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A study on glass transition and crystallization kinetics in $Sb_{0.12}As_{0.36}Se_{0.52}$ glassy alloy by using non-isothermal techniques

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Abstract

Crystallization kinetics of the glassy alloy $Sb_{0.12}As_{0.36}Se_{0.52}$ was studied by made using a method in which the kinetic parameters are deduced bearing in mind the dependence of the reaction rate constant on time, through temperature. The method was applied to the experimental data obtained by differential scanning calorimetry, using continuous-heating techniques. In addition, two approaches are used to analyze the dependence of glass transition temperature, T_g, on the heating rate, β. One is empirical linear relationship between T_g and β. The other approach is the use of straight line $\ln(T_g^2/\beta)$ vs. $1/T_g$ for evaluation of the activation energy for glass transition. The kinetic parameters determined have made it possible to find a bulk nucleation mechanism with decreasing nucleation rate and diffusion controlled growth for the crystallization process. The phases at which the alloy crystallizes after the thermal process have been identified by X-ray diffraction. The diffractogram of the transformed material suggests the presence of microcrystallites of Sb_2Se_3 and AsSe, in the residual amorphous matrix. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Glassy alloy; Non-isothermal process; Heating rate; Glass transition temperature; Crystallization kinetics; Crystalline phases

1. Introduction

Amorphous materials themselves are nothing new. Man has been making glasses (mainly silica) for centuries, as is proven by the coloured glass used artistically in cathedrals and other building during the Middle Age. What is relatively recent is the scientific study of amorphous solids. The advances that have been made in the physics and chemistry of these materials, which are also known as glasses, have been widely appreciated within the research community. A strong theoretical and practical interest in the application of isothermal and non-isothermal experimental analysis techniques to the study of phase transformations has been developed in the last decades. While isothermal experimental analysis techniques are in most cases more definitive, non-isothermal thermo-analytical techniques have several advantages. The rapidity with which non-isothermal experiments can be performed makes these types of experiments attractive. There has been an increasingly widespread use of non-isothermal techniques to study solid-state transformations and to determine the kinetic parameters of the rate controlling processes. The techniques have become particularly prevalent for the investigation of the processes of nucleation and growth that occur during transformation of the metastable phases in the glassy alloy as it is heated. These techniques provide rapid information on such parameters as glass transition temperature and transformation enthalpy, temperature, and activation energy over a wide range of temperatures [1,2]. In addition, the physical form and high thermal conductivity as well as the temperature at which transformations occur in most amorphous alloys make these transformations particularly suited to analysis in a differential scanning calorimeter (DSC).

The study of crystallization kinetics in amorphous materials by differential scanning calorimetry methods has been widely discussed in the literature [2–4]. 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 glassy materials obtained in bulk form, which is the case of the alloy $Sb_{0.12}As_{0.36}Se_{0.52}$, submitted to continuous heating experiments, the reaction rate of the process can be expressed as the product of two separable functions of absolute temperature and the fraction crystallized, thus satisfactory kinetic parameters (activation energy, E, reaction order, n, and pre-exponential factor, q, related to the frequency factor) for describing the crystallization reactions can be obtained.

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The present paper studied the crystallization kinetics of glassy alloy $Sb_{0.12}As_{0.36}Se_{0.52}$, which is characterized by aforementioned parameters, using differential scanning calorimetry with continuous-heating techniques. Finally, the crystalline phases corresponding to the crystallization process were identified by X-ray diffraction (XRD) measurements, using CuK_{α} radiation.

2. Theoretical background

In most solid-state transformations the reaction rate can be expressed as the product of two separable functions of absolute temperature, T, and the fraction transformed, x

$$\dot{x} = \frac{dx}{dt} = g(x)h(T) \tag{1}$$

Some authors [5] introduce two further requirements: that $g(x)$ is independent of the heating rate and that the temperature dependence of the reaction rate constant, K, is exponential. Identifying $h(T)$ as K with an Arrhenian temperature dependence results

$$\frac{dx}{dt} = K_0 g(x) \exp\left(-\frac{E}{RT}\right) \tag{2}$$

where K_0 is the frequency factor, E the activation energy of transformation process, and R is the gas constant. To attain the required relationships, Eq. (2) must be integrated by separation of variables and one obtains

$$G(x') = \int_0^{x'} \frac{dx}{g(x)} = K_0 \int_0^{t'} e^{-E/RT} dt \tag{3}$$

The integration is carried out from the beginning of the reaction until some fraction is transformed. It should be noted that the function $G(x')$ is independent of the heating rate used to obtain the transformed fraction x'.

