DETERMINATION OF KINETIC PARAMETERS OF CRYSTALLIZATION AND STUDY OF GLASS FORMING ABILITY FOR ALLOYS IN THE Ge-As-Te AMORPHOUS SYSTEM

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A mathematical method which makes it possible to calculate the kinetic parameters of crystallization, activation energy, E, reaction order, n, and frequency factor, K_0, was developed. The procedure was applied to chalcogenide glasses $Ge_{0.05}As_{0.20}Te_{0.75}$, $Ge_{0.10}As_{0.20}Te_{0.70}$ and $Ge_{0.14}As_{0.43}Te_{0.43}$, confirming the validity of the method. A criterion is discussed for analyzing the glass forming ability (GFA) of these alloys, from the thermal events observed on heating the glasses, and evaluated in terms of the reaction rate constant of each alloy.

1. Introduction

The study of crystallization kinetics in amorphous materials by DSC (differential scanning calorimetry) methods has been widely discussed in the literature [1–5]. There is a large variety of theoretical models and theoretical functions, proposed to explain the crystallization kinetics. The application of each of them depends on the type of amorphous material studied and how it was made. For chalcogenide glasses obtained in bulk form, which is the case of the alloys we studied [6], the most adequate theoretical model turned out to be the so-called Johnson–Mehl–Avrami model, which, although developed for isothermal processes, can be applied, under certain conditions, to continuous heating experiments [5].

There are techniques for determining the kinetic parameters of the crystallization reaction from data obtained by continuous heating [7,8], based on the maximum values of the DSC curves, but since these methods use only one experimental point from each of the curves obtained for each heating rate, another method is proposed as an alternative, as it makes it possible to use a large number of values obtained from the entire experimental curve for each of the different heating rates.

On the other hand, glass forming ability is usually evaluated in relation to the characteristic temperatures measured during heating of the samples, defining useful parameters such as K_{gl}, introduced by Hruby [9]. In this paper, GFA is analyzed through the use of another criterion: the evaluation of the parameters that define crystallization kinetics.

2. Theoretical

2.1. Kinetic parameters

When, under isothermal conditions, an amorphous material is given the energy needed to go through the energy barrier which separates it from the crystalline state, the crystallized fraction is a time function of the type

$$x(t)=1-\exp[-(Kt)^n], \quad (1)$$

in which K is the rate constant, a temperature function according to the Arrhenius expression

$$K(T)=K_0\exp(-E/RT), \quad (2)$$

K_0 is the frequency factor, related to molecular collision probability [10,11], E is the activation energy for the crystallization process, and n is the kinetic exponent, or order of the reaction, which gives information concerning nucleation and crystal growth mechanisms.

Crystallization rate is obtained by differentiating relationship (1) with respect to time, and by eliminating this variable, the result is

$$\mathrm{d}x/\mathrm{d}t=K(T)f(x), \quad (3)$$

where

$$f(x)=n(1-x)[-\ln(1-x)]^{(n-1)/n} \quad (4)$$

is the characteristic function of the theoretical Johnson–Mehl–Avrami model for the crystallization process, which, again, seems to be most adequate for describing the phenomenon occurring in chalcogenide bulk glasses [5].

Although crystallization rate was determined under isothermal conditions, it is possible to use it with a high degree of accuracy for continuous heating processes, as the activation energy for non-isothermal conditions at low heating rates is practically equal to this energy for isothermal processes, although it diminishes as the heating rate increases. This is why many authors [12–16] use this approximation with satisfactory results.

Allowing relationship (3) to be valid for both isothermal and continuous heating processes, the procedure described below has been developed for calculating E, n and K_0.

By relating expressions (2) and (3) and taking logarithms, the following is obtained:

$$\ln(\mathrm{d}x/\mathrm{d}t)=\ln[K_0f(x)]-E/RT, \quad (5)$$

where it can be seen that, for those values of the crystallized fraction in which $f(x)$ has a constant behaviour, there is linearity between the logarithm of the crystallization rate and the inverse temperature, making it possible to determine activation energy from the slope of the straight regression line of the experimental data obtained for the different temperatures (isothermal method) or for the different heating rates (non-isothermal method).

