,7,8] where the second term in the following expression is not taken into account:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \left(\frac{\partial\alpha}{\partial t}\right)_T + \left(\frac{\partial\alpha}{\partial T}\right)_t \left(\frac{\partial T}{\partial t}\right)_\alpha \tag{8}$$

which it should be when the temperature dependence of the crystallized volume fraction is considered: $\alpha = \alpha(t, T)$. In the crystallization of the metallic glasses, it is assumed that the appearance of one or more crystalline phases is a temperature function, while the growth of these phases is a time function.

When equation (8) is taken into consideration, in equation (1) together with equations (2) and (3), with (4), (5) or (6), the expressions become fairly complicated when investigating approximate possible solutions, but the task can be made easier with the help of:

(a) Special laboratory techniques, such as thermal analysis at constant rate [9], and the integration through small increments of α, t, T, etc. [10];

(b) Neglecting the second term in equation (8), in which circumstance Criado [9] has shown that, by means of equations (2) and (4), and in certain conditions, one can obtain identical expressions as if the neglected term had been considered.

On the other hand, if the expression which has to describe the kinetics of crystallization does not correspond to a state function an expression which considers the fraction of the crystallized volume and its dependence on the thermal history at which the material has been subjected to is needed. Such an expression has been recently proposed [11]:

$$\alpha(t, T) = 1 - \exp\left[-\left(K\int_0^t (T - T_g)\mathrm{d}t\right)^n\right] \tag{9}$$

the values of the kinetic parameters obtained through expression (9) are in accordance with those obtained with the same material by other methods.

In short, the kinetic parameters determination, as a consequence of the integration of equation (1) with the consideration of (2), (4) and (8) leads us to complicated expressions completely different to the classic Johnson–Mehl–Avrami expression (7).

On the other hand, the analysis of a non-isothermal reaction from generalized expressions does not supply, decisively, the correct mechanism of the reaction, it is therefore required to establish the value of n from isothermal experiments: only after this is it possible to obtain the correct value of the activation energy, E, in the non-isothermal case [4].

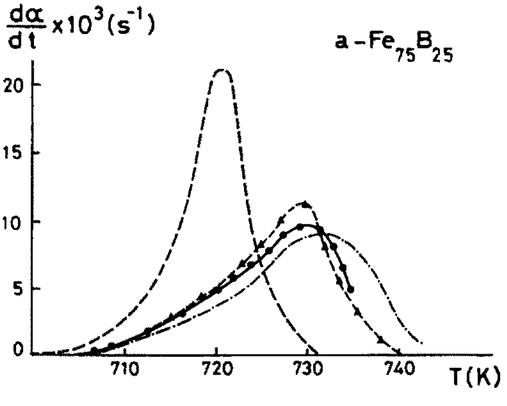

Fig. 1. The measured crystallization rate (●——●) is compared with that calculated from [6] (— — —), [8] (–·–) and isothermal expression (7) (▲——▲). (Adapted from [12].)

For these reasons, and as the agreement of the experimental results with the values calculated using the classical model is reasonable, some authors suggest that there is no reason for which any correction should have been made in the treatment of the data obtained for non-isothermal kinetics of crystallization [12,13] (Fig. 1). Thus, kinetic parameters (n, E) are obtained experimentally [14,15]. Mathematically speaking, this means that the fraction of crystallized volume does not depend on the thermal history of the process at which the sample is subjected to. Thus, it is considered that a general correcting term does not exist in the classic expression of the kinetics of crystallization described by equation (7).

The aim of this paper is to study the differential equation which describes the kinetics of crystallization in a generalized model in order to substantiate these observations.

2. MATHEMATICAL APPROACH

2.1. The model

We consider a disordered solid solution in which the hypotheses for the kinetic crystallization mechanisms from the glass state are:

(a) Nucleation is randomly distributed;

(b) The growth rate of the new phase depends only on temperature but not on time.

We consider that the increment rate of the crystallized volume is given by equation (1), and that the characteristic function of the reaction mechanism, $\mathrm{f}(\alpha)$, is

$$\mathrm{f}(\alpha) = \exp\left(-K\alpha\left(T - T_{\mathrm{g}}\right)\right) \tag{10}$$

from which it is easily seen that it is a generalization of equation (2) by letting $n = 1$ (except for the multiplicative constant K). Due to the short interval between the glass transition and the glass temperatures, T_{c} and T_{g}, which is usual in metallic glasses, the independent characterization of the devitrification phenomenon used to be difficult for their distinction. For this reason we use the glass transition temperature, T_{g}, only.

