JOURNAL OF MATERIALS SCIENCE 26 (1991) 211–215

A study of the crystallization kinetics of some Cu–As–Te glasses

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The crystallization kinetics of two amorphous alloys in the Cu–As–Te system was studied by differential scanning calorimetry, using continuous heating methods, and applying a new analysis procedure in order to calculate the kinetic parameters which define the crystallization reactions, in the Johnson–Mehl–Avrami model. In this analysis, the crystallized fraction interval at which the characteristic function of said model is constant was taken into account. The values obtained for these parameters made it possible to discuss the glass-forming ability of the compounds under study, and the types of crystalline growths in the alloys.

1. Introduction

Recent years have seen a growing interest in the theory and practical aspects of the application of experimental analysis techniques to the study of the crystallization of glasses. Two popular techniques, isothermal and non-isothermal, have been widely used [1–4]. While isothermal experimental analysis techniques are in most cases more definite, non-isothermal experiences have several advantages. The speed with which non-isothermal experiments can be performed makes them attractive. Many phase transformations occur too rapidly to be measured under isothermal conditions, because of transients inherently associated to the experimental devices. Non-isothermal experiments can be used to extend the temperature range of measurements beyond the range accessible to isothermal experiments. Non-isothermal analysis of the crystallization kinetics of glasses has thus become increasingly attractive.

The crystallization kinetics of glass-forming materials are controlled by nucleation and growth mechanisms which can be characterized by kinetic constants. In the late 1930s, Johnson, Mehl and Avrami [5–7] developed a formal theory of transformation kinetics, relating the volume fraction of crystals to these kinetic parameters, which has turned out to be very efficient in describing the behaviour of the crystallization processes experienced by the glasses.

The present paper proposes a method which makes it possible to determine the kinetic parameters through the application of this formal theory. In order to ascertain its validity, the method presented is applied to the crystallization process of the chalcogenide glassy alloys $Cu_{0.05}As_{0.50}Te_{0.45}$ (M1) and $Cu_{0.15}As_{0.40}Te_{0.45}$ (M2).

2. Thermal analysis

Isothermal crystallization processes in glasses are usually interpreted [5–8] according to the Johnson–Mehl–Avrami transformation equation, which is normally written as

$$x = 1 - \exp[-(Kt)^n] \qquad (1)$$

where x is the transformed volume fraction, t is the effective time, n is the Avrami exponent and K is the rate constant which has an Arrhenian temperature dependence

$$K = K_0 e^{-E/RT} \qquad (2)$$

in which K_0 is the frequency factor, E is the activation energy and T is the absolute temperature.

Taking the first derivative of x with respect to t, we obtain the crystallization rate at each instant

$$\frac{dx}{dt} = (1 - x)nK^n t^{n-1} \qquad (3)$$

and by eliminating parameter t, through Equation 1, we can write

$$\frac{dx}{dt} = n(1 - x)K[-\ln(1 - x)]^{n-1/n} \qquad (4)$$

which is usually expressed in the generic form

$$\frac{dx}{dt} = K(T)f(x) \qquad (5)$$

where

$$f(x) = n(1 - x)[-\ln(1 - x)]^{n-1/n} \qquad (6)$$

Although the above equations have been derived for isothermal crystallization processes, it has been proved that, under certain restrictions [1, 2, 8–10], they can be applied to non-isothermal experiments with satisfactory results.

Taking logarithms in Equation 5 we obtain

$$\ln\left(\frac{dx}{dt}\right) = \ln[K_0 f(x)] - \frac{E}{RT} \qquad (7)$$

an expression which establishes that, for that interval of values of the crystallized fraction in which $f(x)$

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TABLE I Intervals of glass transition temperature, T_g, initial peak temperature, T_{in}, maximum peak temperature, T_p, peak width, ΔT, corresponding to the different experimental heating rates, and calculated enthalpies