The time integral in Eq. (3) is transformed to a temperature integral by recalling that the heating rate is $\beta = dT/dt$, and by a substitution of variables $y = E/RT$ one obtains

$$G(x') = \frac{-K_0 E}{\beta R} \int_{y_0}^{y'} \frac{e^{-y}}{y^2} dy \tag{4}$$

This integral can be evaluated using the exponential integral function if it is assumed that $T_0 \ll T'$, so that y_0 can be taken as infinity. This assumption is justifiable for any heating treatment which begins at a temperature where nucleation and crystal growth are negligible [6].

The exponential integral function is not integrable in closed form and the authors [7] have developed an approximation to evaluate it. In the case of the exponential integral of order two, $E_2(-y')$, considering that in alternated series the error is less than the first term neglected and bearing in mind that in most transformation reactions $y' = E/RT' \gg 1$ (usually $E/RT' \geq 25$), it is possible to rewrite the Eq. (4), in logarithmic form, without making any appreciable error, yielding

$$\ln[G(x')] = \ln\left(\frac{T'^2}{\beta}\right) + \ln\left(\frac{K_0 R}{E}\right) - \frac{E}{R} \cdot \frac{1}{T'} \tag{5}$$

The Eq. (5) represents a straight line, whose slope yields a value of E/R, which permits to obtain the activation energy of the process. If it can be assumed that the fraction x' at the peak of exotherms, x_p, is constant, then T' can be taken as the temperature at the peak, T_p.

On the other hand, an important kinetic parameter, which supplies information on the reaction mechanism and the dimensionality of the crystal, is the kinetic exponent or reaction order, n. A theoretical expression of the above mentioned parameter can be obtained starting of the volume fraction transformed

$$x = 1 - \exp\left[-Q\left(\frac{KT^2}{\beta}\right)^n\right] \tag{6}$$

deduced by Vázquez et al. [7] from the equation of the evolution with time of the fraction transformed [8].

In this sense, the crystallization rate is obtained by deriving the volume fraction transformed (Eq. (6)) with respect to time, bearing in mind the fact that in non-isothermal processes, the reaction rate constant is a time function through its Arrhenian temperature dependence, resulting in

$$\frac{dx}{dt} = \frac{Qn}{\beta}\left(\frac{KT^2}{\beta}\right)^{n-1}(1-x)\left[T^2\frac{dK}{dt} + 2\beta TK\right] \tag{7}$$

The maximum transformation rate is found by making $d^2x/dt^2 = 0$, thus obtaining the relationship

$$Q\left(\frac{K_p T_p^2}{\beta}\right)^n = 1 - \frac{1}{n}\left\{\left[T_p^4\left(\frac{dK}{dt}\right)_p^2 + 2\beta^2 K_p^2 T_p^2 - K_p T_p^4 \left.\frac{d^2K}{dt^2}\right|_p\right] \times \left[T_p^2 \left.\frac{dK}{dt}\right|_p + 2\beta K_p T_p\right]^{-2}\right\} \tag{8}$$

where the subscript p is denoted to the maximum crystallization rate.

Substituting the first and the second derivative of the reaction rate constant with respect to time, in Eq. (8) and bearing in mind the above mentioned fact that, in most transformation reactions $E \gg RT_p$, it is possible to express the Eq. (7) by following relationship

$$\left.\frac{dx}{dt}\right|_p = n\beta Q\left(\frac{K_p T_p^2}{\beta}\right)^n (1-x_p)\frac{E}{RT_p^2} = 0.37\frac{\beta E}{RT_p^2} n \tag{9}$$

which makes it possible to calculate the reaction order for each heating rate.

Finally, the pre-exponential factor, $q = Q^{1/n} K_0$ in Eq. (6), which measures the probability of effective molecular collisions for the formation of the activated complex, can be obtained from the expression (9), which can be approximated by

$$\frac{T_{\mathrm{p}}^{2}}{\beta} q e^{-E/RT_{\mathrm{p}}} = 1 \qquad (10)$$

where using the above obtained value of the activation energy, E, and the value of the temperature T_{p} for each heating rate it is possible to find different values of the above mentioned factor q (in $(\mathrm{K\,s})^{-1}$). The corresponding mean value may be taken as the most probable value of the pre-exponential factor, related with the frequency factor of the transformation reaction.