In order to determine n and K_0, the relationship which defines $f(x)$ in the Johnson–Mehl–Avrami model is introduced into expression (5), with the result:

$$\ln(\mathrm{d}x/\mathrm{d}t)=A-B+\ln n+y+[(n-1)/n]\ln(-y), \quad (6)$$

where $y=\ln(1-x)$, $A=\ln K_0$ and $B=E/RT$.

Through a least-squares method, this expression fits the experimental data: $y_i=\ln(1-x_i)$, $z_i=\ln(\mathrm{d}x/\mathrm{d}t)_i$ minimizing the function:

$$S=\sum_{i=1}^{N}\{z_i-A+B-\ln n-y_i-[(n-1)/n]\ln(-y_i)\}^2, \quad (7)$$

depending on variables A and n, originating the system of equations

$$\partial S/\partial A=\sum_{i=1}^{N}\{z_i-A+B-\ln n-y_i-[(n-1)/n]\ln(-y_i)\}=0,$$

$$\partial S/\partial n=\sum_{i=1}^{N}\{z_i-A+B-\ln n-y_i-[(n-1)/n]\ln(-y_i)\}[1+(1/n)\ln(-y_i)]=0,$$

whose solution gives the kinetic parameters:

$$n=\left[\left(\sum_{i=1}^{N}\ln(-y_i)\right)^2-N\sum_{i=1}^{N}[\ln(-y_i)]^2\right]\left[\sum_{i=1}^{N}\ln(-y_i)\left(\sum_{i=1}^{N}y_i-\sum_{i=1}^{N}z_i+\sum_{i=1}^{N}\ln(-y_i)\right)\right.$$
$$\left.+N\left(\sum_{i=1}^{N}z_i\ln(-y_i)-\sum_{i=1}^{N}y_i\ln(-y_i)-\sum_{i=1}^{N}[\ln(-y_i)]^2\right)\right]^{-1} \tag{8}$$

$$\ln K_0=\frac{1}{N}\left(\sum_{i=1}^{N}z_i-\sum_{i=1}^{N}y_i-\frac{n-1}{n}\sum_{i=1}^{N}\ln(-y_i)\right)-\ln n+\frac{E}{ER}, \tag{9}$$

which may be observed to be functions of experimental data such as crystallized fraction and crystallization rate.

2.2. Glass forming ability

The study of glass forming ability is usually based on the values measured for quantities such as crystallization enthalpies, temperatures or rates.

Crystallization enthalpy is the specific energy released during the whole process, and so it gives information on the energetic difference between the amorphous state and the corresponding crystalline state. Crystallization temperatures, usually identified with the temperatures corresponding to the maximum values of the DSC curves, also make it possible to establish a criterion for the evaluation of GFA.

Crystallization rates make it possible to evaluate, in the form of a time interval, the path which separates the glass transition temperature, T_g, from crystallization temperature, T_c, and allows us to establish a criterion for the crystallization ability of the alloys.

In this work, a criterion has been preferred which, based on the values found for the kinetic parameters, is considered to be more accurate and related to the crystallization process.

Starting from an amorphous compound, the molecules participating in the crystallization reaction will acquire an energy excess, forming an activated complex which, after the corresponding energy release, results in the crystalline state. This energy excess is captured through molecular collisions, according to modern chemical rate theory. The Arrhenius function is introduced in the theoretical model as a reaction rate constant, so its evaluation makes it possible to define a criterion for crystallization. The frequency factor, K_0, is usually written as a product of two factors: molecular collision probability and the so-called steric factor, a number less than one which gives information on whether the relative directions in which the molecular collisions take place are such that the impact will lead to the crystallization reaction. Activation energy can be interpreted as the energy excess that a molecule must acquire in order to be a part of the activated complex [10,11]. The evaluation of the rate constant is, therefore, a way of estimating GFA.

