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A comparative study of different methods for calculating the set of kinetic parameters which describe the crystallization reaction of a glassy alloy

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Abstract

The crystallization reaction of an As–Se–Te alloy was taken as a reference for determining the kinetic parameters which describe the said reaction by differential scanning calorimetry and using non-isothermal techniques.

Three sets of kinetic parameters were obtained, using three calculation methods within the theoretical Johnson–Mehl–Avrami model. Each of the results obtained is discussed regarding its agreement with previous experimental data.

INTRODUCTION

The crystallization kinetics of amorphous alloys have been intensively studied using the classic Johnson–Mehl–Avrami (JMA) theoretical model [1], according to which

$$x(t) = 1 - \exp\left[-(Kt)^n\right] \tag{1}$$

where $x(t)$ is the crystallized volume fraction, t is the effective time (transformation time minus incubation time), n is the Avrami exponent, which reflects the characteristics of nucleation and the growth process, and K is an Arrhenius function of the temperature

$$K(T) = K_0 \exp(-E/RT) \tag{2}$$

where the pre-exponential term K_0 is the frequency factor, E is the activation energy describing the overall crystallization process and T is the absolute temperature.

The crystallization process is generally admitted to be well understood when the three kinetic parameters E, n and K_0 are determined.

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Different authors have developed very diverse methods, based on the aforementioned JMA theoretical model, for calculating these parameters [2–7]. These methods are widely used in the literature, with varying results depending on the nature of the glassy alloys to which they are applied. In general, these developments are carried out under the hypothesis that the temperature is constant during the crystallization reaction, which means that the conclusions are strictly applicable only to experimental data obtained through isothermal techniques. However, these techniques are not always feasible, and it is sometimes more interesting to carry out DSC measurements by linear heating at a controlled rate β. It has been proved [8] that the application of results deduced under isothermal conditions to non-isothermal experimental data leads to satisfactory conclusions, with certain restrictions.

It has logically been observed that, given a fixed composition of alloy glass, the same set of kinetic parameters enables us to interpret the results obtained under both calorimetric conditions (isothermal and non-isothermal) [6]. It should also be interesting to find the sets of kinetic parameters supplied by different methods of analysis applied to experimental data obtained for a single alloy. In this work we will use three methods of analysis, which are briefly described in the Theory section below.

EXPERIMENTAL

The alloy $As_{0.30}Se_{0.25}Te_{0.45}$ was made in bulk form, from its 99.999% pure components, in the usual way [4]. The glassy nature of the material was confirmed by X-ray diffractometric scanning in a Siemens D-500 diffractometer, showing an absence of the peaks that are characteristic of crystalline phases.

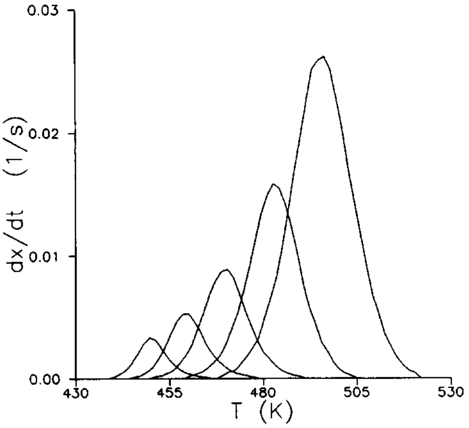

Fig. 1. Experimental curves of dx/dt versus T.

The calorimetric measurements were carried out in a Rigaku Thermoflex DSC instrument, to which an inert gas external installation was connected in order to ensure a constant He-55 flow of 60 ml min^{-1} to purge the gases generated during the crystallization reaction, which, as is characteristic of chalcogenide materials, are damaging to the DSC sensory equipment. The instrument was calibrated at the temperatures corresponding to the In, Sn and Pb melting points, and at a heating rate of 2–32 K min^{-1}.

The crystallization experiments were carried out through continuous heating at β rates of 2, 4, 8, 16 and 32 K min^{-1}. The pulverized samples were crimped (but not hermetically sealed) into aluminium pans, and empty aluminium pans were used as reference.

Figure 1 shows the curves of $\mathrm{d}x/\mathrm{d}t$ versus T, obtained through calorimetric scans for the different experimental heating rates.