3. Experimental details

High purity (99.999%) antimony, arsenic and selenium in appropriate atomic percentage proportions were weighed into a quartz glass ampoule (6 mm diameter). The contents of the ampoule (7 g total) were sealed at a pressure of 10^{-4} Torr (10^{-2} N m^{-2}) and heated in a rotating furnace at around 950°C for 24 h, submitted to a longitudinal rotation of 1/3 rpm in order to ensure the homogeneity of the molten material. It was then immersed in a receptacle containing water in order to solidify the material quickly, avoiding the crystallization of the compound. The amorphous nature of the material was checked through a diffractometric X-ray scan, in a Siemens D500 diffractometer. The thermal behaviour was investigated using a Perkin–Elmer DSC7 differential scanning calorimeter. The temperature and energy calibrations of the instrument were performed, for each heating rate, using the well-known melting temperatures and melting enthalpies of high-purity zinc and indium supplied with the instrument. Powdered samples weighing about 20 mg (particle size ~ 40 μm) were crimped in aluminium pan and scanned from room temperature through their glass transition temperatures, T_{g}, at different heating rates of 1, 2, 4, 8, 16, 32 and 64 K min^{-1}. An empty aluminium pan was used as reference and in all cases a constant flow of nitrogen was maintained in order to drag the gases emitted by the reaction, which are highly corrosive to the sensory equipment installed in the DSC furnace. The glass transition temperature was considered as a temperature corresponding to the intersection of the two linear portions adjoining the transition elbow in the DSC trace, as is shown in Fig. 1.

The crystallized fraction, x, at any temperature, T, is given as $x = A_T/A$, where A is the total area of the exotherm between the temperature, T_{i}, where the crystallization just begins and the temperature, T_{f}, where the crystallization is completed and A_T is the area between the initial temperature and a generic temperature T, see Fig. 1.

With the aim of investigating the phases at which the samples crystallize during thermal process, diffractograms of the material transformed after the process were obtained. The experiments were performed with a Philips diffractometer (type PW 1830). The patterns were run with Cu as target and Ni as filter ($\lambda = 1.542$ Å) at 40 kV and 40 mA, with a scanning speed of 0.1 deg s^{-1}.