3. Experimental

Three glasses were prepared: $Ge_{0.05}As_{0.20}Te_{0.75}$ (M-I), $Ge_{0.10}As_{0.20}Te_{0.70}$ (M-II), and $Ge_{0.14}As_{0.43}Te_{0.43}$ (M-III). The calorimetric analysis was carried out using a DSC Perkin-Elmer DC2, calibrated with a Pb.

The samples were pulverized, placed on aluminium pans and crimped (but not hermetically sealed). The scannings were done in an inert gas atmosphere, using heating rates of 2.5, 5, 10, 20 and 40 K/min.

Fig. 1 shows, as an example, the DSC curves for alloy $Ge_{0.14}As_{0.43}Te_{0.43}$. The areas under the crystallization peaks and their fractions were determined by two different ways: by measuring directly, with a planimeter on the DSC plots, and by numeric integration by use of a computer; the results differed by less than 1%.

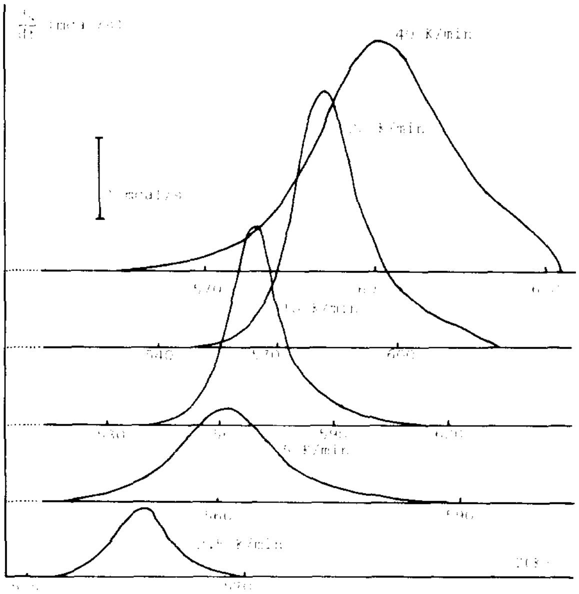

Fig. 1. DSC curves for alloy $Ge_{0.14}As_{0.43}Te_{0.43}$ at different heating rates.

3.1. Kinetic parameters

In order to apply the proposed method, experimental data, $\ln(dx/dt)$ versus $1/T$ of the DSC curves obtained for each compound were taken, corresponding to the interval $0.1<x<0.9$, with the same value for x for each heating rate, to keep the factor $\ln[K_0f(x)]$ constant. In this way a first value for E is estimated, with which the value of $\ln[K_0f(x)]$ is found from expression (5). Representative curves of $\ln[K_0f(x)]$ versus $-\ln(1-x)$ are like the ones indicated in fig. 2 for each heating rate, for alloy M-III, and this makes it possible to select a new interval of the crystallized fractions which, with good approximation, meets the linearity conditions required for this method to be applicable to non-isothermal experiments.

By repeating the procedure for values of x within the aforementioned interval, a series of convergent values are found for E, until a satisfactory linear correlation coefficient is obtained. Fig. 3 shows, for the same alloy, the cloud of points corresponding to different experimental values of said interval, which make it possible to find the activation energy for the crystallization process.

Table 1 shows the crystallized fraction intervals in which the above approximation is adequate, for the three alloys, and the activation energies calculated for each case. By applying expressions (8) and (9), already deduced, parameters n and K_0 were deter-

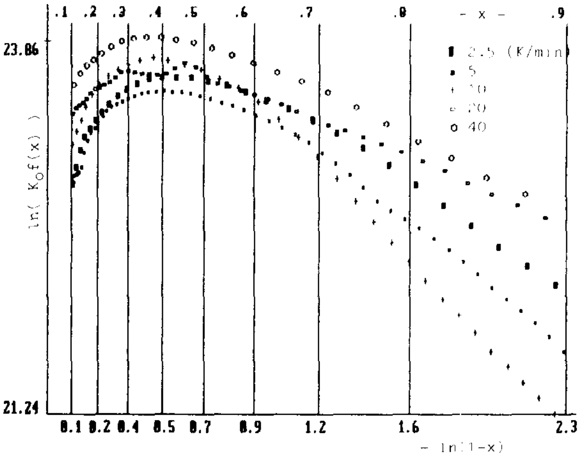

Fig. 2. Plots of $\ln[K_0f(x)]$ versus $-\ln(1-x)$ for alloy $Ge_{0.14}As_{0.43}Te_{0.43}$, at each of the heating rates.