	$Cu_{0.05}As_{0.50}Te_{0.45}$		$Cu_{0.15}As_{0.40}Te_{0.45}$	
	Peak I	Peak II	Peak I	Peak II
T_g (K)	410–423		423–435	
T_{in} (K)	450.6–471.6	484.5–508.2	456.4–477	481.5–507
T_p (K)	466.1–491.4	496.9–520.6	473.5–495.6	500.2–528.8
ΔT (K)	46.7–52.8	19.8–37.2	33.6–41.4	32.1–44.1
ΔH (mcal mg^{-1})	6.87	4.08	4.65	8.01

is constant, there is a linear relationship between $\ln(dx/dt)$ and the absolute temperature inverse. Bearing in mind that both the logarithm of the crystallization rate and the temperature are data which can be obtained from the experimental exothermal curves given by differential scanning calorimetry of the glasses, it is possible to carry out an adjustment, by least square method, of the experimental data, to a straight line whose slope gives us the activation energy, E, of the crystallization process.

In the crystallized fraction interval, it is verified that $\ln[K_0 f(x)] = C$, C being a constant, a condition which, taking Equation 6 into account, can be stated as

$$\ln K_0 + \ln n + \ln(1-x) + \frac{n-1}{n}\ln[-\ln(1-x)] = C \qquad (8)$$

an equation which must be true for any given value of x contained in the interval. By writing Equation 8 for two given values of the crystallized fraction, x_1 and x_2, and subtracting the expressions obtained in each case

$$\ln\frac{1-x_1}{1-x_2} = \frac{n-1}{n}\ln\frac{\ln(1-x_2)}{\ln(1-x_1)} \qquad (9)$$

from which

$$n = \ln\left[\frac{\ln(1-x_2)}{\ln(1-x_1)}\right]\left\{\ln\left[\frac{(1-x_2)\ln(1-x_2)}{(1-x_1)\ln(1-x_1)}\right]\right\}^{-1} \qquad (10)$$

which gives us the Avrami exponent for the process under consideration.

The third kinetic parameter characteristic of the crystallization reaction, the frequency factor K_0, can be determined from Equation 8, by substituting the previously found values of n and C and using any one of the values of the crystallized fraction, within the constancy interval of the function $K_0 f(x)$.

3. Experimental procedure

The two alloys under study were made in bulk form, by homogeneously mixing their highly pure (99.99%) components. After the usual melting (950 °C) and quenching in air, to avoid crystallization, their amorphous nature was tested by X-ray diffraction. Fig. 1 shows the glass-forming region of the Cu–As–Te system [11] and the position, within the system, of the two compositions under study, whose structures and electrical properties have already been studied [12, 13].

The calorimetric crystallization experiments were done in a DSC Thermoflex by Rigaku Corporation, keeping a constant flow of 60 cm^3 min^{-1} of inert gas inside the oven, and using the continuous heating method, at heating rates of 2, 4, 8, 16 and 32 K min^{-1}.

The analysed samples, were pulverized, crimped into aluminium pans, and their masses were kept within the 11 to 35 mg interval. An empty aluminium pan was used as reference.

Fig. 2 shows the thermograms obtained for each of the alloys, at a heating rate of 16 K min^{-1}, where we may observe that both alloys exhibit two crystallization peaks (I and II).

Table I shows the characteristic temperatures of all the thermograms, as well as the enthalpies, for each

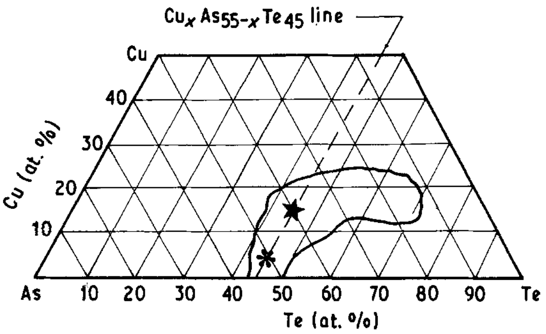

Figure 1 Glass forming region of the Cu–As–Te system.