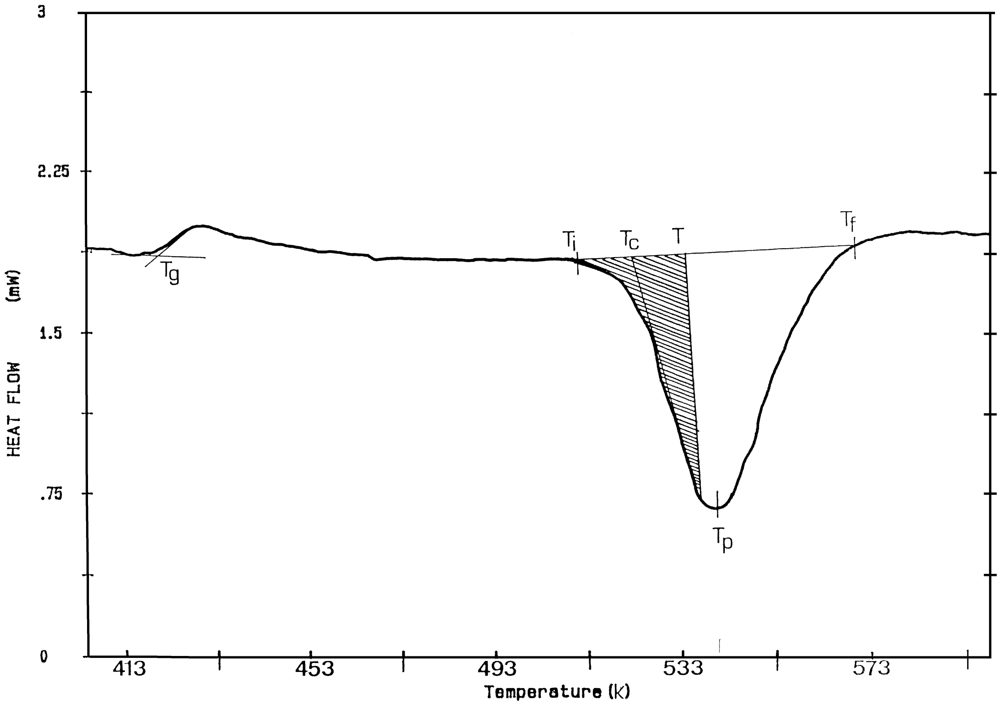

Fig. 1. Typical DSC trace of $\mathrm{Sb_{0.12}As_{0.36}Se_{0.52}}$ glassy alloy at a heating rate 4 K min^{-1}. Hatched area shows A_T, the area between T_{i} and T.

4. Results and discussion

The typical DSC trace of $Sb_{0.12}As_{0.36}Se_{0.52}$ chalcogenide glass obtained at a heating rate of 4 K min^{-1} and plotted in Fig. 1 shows three characteristic phenomena in the studied temperature region. The first one ($T = 425$ K) corresponds to the glass transition temperature, T_g, the second one ($T = 525$ K) to the extrapolated onset crystallization temperature, T_c, and the last one ($T = 543$ K) to the peak temperature of crystallization T_p of the above mentioned chalcogenide glass. This behaviour is typical for a glass-crystalline transformation. The values of temperature T_g, T_c and T_p increase by increasing the heating rate, β.

4.1. The glass transition

Two approaches are used to analyze the dependence of T_g on the heating rate. One is the empirical relationship of the form $T_g = A + B \ln\beta$, where A and B are constants for a given glass composition [9]. This has been originally suggested based on results for $Ge_{0.15}Te_{0.85}$ glass. The results shown in Fig. 2 indicate the validity of this relationship for the $Sb_{0.12}As_{0.36}Se_{0.52}$ chalcogenide glass. For this glass, the empirical relationship can be written in the form

$$T_g = 458.5 + 11.943 \ln\beta \qquad (11)$$

where a straight regression line has been fitted to the experimental data.

The other approach is the use of the Eq. (5) for the evaluation of the activation energy for glass transition, E_g. For homogeneous crystallization with spherical nuclei, it has been shown [10,11] that the dependence of crystallization temperature on β is given by

$$\ln\left(\frac{T_c^2}{\beta}\right) = \frac{E}{R}\frac{1}{T_c} + \text{constant} \qquad (12)$$

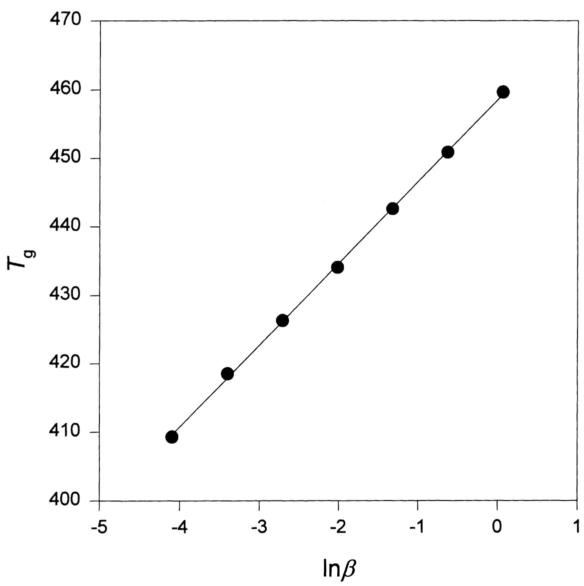

Fig. 2. Glass transition temperature vs. lnβ of $Sb_{0.12}As_{0.36}Se_{0.52}$ alloy.

Though originally deduced for the crystallization process, it is suggested that this expression is valid in very general case [12] and has often been used [10–13] to calculate E_g.

In addition, the activation energy for glass transition can also be evaluated assuming that, usually, the change of $\ln(T_g^2)$ with β is negligibly small compared with the change of lnβ [14–16]. Thus, it is possible to write the Eq. (5) as

$$\ln\beta = -\frac{E_g}{R}\frac{1}{T_g} + \text{constant} \qquad (13)$$

a straight line, whose slope yields a value of E_g and where the subscript g denotes to the glass transition temperature.