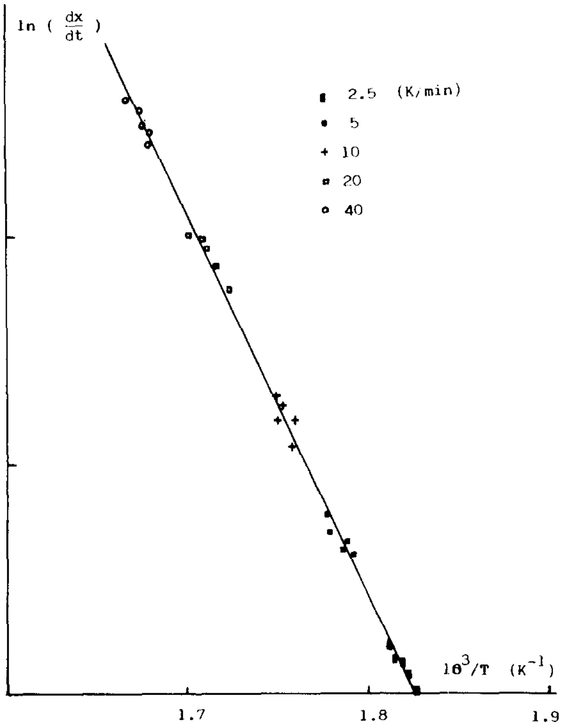

Fig. 3. Plot of $\ln(dx/dt)$ versus $1/T$ for different values of the crystallized fraction.

Table 1
Kinetic parameters calculated by the proposed method, and from peak values of the DSC curves obtained

Method	Kinetic parameters	Alloy		
		M-I	M-II	M-III
proposed	validity interval	$0.30<x<0.60$	$0.20<x<0.60$	$0.30<x<0.70$
	E (kJ/mol)	217.06	192.71	144.31
	n	2.1	2.6	3.5
	$\ln K_0$ [a]	52.70	47.70	25.55
peak	E (kJ/mol)	216.25	200.00	144.30
	n	1.7	2.1	2.9
	$\ln K_0$	53.22	48.17	25.80

[a] K_0 in units of s^{-1}.

mined for each heating rate; their mean value will give the best value for them, for each of the alloys. Table 1 shows these values for the aforementioned parameters for each alloy.

In order to verify the efficacy of our proposed method, the kinetic parameters of the three alloys under study have also been evaluated through the technique used by Gao et al. [7,8]. In it, the peak values of the DSC curves are used, and the relationships deduced by the authors mentioned:

$$\beta E/RT_c^2 K_c = 1, \qquad (10)$$

$$(dx/dt)_c = 0.37\, nK_c, \qquad (11)$$

$$\ln(dx/dt)_c = \ln(0.37 nK_0) - (E/R)(1/T_c), \qquad (12)$$

where subscript c indicates the value of the parameters corresponding to the peak. In expression (12), the linear dependence between the experimental quantities $\ln(dx/dt)_c$ and $(1/T_c)$ is observed.

Using the experimental data for the different heating rates, a cloud of points is obtained for which a straight line can be fitted whose slope gives the activation energy, E. K_c is determined through relationship (10), for each value of the heating rate, β, and Avrami's index, n, can be found through expression (11). The frequency factor K_0 can be determined by use of the Arrhenius relationship itself, or through the origin ordinate of the aforementioned line.

Table 1 shows the values which this procedure gives for the three alloys studied. The agreement with those determined above confirms the proposed method. The validity of the proposed method is also evident when the values given by it are compared to the results obtained by Sugi et al. [12] for these parameters in similar alloys in the Ge–As–Te system.