THEORY

Method 1

This method, proposed by Yi Qun Gao et al. [3], determines the crystallization rate by taking the first derivative of x relative to t in eqn. (1) and imposing the condition of maximum $\mathrm{d}^2x/\mathrm{d}t^2 = 0$ to locate the maximum crystallization rate. In a satisfactory approximation, the following relationship is found

$$\ln\left(\left.\frac{\mathrm{d}x}{\mathrm{d}t}\right|_p\right) = \ln(0.37nK_0) - \frac{E}{R}\frac{1}{T_p} \tag{3}$$

indicating that, between the experimental values of the crystallization rate logarithm and its temperature inverse (both of which magnitudes are measured at the instant when the maximum value is reached), corresponding to the different values of β, there is a linear relationship whose slope gives us the activation energy E of the process.

The other two kinetic parameters are obtained using the conditions

$$\frac{\beta E}{RK_pT_p^2} = 1 \qquad \left.\frac{\mathrm{d}x}{\mathrm{d}t}\right|_p = 0.37nK_p \tag{4}$$

which are also derived from the aforementioned mathematical reasoning.

Method 2

This method is based on the one developed by Augis and Bennet [7], with a slight variation as to the way of determining the parameters n and K_0 [4]. The reasoning is similar to that carried out for the previous method, but it takes into account that the method will be applied to non-isothermal experiments. From this point of view, the crystallization rate is obtained by taking the derivative of expression (1) with respect to time, bearing in mind the fact that the reaction rate constant is a time function through its Arrhenius temperature dependence, resulting in

$$\frac{\mathrm{d}x}{\mathrm{d}t} = n(Kt)^{n-1}\left[t\frac{\mathrm{d}K}{\mathrm{d}t} + K\right](1-x) \tag{5}$$

The maximum crystallization rate is found by making $\mathrm{d}^2x/\mathrm{d}t^2 = 0$, thus obtaining the relationship

$$\left[\frac{K_p(T_p - T_0)}{\beta}\right]^n = 1 - \frac{1}{n\left[1 + \left(E/RT_p^2\right)\left(T_p - T_0\right)^2\right]} \tag{6}$$

T_0 being the initial temperature.

Because in most crystallization reactions $E/RT \geqslant 25$ [9], an interesting approximation has been specified for the case where $E \gg RT$, the result of which is

$$\ln\frac{(T_p - T_0)}{\beta} = \frac{E}{R}\frac{1}{T_p} - \ln K_0 \tag{7}$$

a linear relationship which makes it possible to calculate the activation energy E and the frequency factor K_0.

Another relationship derived from the approximation used is

$$n = \frac{\left.\frac{\mathrm{d}x}{\mathrm{d}t}\right|_p RT_p^2}{0.37EK_p(T_p - T_0)} \tag{8}$$

which allows us to find the Avrami exponent n.

A comparison of eqns. (3) and (7) and eqns. (4) and (8) shows a formal similarity between both methods, although method 2 explicitly takes into account the experimental dependence of temperature on time $T = T_0 + \beta t$.

Method 3

This procedure for calculating the kinetic parameters of the crystallization reaction uses many experimental points in the DSC curves, unlike the two previous ones, which after all consider only the maximum experimental values. Method 3 has been amply described in a previous work [10] and, together with the same JMA theoretical model, is based on the expression for the crystallization rate

$$\ln\left(\frac{\mathrm{d}x}{\mathrm{d}t}\right) = \ln[K_0 f(x)] - \frac{E}{R}\frac{1}{T} \tag{9}$$

where $f(x) = n(1-x)[-\ln(1-x)]^{(n-1)/n}$.

The above relationship in the constancy interval $\ln[K_0 f(x)]$, makes it possible to construct a straight regression line between the inverse of the experimental temperature values and the corresponding logarithm of the crystallization rate, from whose slope, by an iterative method, the value of the activation energy E is deduced. If we take into account the value of $f(x)$, the above mentioned condition of constancy leads to the expression

$$\ln K_0 + \ln n + \ln(1-x) + [(n-1)/n]\ \ln[-\ln(1-x)] = C \tag{10}$$

where C is a constant.

By imposing condition (10) for any two values x_1 and x_2 of the crystallized fraction within the said interval, it is possible to obtain the following for the kinetic exponent of the reaction

$$n = \frac{\ln[\ln(1-x_2)/\ln(1-x_1)]}{\ln[(1-x_2)\ln(1-x_2)/(1-x_1)\ln(1-x_1)]} \tag{11}$$

Expressions (10) and (11) make it possible to find the kinetic parameters n and K_0 from data derived from the records obtained during the non-isothermal DSC experiments.