Fig. 3 shows the plots of $\ln(T_g^2/\beta)$, curve (a) and lnβ, curve (b), vs. $1/T_g$ for the $Sb_{0.12}As_{0.36}Se_{0.52}$ chalcogenide glass, where it is observed the linearity of the used equations. The obtained values of the activation energy for glass transition are respectively 29.8 kcal/mol (plot (a)) and 31.5 kcal/mol (plot (b)). It is observed that the values obtained agree with the quoted data in the literature for similar compounds [17,18].

4.2. The crystallization

The usual analytical methods, proposed in the literature for analyzing the crystallization kinetics in glass-forming liquids, assume that the reaction rate constant can be defined by an Arrhenian temperature dependence. In order for this assumption to hold, one of the following two sets of conditions should apply:

1. The crystal growth rate, u, has an Arrhenian temperature dependence; and over the temperature range where

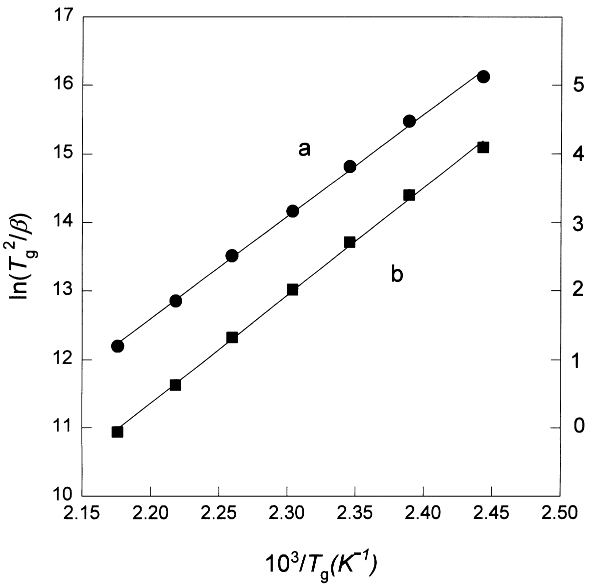

Fig. 3. (a) Plot of $\ln(T_g^2/\beta)$ vs. $10^3/T_g$ of analyzed material. (b) Plot of lnβ vs. $10^3/T_g$ of studied glass.

Table 1
The characteristic temperatures, enthalpy of the crystallization process of $Sb_{0.12}As_{0.36}Se_{0.52}$ alloy. Maximum crystallization rates, reaction order and pre-exponential factor for different heating rates

β (K min^{-1})	$(dx/dt)\|_p$ (s^{-1})	T_g (K)	T_i (K)	T_p (K)	ΔT (K)	ΔH (mcal mg^{-1})	n	$<n>$	$q=Q^{1/n}K_0$ ((K s)$^{-1}$)	$<q>$ ((K s)$^{-1}$)
1	0.00096	409.3	503.8	523.5	36.0	4.2	2.61		2.33×10^6	
2	0.00164	419.1	509.3	533.2	44.8	4.4	2.31		2.54×10^6	
4	0.00275	425.4	512.9	542.6	55.5	4.8	2.00		2.88×10^6	
8	0.00489	434.0	520.3	553.4	64.2	4.9	1.85	1.91	3.07×10^6	2.76×10^6
16	0.00918	443.2	525.6	562.6	65.3	5.0	1.80		3.67×10^6	
32	0.01155	450.8	528.0	582.7	80.2	5.3	1.21		2.50×10^6	
64	0.02545	459.6	534.8	597.7	80.1	5.3	1.41		2.35×10^6	

the thermoanalytical measurements are carried out, the nucleation rate is negligible (i.e., the condition of site saturation).

2. Both the crystal growth and the nucleation frequency have Arrhenian temperature dependences.

In the present work is assumed the second condition, and therefore, the overall effective activation energy for crystallization, E_c, is given by the relationship [7]

$$E_c = \frac{E_N + mE_G}{n}$$

where E_N and E_G are the effective activation energies for nucleation and growth respectively, m is a dimensionless quantity, which depends on the mechanism of growth and the dimensionality of the crystal and n is the reaction order. From this point of view, and considering that, in most crystallization processes, the overall activation energy is much larger than the product RT, the crystallization kinetics of the alloy $Sb_{0.12}As_{0.36}Se_{0.52}$ may be studied according to the appropriate approximation, described in the preceding theory.