3.2. *Glass forming ability*

The DSC curves of the three alloys make it possible to determine the crystallization temperatures, which have been identified with the peak value and glass transition temperatures, the latter of which were taken in the centre of the two inflections which are characteristic of the curves, for each heating rate. Crystallization enthalpy was found for the same heating rate at which the instrument was calibrated.

The reaction rate constant was evaluated using the average crystallization temperatures of those measured for the different heating rates.

Table 2 shows the experimental data used which makes it possible to evaluate the GFA of the compounds and to calculate the value for the aforementioned reaction rate constant.

The results obtained give a sequence, according to crystallization ability, increasing with Te concentration, which agrees with the conclusions reached by other criteria. Our method has the advantage that it can be expressed quantitatively in terms of chemical kinetics.

Note that the energy barrier, E, is greater as the crystallization ability increases, a fact which, far from being contradictory, could reinforce the concept of glass stability.

Table 2
Experimental data which make it possible to evaluate GFA in the corresponding alloys

Alloy	H (kJ/mol)	T_g (K)	T_c (K)	T_c-T_g	$K=K_0\exp(-E/RT)$
M-I	1.7	383	458	75	0.021
M-II	1.8	390	456	66	0.020
M-III	4.3	453	572	119	0.009

4. Conclusions

The method described above gives values for the kinetic parameters of the crystallization reactions, which must be considered more accurate, as they are numerically adjusted in a deterministic way, for all possible values of the crystallized fraction, thus including all the experimental data given by the DSC curves.

In the numerical development done in order to apply the described method for determining *n*, there is an oscillation in the values obtained for each heating rate. This is due to the aforementioned fact that the theoretical deductions were done for isothermal techniques, and the experimental data were taken from non-isothermal experiments. There was found to be very little energetic difference between the amorphous state and the corresponding crystalline state, which could somehow explain the stability of these Ge–As–Te system glassy alloys. Analysis of the crystallization reaction rate constant in these compounds shows that their crystallization ability increases with Te content.

References

[1] H.E. Kissinger, Anal. Chem. 29 (1957) 1702.
[2] D.J. Sarrach and J.P. DeNeufville, J. Non-Cryst. Solids 22 (1976) 245.
[3] K. Tanaka, Y. Osaka, M. Sugi, S. Iizima and M. Kikuchi, J. Non-Cryst. Solids 12 (1973) 100.
[4] D.W. Henderson, J. Non-Cryst. Solids 30 (1979) 301.
[5] S. Surinach, M.D. Baró, M.T. Clavaguera-Mora and N. Clavaguera, J. Non-Cryst. Solids 58 (1983) 209.
[6] R.A. Ligero, J. Vázquez, P. Villares and R. Jiménez-Garay, Mater. Letters 5 (1987) 301.
[7] Y.Q. Gao, W. Wang, F.-Q. Zheng and X. Liu, J. Non-Cryst. Solids 81 (1986) 135.
[8] Y.Q. Gao and W. Wang, J. Non-Cryst. Solids 81 (1986) 129.
[9] A. Hruby, Czech. J. Phys. B22 (1972) 1187.
[10] H.E. Kissinger, J. Res. Natl. Bur. Std. US 57 (1956) 217.
[11] H.E. Avery, Cinética química básica y mecanismos de reacción (Reverté, Barcelona, 1977).
[12] M. Sugi, S. Iizima, M. Kikuchi and K. Tanaka, J. Non-Cryst. Solids 5 (1971) 358.
[13] Y.Q. Gao and S.H. Wang, J. Non-Cryst. Solids 70 (1985) 85.
[14] H. Yinnon and D.R. Uhlmann, J. Non-Cryst. Solids 54 (1983) 253.
[15] E.A. Marseglia, J. Non-Cryst. Solids 41 (1980) 31.
[16] J. Colmenero and J.M. Barandiarán, J. Non-Cryst. Solids 30 (1979) 263.