RESULTS AND DISCUSSION

Table 1 shows the experimental data corresponding to the peak values for the alloy on which this study is based. With these values it is possible to build the plots corresponding to eqns. (3) and (7) and the compromise straight lines, from whose slope the activation energies predicted by methods 1 and 2 are deduced.

TABLE 1

Experimental values corresponding to the DSC thermograms

β (K min^{-1})	T_0 (K)	T_p (K)	$10^3 x(\mathrm{d}x/\mathrm{d}t)_p$ (s^{-1})
2	438.5	449.7	3.30
4	444.1	460.1	5.27
8	450.0	470.5	8.91
16	458.8	482.8	15.85
32	467.6	496.4	26.16

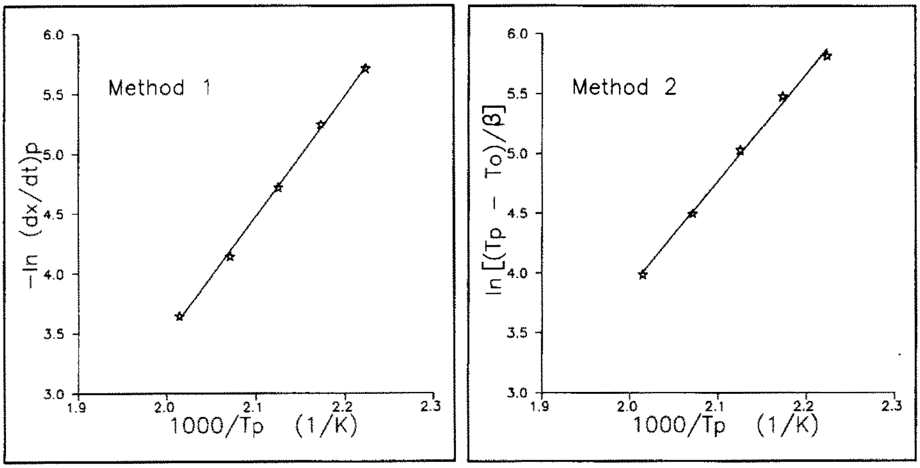

Fig. 2. Experimental plots and compromise straight lines for determining activation energy.

Figure 2 shows the plots and compromise straight lines obtained by both methods, and Table 2 shows the values deduced for the activation energy E.

By applying eqns. (4) and (8) it is possible to calculate the other two kinetic parameters, which are also shown in Table 2 for both methods.

The application of method 3 used an average of 186 experimental data points per heating rate, with which the activation energy was calculated in a first approximation. From this activation energy the values of $\ln[K_0 f(x)]$ were determined, and are represented in Fig. 3. Once a more restricted interval was selected for the crystallized fraction, where the constancy of $\ln[K_0 f(x)]$ is more strictly met with, E was again calculated. By iterating the process, a converging value was found for this parameter, the variation of $\ln[K_0 f(x)]$ being less than 2%, valid in an interval for the crystallized fraction between $x = 0.20$ and $x = 0.65$, and where it is still possible to count on 141 experimental data points for carrying out the adjustment. For $x < 0.2$ and $x > 0.65$, the variation of $\ln[K_0 f(x)]$ stays below 5%. The final results for the three kinetic parameters are shown in Table 2.

A study of the results supplied by the three methods used shows certain differences. As to the activation energy, the three values may be considered

TABLE 2

Set of kinetic parameters calculated by the three methods for the reference glassy alloy

Method	E (kJ mol^{-1})	n	K_0 (s^{-1})
1	83	4.16	1.14×10^7
2	74	4.70	1.15×10^6
3	85	2.00	3.40×10^7