With the aim of analyzing the crystallization kinetics of the above mentioned alloy, the magnitudes described by the thermograms, for the different heating rates, quoted in Section 3, are obtained and given in Table 1, where T_i and T_p are the temperatures at which crystallization begins and that corresponding to the maximum crystallization rate, respectively, ΔT is the width of the peak and ΔH is the crystallization enthalpy.

The area under DSC curve is directly proportional to the total amount of alloy crystallized. The ratio between the ordinates and the total area of the peak gives the corresponding crystallization rates, which makes it possible to build the curves of the exothermal peaks represented in Fig. 4. The $(dx/dt)_p$ values increase in the same proportion that the heating rate, a property which has been widely discussed in the literature [19].

The plot of $\ln(T_p^2/\beta)$ vs. $1/T_p$ at each heating rate and its straight regression line is shown in Fig. 5. From the slope of this experimental straight line it is possible to deduce the value of the activation energy, $E = 32.7$ kcal mol^{-1}, for the

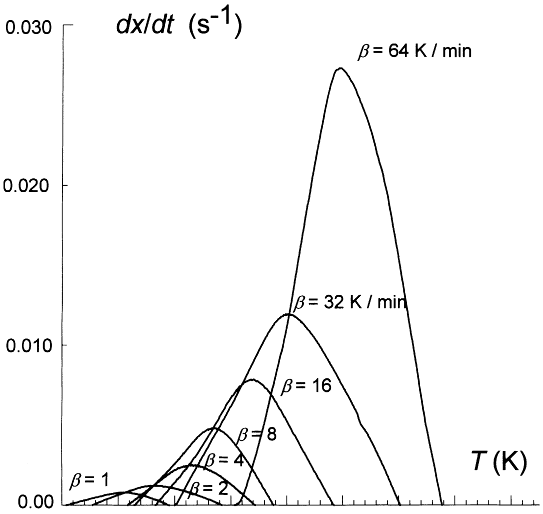

Fig. 4. Crystallization rate, vs. temperature, of the exothermal peaks at different heating rates.

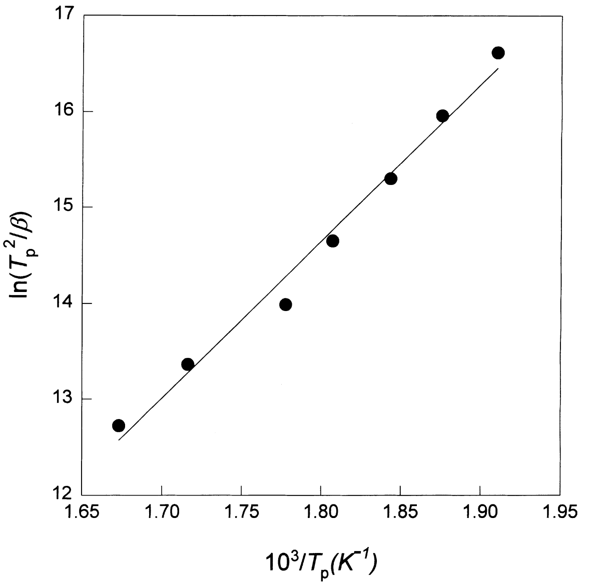

Fig. 5. Experimental plot of $\ln(T_p^2/\beta)$ vs. $10^3/T_p$ and straight regression line of $Sb_{0.12}As_{0.36}Se_{0.52}$ alloy (β in K s^{-1}).