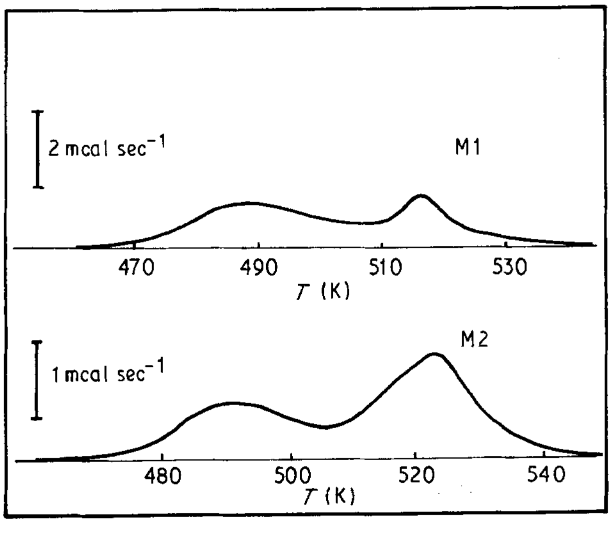

Figure 2 Thermograms obtained for the alloys, for β = 16 K min^{-1}.

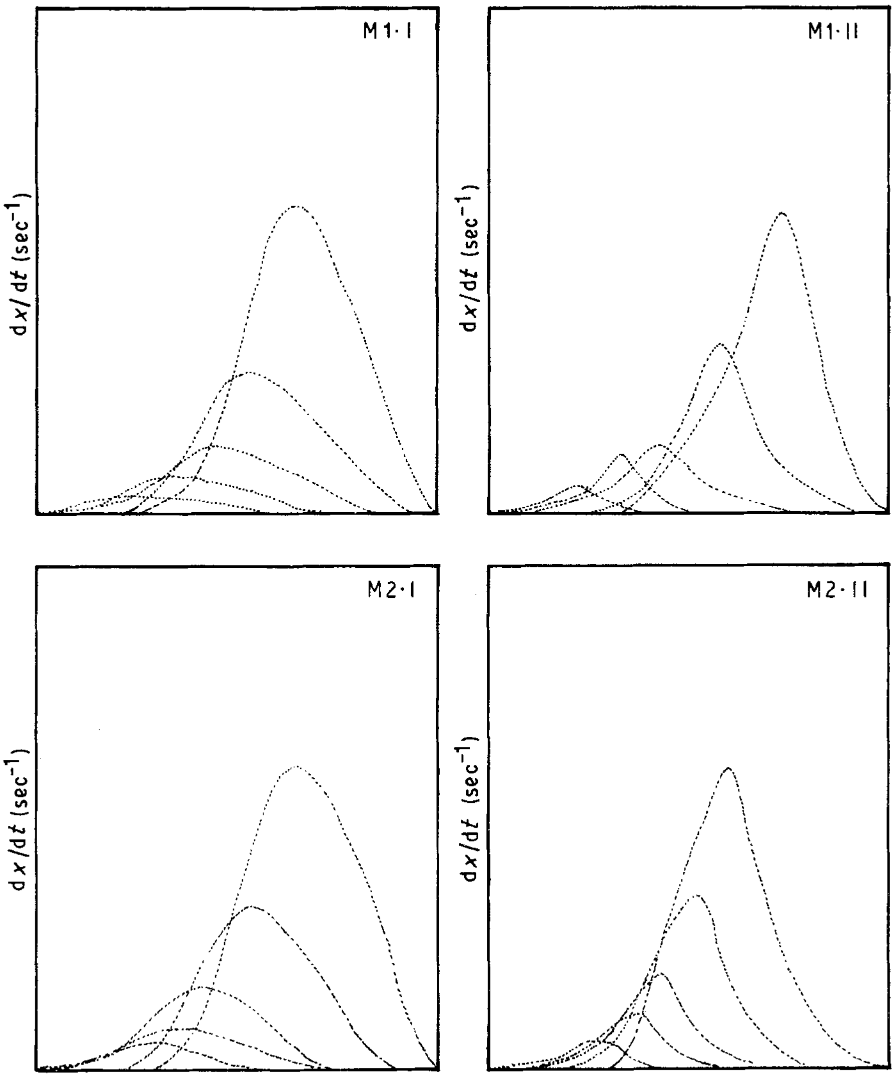

Figure 3 Representation of (dx/dt) against T for the exothermal peaks registered in both alloys.

reaction, calculated at the same heating rate at which the instrument was calibrated ($\beta = 16\ \mathrm{K\,min}^{-1}$).