Let us consider a process described by a linear evolution of temperature, $T = T_0 + \beta t$. Although this expression can be a simplification of the problem, some of its results can be considered valuable for general situations, as any treatment can approximate to expressions of such types at different intervals of time (Fig. 2).

Then, expression (1) is described by the differential equation:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \exp\left(-K\alpha\left(T_0 + \beta t - T_{\mathrm{g}}\right)\right) A \exp\left(-E/\mathrm{R}\left(T_0 + \beta t - T_{\mathrm{g}}\right)\right) \tag{11}$$

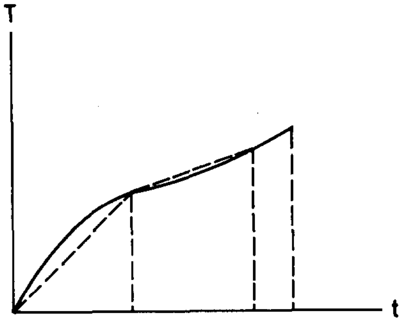

Fig. 2. Linear approximation of a non-isothermal process.

The initial condition which is needed to facilitate the solution of equation (11) is $\alpha(0) = 0$.

2.2. *Asymptotic solutions*

Let us change

$s = T_0 + \beta t - T_g$; $\beta' = K\beta$

$$\bar{\alpha} = (E/\mathrm{R})\alpha; \; \bar{s} = (\mathrm{R}/E)s \tag{12}$$

from where

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}(t) = \frac{\mathrm{d}\bar{\alpha}}{\mathrm{d}s}(s)\beta' \tag{13}$$

and

$$\frac{\mathrm{d}\bar{\alpha}}{\mathrm{d}s} = \exp(-\alpha(s)s)A/\beta \cdot \exp(-E/\mathrm{R}s) \tag{14}$$

with A, β', E, $\mathrm{R} > 0$. From which the differential equation is

$$\frac{\mathrm{d}\bar{\alpha}}{\mathrm{d}\bar{s}} = \exp(-\bar{s}\bar{\alpha}(\bar{s}))K \exp(-1/\bar{s}) \tag{15}$$

with the following change:

$$K = \frac{E^2}{\mathrm{R}^2}\frac{A}{\beta}$$

First we notice that

$$\frac{\mathrm{d}\bar{\alpha}}{\mathrm{d}\bar{s}} > 0$$

therefore $\bar{\alpha}(\bar{s})$ is a monotonous, increasing function.

On the other hand, for $\bar{s} > 0$:

$$\exp(-\bar{s}\bar{\alpha}(\bar{s}))K \exp(-1/\bar{s}) < K \exp(-\bar{s}\bar{\alpha}(\bar{s})) \tag{16}$$

Therefore, if $\bar{s} > 0$, the solutions of equation (15) will be bounded by the solutions to the equation:

$$\frac{d\bar{\alpha}}{d\bar{s}} = K \exp(-\bar{s}\bar{\alpha}) \tag{17}$$

But, if the solution of equation (17) at the initial condition $\bar{\alpha}(0) = 0$ applies only for $\bar{s} \geqslant 0$ then either $\bar{\alpha} \leqslant 1$ for all $\bar{s} \geqslant 0$ or $\bar{s}_1$ is such that $\bar{\alpha}(\bar{s}_1) = 1$. If this is the case and due to the constancy of $\bar{\alpha}$, we have

$$K \exp(-\bar{s}\bar{\alpha}) < K \exp(-\bar{s})\bar{\alpha} \tag{18}$$

then

$$\frac{d\bar{\alpha}}{d\bar{s}} = K \exp(-\bar{s})\bar{\alpha} \tag{19}$$

with an identical initial condition. Notice that the solution has a limit when $\bar{s} \rightarrow \infty$ (equation (19) is of separated variables).