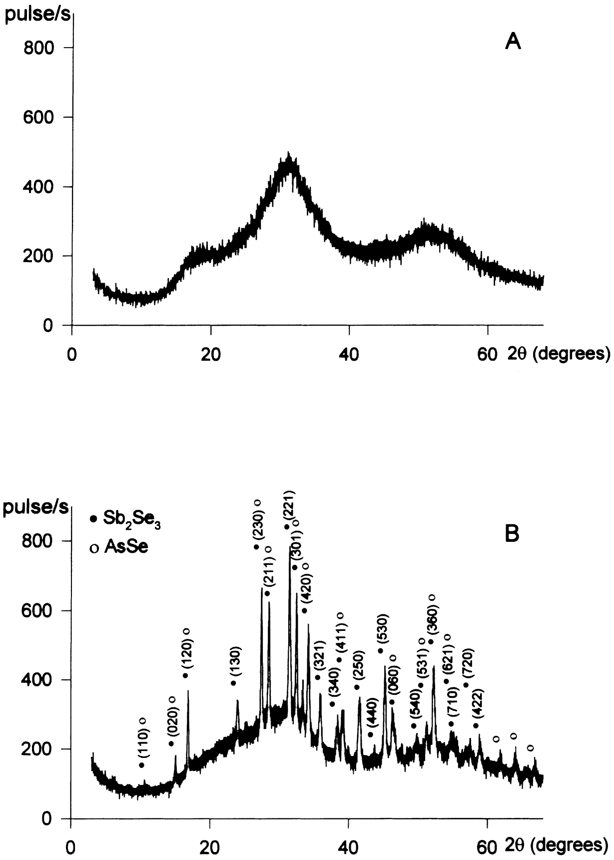

Fig. 6. (A) Diffractogram of amorphous alloy $Sb_{0.12}As_{0.36}Se_{0.52}$. (B) Diffraction peaks of alloy crystallized in DSC.

crystallization process studied. The experimental data T_p and $dx/dt|_p$ (see Table 1), which correspond to the maximum crystallization rate for each heating rate and the above mentioned value of the activation energy make it possible to determine, through relationship (9), the reaction order, n, whose values are also given in Table 1.

Finally, the values of the pre-exponential factor, q, shown in Table 1, have been obtained from the expression (10), by using the above deduced value of the activation energy and the value of T_p (see Table 1) for each heating rate.

It should be noted that the calorimetric analysis is an indirect method to obtain mean values for the parameters which control the kinetics of a reaction. The mentioned mean values in this study were given in Table 1. From these mean values and the Avrami theory of nucleation, the value found for the pre-exponential factor (related to the probability of molecular collisions) seems to confirm that, there is a diffusion controlled growth, coherent with the basic formalism used.

Bearing in mind the usual criteria for the interpretation of reaction order [8,20,21] some observations relating to the morphology of the growth can be worked out. In glassy alloy $Sb_{0.12}As_{0.36}Se_{0.52}$ there is a relatively stable crystallization phase ($E = 32.7$ kcal mol^{-1}) exhibiting a bulk nucleation mechanism and in accordance with the literature [8] the exponential growth law of Avrami [22–24] is valid for growth under most circumstances, and approximately valid for the early stages of diffusion controlled growth. The crystalline phase may exhibit all shapes growing from small dimensions, decreasing nucleation rate, since the mean value of the reaction order, $<n> = 1.91$, is within the interval (1.5–2.5) [8].

5. Identification of the crystalline phases

For the purpose to identify the possible phases that crystallize during the thermal treatment supplied to the samples, these were submitted to a XRD measurements. In Fig. 6 it is shown the significant portion of diffractometer recording for the glassy alloy $Sb_{0.12}As_{0.36}Se_{0.52}$, as-quenched and crystallized after the thermal process, respectively. Trace A of Fig. 6 has broad humps characteristic of the amorphous phase of the starting material at diffraction angles (2θ) between 20° and 60°. The diffractogram of the transformed material after the crystallization process (trace B) suggests the presence of microcrystallites of Sb_2Se_3 and AsSe, indexed in the pattern, respectively, with • and ○, remaining an residual amorphous phase. The found Sb_2Se_3 phase crystallizes in the orthorhombic system [25] with a cell unit defined by $a = 11.633$ Å, $b = 11.78$ Å and $c = 3.895$ Å.

6. Conclusions

Crystallization of bulk $Sb_{0.12}As_{0.36}Se_{0.52}$ glass has been studied using calorimetric and X-ray powder diffraction techniques. The study of crystallization kinetics was made using a method in which the kinetic parameters are deduced bearing in mind the dependence of the reaction rate constant on time. This method for thermal analysis of glassy alloys proved to be efficient and accurate, giving results which were in good agreement with the nature of the alloy under study, which are representative of a nucleation and crystalline-growth process, according to the value found for the reaction order. In addition, two approaches have been used to analyze the glass transition. One has been the linear dependence of the glass transition temperature on logarithm of the heating rate. The other approach has been the linear relationship between the logarithm of the quotient T_g^2/β and the reciprocal of the glass transition temperature. Finally, the identification of the crystalline phases was done by recording the XRD pattern of the transformed material. This pattern shows the existence of microcrystallites of Sb_2Se_3 and AsSe in an amorphous matrix.

Acknowledgements

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