4. Results and discussion

The areas under the exothermal peaks were integrated using Simpson's numerical method. The quotient between the area below the peak up to a certain value of the abscissa, and the total area of the peak, represents the value of the crystallized fraction corresponding to the instant under consideration. The proportion between each ordinate and the total area gives the crystallization rate corresponding to the respective temperatures, which makes it possible to obtain the graphic representation of the experimental peaks in the way indicated in Fig. 3, that is, dx/dt against temperature.

In order to analyse the kinetics of each of the crystallization processes, we will proceed as follows. In a first approximation we may admit, according to Equation 7, that there exists linearity between the experimental values of $\ln(dx/dt)$ and the temperature inverse, corresponding to all the heating rates at which the peak has been measured, in a wide interval of the crystallized fraction. Through a least squares method, it is possible to adjust these experimental values to a straight line, whose slope gives a first value for the activation energy, which will usually be far from the truth, as linearity has been assumed for values of the crystallized fraction in which the value of $\ln[K_0 f(x)]$ does not remain constant.

This first estimation for the activation energy makes it possible to calculate, through Equation 7, the value of $\ln[K_0 f(x)]$ that corresponds to each crystallization rate, and therefore to each crystallized fraction. The plots of $\ln[K_0 f(x)]$ against x allow us to select an interval for the crystallized fraction in which the behaviour of $\ln[K_0 f(x)]$ is nearer that of a constant. Fig. 4 shows the representation mentioned for the two alloys under study in this work, corresponding to an initial interval of $0.1 \leqslant x \leqslant 0.9$. The linear adjustment method can be carried out again, with experimental data limited to the new interval, thus obtaining a second value for the activation energy which is more accurate, as the condition of constancy for $\ln[K_0 f(x)]$ is fulfilled in a greater measure. The repetition of the procedure gives more and more accurate values for parameter E. The decision of when to interrupt this reiterative process is conditioned by three factors: the width of the crystallized fraction interval itself, in which the proposed method leads to satisfactory results in the process described by the