We consider γ this limit, that is

$$\lim_{\bar{s} \rightarrow \alpha} \bar{\alpha}(\bar{s}) = \gamma \tag{20}$$

We transform equation (15) in the following integral equation:

$$\int_{\bar{s}}^{\infty} \frac{d\bar{\alpha}(\sigma)}{d\sigma} d\sigma = \int_{\bar{s}}^{\infty} K \exp(-\sigma\bar{\alpha}(\sigma))\exp(-1/\sigma)d\sigma \tag{21}$$

from which

$$\bar{\alpha}(\bar{s}) = \gamma - K\int_{\bar{s}}^{\infty} \exp(-\sigma\bar{\alpha}(\sigma))\exp(-1/\sigma)d\sigma \tag{22}$$

In order to obtain an asymptotic expression for large values of $\bar{s}$ we make the following approximations:

$$\begin{gathered} \bar{\alpha}(\sigma) \simeq \gamma \\ \exp(-1/\sigma) \simeq 1 \end{gathered} \tag{23}$$

so,

$$\bar{\alpha}(\bar{s}) \simeq \gamma - K\int_{\bar{s}}^{\infty} \exp(-\sigma\gamma)d\sigma = \gamma - K\frac{\exp(-\gamma\bar{s})}{\gamma} \tag{24}$$

Returning to the old variables, we obtain the next solution for equation (11) with $\alpha(0) = 0$:

$$\alpha(t, T) \simeq \frac{\mathrm{R}}{E}\gamma - \frac{EA1}{\mathrm{R}\beta'\gamma}\exp\left(-\gamma\mathrm{R}/E\left(T_0 + \beta t - T_g\right)\right) \tag{25}$$

The Johnson–Mehl–Avrami classic model, expression (7), is easily accessible from this expression, except for terms which can be fixed to unity by

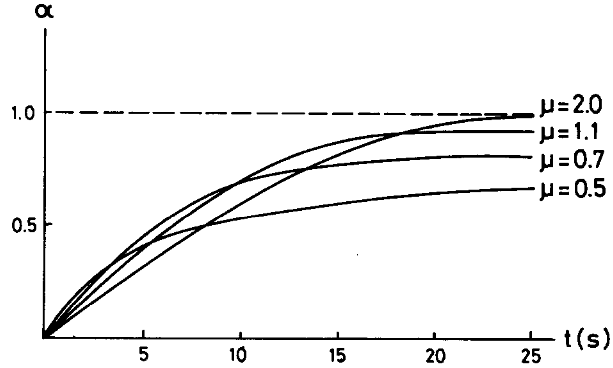

Fig. 3. Temporal evolution of the solutions of equation (15) for different values of parameter μ, numerically calculated by Runge–Kutta's method of 7, 8 order.

means of the parameters K, γ and A: initial conditions required at the solution $\alpha(0) = 0$ must be respected.

2.3. Non asymptotic behaviour

The question to be answered concerns the determination of temporal and temperature value ranges, in which the asymptotic solution can be considered valid as a solution for equation (15).

The model described by expression (7) is applicable to everywhere if, for small time values, and for $T > T_g$, the solutions quickly converge to their asymptotic behaviour.

In order to carry out this study, numerical calculation methods should be used: analytical solutions to equations (15) do not exist. For this reason, a computer study, based on Runge–Kutta's method of order 7, 8 [16], has been done, and which we will not describe here.

The results obtained for different values of the defined parameter $\mu = (E^2A)/(R^2\beta)$ are shown in Fig. 3. Notice that the solutions converge in each case to the asymptotic solution at approximately 10 s, and, because of this, our conclusion is that the asymptotic solution becomes the physical solution to the problem studied here.

3. CONCLUSION

The result from the asymptotic behaviour of the solutions of equation (1) is that the volume of the crystallized fraction is described in this situation by the Johnson–Mehl–Avrami classic expression (7), as has been proposed by different authors [14,15]. This solution can be adopted over the whole temporal range due to its quick asymptotic convergence.

Important consequences concerning the correct determination of the kinetic parameters of the reactions which can take place in disordered solutions are deduced from this result.

However, from a physical point of view, more accurate models can be investigated and, in fact, some works about this subject have been published, in relation to stochastic techniques [17], and, in the future, approximations from Monte-Carlo simulation techniques or from fractal objects [18] will allow us to reach a better understanding of the elemental physical processes of crystallization based on more realistic hypotheses of the structural transformations which take place in disordered solid solutions.

Some of the crystallization phenomena, such as metallic glasses of eutectic composition, in two crystalline phases should be treated by means of non-lineal models, in which the possibility of an evolution of the two different kinetic processes should be considered at the same time [19].

At present, the Johnson–Mehl–Avrami expression (7) should be considered as a valid approximation of the macroscopic description of the kinetic crystallization for both isothermally and non-isothermally activated processes.

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