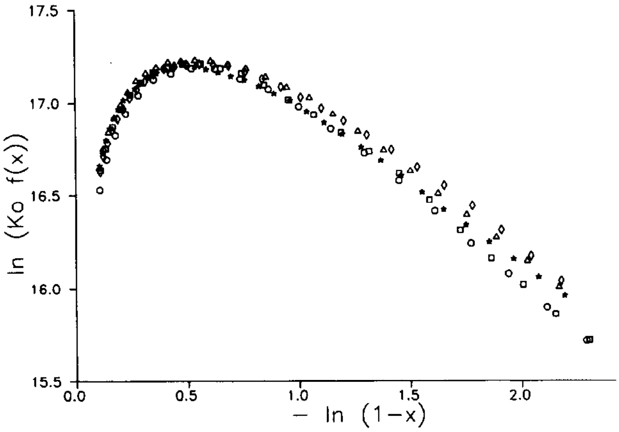

Fig. 3. Plots of $\ln[K_0 f(x)]$ versus x determined in the first approximation in method 3. (○ 2 K min^{-1}, □ 4 K min^{-1}, △ 8 K min^{-1}, ◇ 16 K min^{-1}, ★ 32 K min^{-1}).

satisfactory, being within the margin of error accepted in the literature, but the differences in parameter *n* are greater, and if individually considered would lead to very different conclusions as to, for instance, the mechanisms of nucleation and growth [11].

The problem centres therefore on evaluating which of the methods of calculation described is the most suitable for finding the set of kinetic values; this may depend on the type of glassy material studied.

In order to do this, we propose to reconstruct the crystallization reactions, taking each set of kinetic parameters, according to expression (1), and comparing them with the experimental one. Figure 4 shows this reconstruction, representing crystallized fractions versus times, with the data corresponding to a heating rate of 8 K min^{-1}.

In order to establish a criterion allowing us to decide on the most adequate calculation method, the mean square deviation between the curves reconstructed with each set of kinetic parameters and the experimental curve was found for each heating rate. The average values found are shown in Table 3.

TABLE 3

Average of the mean square deviations σ between the experimental curves and the reconstructed curves

Method	$\bar{\sigma}$
1	0.096
2	0.108
3	0.229

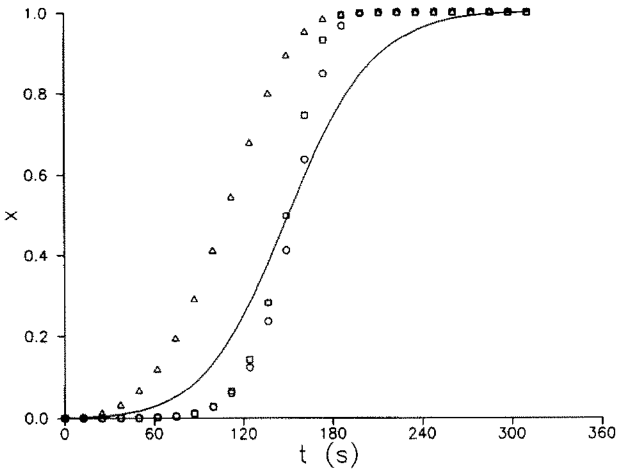

Fig. 4. Crystallized fraction versus *t* for the experimental curve and the derivations of the three sets of kinetic parameters calculated by the three methods for data corresponding to $\beta = 8$ K min^{-1}. (○ method 1, □ method 2, △ method 3, —— experimental).

The parameters calculated through methods 1 and 2 give the lowest values for the mean square deviation; they are both of the same order and quantitatively acceptable. The same is not true of the parameters obtained through method 3, whose deviation from the experimental values is too great, although the slope and shape of the sigmoids are the most similar to those described by the experimental values.

The greater mathematical strictness used in method 2, which lies in the fact that, in the two derivation steps for the crystallized fraction, the temperature dependence is taken into account, did not show any improvement in relation to the values given by method 1, which considers only the peak values of the experimental DSC curves.

The results obtained, even in the most favourable cases, show the approximate character of the methods used for calculating the set of kinetic parameters which describe the crystallization reaction.

The application of conclusions deduced under isothermal conditions to experimental data obtained through continuous heating techniques, even if the aforementioned restrictions are met with, is perhaps not equally suitable for all amorphous alloys.

The comparison of the sigmoid curves represented in Fig. 4 even leads us to question whether the theoretical JMA model, as summarized in eqns. (1) and (2), equally describes the whole crystallization reaction.

In any case, the final comparison of curves of *x* versus *t*, reconstructed from the set of kinetic parameters, with the experimental curves is suggested as a good procedure for verifying the agreement between the actual behaviour of the amorphous alloy when it crystallizes and the theoretical model describing this crystallization reaction.

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