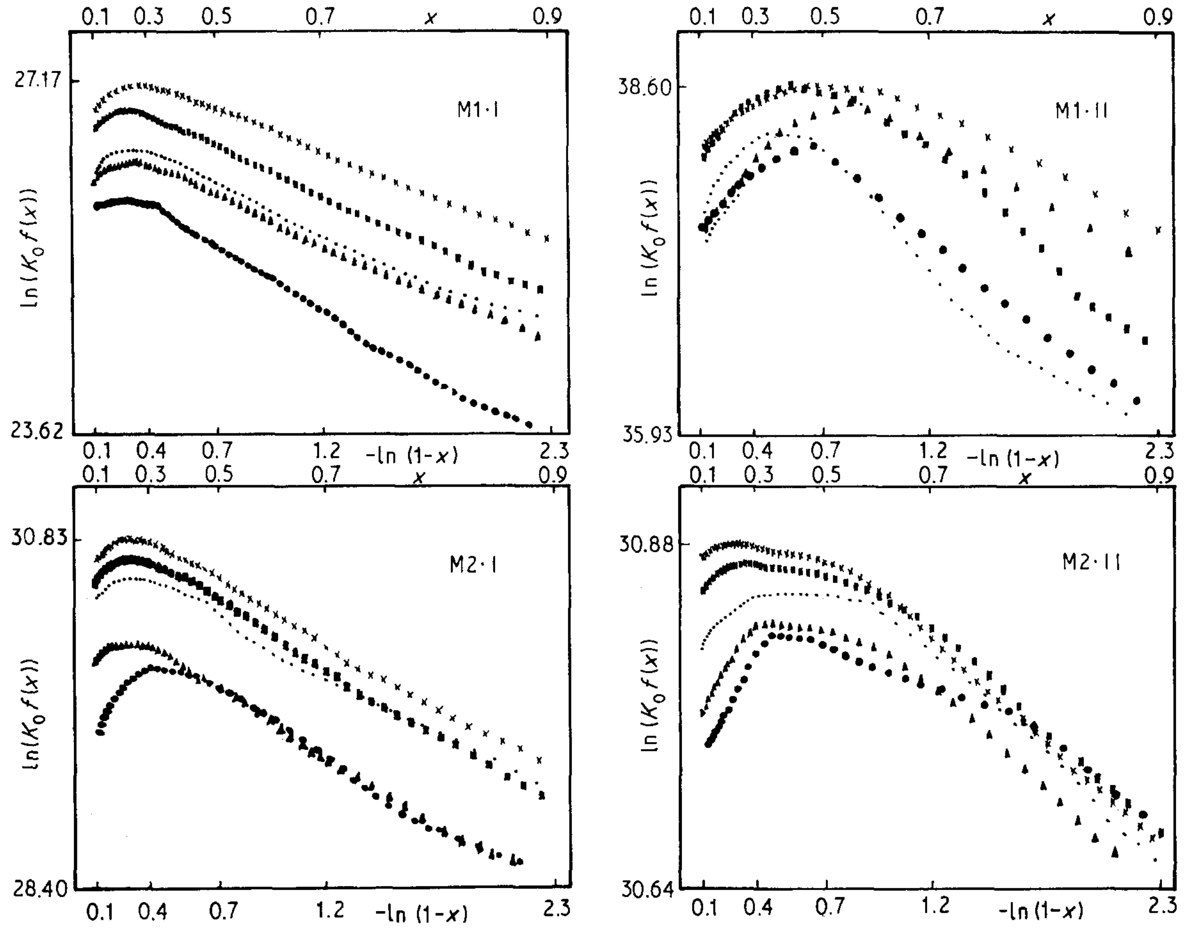

Figure 4 Plots of $[\ln K_0 f(x)]$ against x for the first approximation of the method described in both alloys.

Johnson–Mehl–Avrami model; the linear adjustment correlation coefficient, which tells us the degree of linearity that exists between the experimental data; the variation, Δ, of the function $\ln[K_0 f(x)]$ in the interval mentioned, which makes it possible to evaluate the relative error, Σ_r, made when considering it constant.

Table II gives the values obtained for the factors mentioned in all the peaks analysed, in successive runs of the method. In all the cases, the most satisfactory approximation was considered to be that given by an interval of $0.2 \leqslant x \leqslant 0.6$, which is wide enough to be considered representative of the calculation carried out for the crystallization reaction with the theoretical model used, and possesses adequate correlation coefficients, with small relative errors. We may observe that other intervals give better correlation coefficients, and even smaller relative errors, but it does not seem suitable to choose them because they reduce the crystallized fraction range in which the kinetic description is valid, in exchange for an insignificant improvement in the correlation coefficient and a diminishing Σ_r which, in any case, is already lower than the error inherent in the experimental procedure.

The Avrami exponent of each crystallization process is independently calculated for each exothermal curve corresponding to a heating rate, β. The results obtained for all the experimental heating rates are finally averaged in order to evaluate the reaction order associated with the crystallization process mentioned.

TABLE II Constancy intervals, Δx, linear regression correlation coefficients, r, activation energies, E, variations of function $\ln[K_0 f(x)]$ in the interval, Δ, and relative errors, Σ_r, obtained in the successive repetitions of the proposed method, in both alloys

	Peak	Δx	r	E	Δ	Σ_r
$Cu_{0.05}$ $As_{0.50}$ $Te_{0.45}$	I	0.2–0.7	0.8916	45.6	1.9/43	0.022
		0.2–0.65	0.9203	47.5	1.6/45	0.018
		0.2–0.60	0.9435	48.6	1.4/46	0.015
		0.2–0.55	0.9610	49.5	1.2/47	0.013
		0.2–0.50	0.9732	50.0	1.0/48	0.010
		0.15–0.60	0.9394	47.3	1.4/45	0.016
		0.20–0.61	0.9383	48.4	1.4/46	0.015
	II	0.2–0.70	0.9494	56.5	1.7/52	0.016
		0.2–0.65	0.9737	57.2	1.2/53	0.011
		0.2–0.63	0.9791	57.4	1/53	0.009
		0.2–0.61	0.9824	57.6	0.9/53	0.008
		0.2–0.60	0.9828	57.6	0.9/53	0.008
		0.16–0.60	0.9823	59.5	0.91/55	0.008
$Cu_{0.15}$ $As_{0.40}$ $Te_{0.45}$	I	0.2–0.7	0.9202	44.8	1.5/42	0.018
		0.2–0.65	0.9415	46.3	1.4/44	0.016
		0.2–0.64	0.9449	46.6	1.3/44	0.015
		0.2–0.63	0.9479	47.0	1.3/45	0.014
		0.2–0.60	0.9568	47.8	1.1/46	0.012
		0.18–0.60	0.9565	47.7	1.2/45	0.013
	II	0.2–0.7	0.9790	49.5	0.9/44	0.010
		0.2–0.65	0.9872	51.3	0.7/46	0.008
		0.2–0.63	0.9890	51.6	0.6/46	0.007
		0.2–0.61	0.9900	52.0	0.6/47	0.006
		0.2–0.60	0.9908	52.3	0.5/47	0.005
		0.2–0.60	0.9914	51.8	0.5/46	0.005

TABLE III Kinetic parameters obtained for the crystallization processes of both alloys

	$Cu_{0.05}As_{0.50}Te_{0.45}$		$Cu_{0.15}As_{0.40}Te_{0.45}$	
	Peak I	Peak II	Peak I	Peak II
E (kcal mol^{-1})	48.6	57.6	47.8	52.3
n	1.98	1.83	1.94	1.84
K_0 (sec^{-1})	1.2×10^{20}	1.2×10^{23}	4.5×10^{19}	2.3×10^{20}

TABLE IV Average values of the rate constant, corresponding to the temperature at which crystallization rate is maximum, for the four exothermal peaks analysed, and mean co-ordination of both alloys [13]

	$Cu_{0.05}As_{0.50}Te_{0.45}$		$Cu_{0.15}As_{0.40}Te_{0.45}$	
	Peak I	Peak II	Peak I	Peak II
$\langle K_p \rangle$ (sec^{-1})	0.0108	0.0149	0.0128	0.0177
$\bar{C}$ (at.)	2.44		2.86	

In each case, two experimental values, x_1 and x_2, are taken for the crystallized fraction, and the value of n is calculated by applying Equation 10. In this work, many pairs of values for x were actually taken, inside the interval selected as described above, and the average value obtained was assigned to n.

It must be borne in mind that the mathematical error made in the determination of n, through Equation 10, increases as the values of x_1 and x_2 get closer together, so it is advisable to distinguish previously the minimum difference between the crystallized fractions to be used, in order to keep this mathematical error lower than the experimental error. In this case, we have found that this condition is complied with if the difference between x_1 and x_2 is greater than one-ninth of the amplitude of the constancy interval chosen, that is, $|x_1 - x_2| \geqslant 0.11$.

Finally, the frequency factor is determined by applying Equation 8, where n is substituted by the value previously calculated for each process, and constant C is substituted by the value taken by the function $\ln[K_0 f(x)]$ in the constancy interval for each heating rate. By using different experimental values of the crystallized fraction, it is possible to calculate an average value for $\ln K_0$ corresponding to each heating rate. By carrying out analogous calculations for all the continuous heating experiments corresponding to one exothermal peak, a series of values for $\ln K_0$ is obtained, whose average is the value of the frequency factor associated with the crystallization reaction.

Table III gives the values which were calculated for the kinetic parameters of the alloys under study by following the method described.

According to the common interpretation of the Avrami index [14, 15], the values obtained for it, in the two crystallization stages undergone by each of the alloys, suggest that both go through a one-dimensional critical growth, very near the conditions required for two-dimensional growth. The practical equality between the activation energies obtained in all the cases, and the similarity between the rest of the parameters, indicate that the variation in copper concentration in both alloys did not cause any significant change in the phases in which each one of them crystallizes.

The crystallization reaction rate constants corresponding to the temperature at which the crystallization rate is maximum, K_p, were calculated for each of the thermograms analysed, and by averaging the values found for each exothermal peak of both alloys, at the different experimental heating rates, the values of $\langle K_p \rangle$ shown in Table IV, were obtained which, according to the meaning of the rate constant [16, 17], shows that both compounds exhibit a similar glass forming ability, although it decreases slightly as the copper concentration increases, a fact which agrees with the structural results obtained for both compounds [13]. Composition M2, having a higher co-ordination number than M1, has a greater number of cross-links, which give rise to greater structural rigidity and stability.

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Received 26 June 1989
and accepted 21 February 1990