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Kinetic study of non-isothermal crystallization in $Sb_{0.18}As_{0.34}Se_{0.48}$ glassy alloy

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Abstract

A study of the crystallization kinetics of glassy alloy $Sb_{0.18}As_{0.34}Se_{0.48}$ was made using a method in which the kinetic parameters were 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, from the heating rate dependence of the glass transition temperature, the glass transition activation energy was derived. The kinetic parameters determined have made it possible to discuss the type of nucleation and crystal growth exhibited in 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, remaining an additional amorphous matrix.

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

1. Introduction

Traditionally, solid state physics has meant crystal physics. Solidity and crystallinity are considered as synonymous in the texts on condensed matter. Yet one of the most active fields of solid state research in recent years has been the study of solids that are not crystals, solids in which the arrangement of the atoms lacks the slightest vestige of long-range order. The advances that have been made in the physics and chemistry of these materials, which are known as amorphous solids or glasses, have been widely appreciated within the research community. The last decades have seen a strong theoretical and experimental interest in the application of isothermal and non-isothermal experimental analysis techniques to the study of phase transformations. While isothermal experimental analysis techniques are, in most cases, more definitive, non-isothermal thermoanalytical techniques have several advantages. The rapidity with which non-isothermal experiments can be performed makes these types of experiment 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 determination of the thermal stability of amorphous alloys and in 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 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 [2–5]. There is a large variety of theoretical models and theoretical functions proposed to explain the crystallization kinetics. The application of each depends on the type of amorphous material studied and how it was made. For glassy materials obtained in bulk form, which is the case for the alloy $Sb_{0.18}As_{0.34}Se_{0.48}$, submitted to continuous heating experiments, it is usual to consider the reaction rate of the process as

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expressed by the product of two separable functions of absolute temperature and fraction crystallized, thus obtaining satisfactory kinetic parameters (activation energy E, reaction order n, and pre-exponential factor q related to the frequency factor) describing the crystallization reactions.

The present paper studies the crystallization kinetics of the glassy alloy $Sb_{0.18}As_{0.34}Se_{0.48}$, which is characterized by the 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 Cu Kα radiation.

2. Theoretical background

In the derivation of relationships for calculating kinetic parameters of the solid state transformations it is useful to examine the parametric dependence of the rate $\dot{x}$ of fraction transformed per unit time t. Any operation on dx/dt, such as differentiation or integration, is greatly simplified if the reaction rate can be expressed as the product of two separable functions of absolute temperature T and fraction transformed

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

i.e. if the dependence of $\dot{x}$ on temperature can be separated from its dependence on x. There are a number of ways in which $g(x)$ and $h(T)$ can be formulated, since both x and T are functions of time t. Different methods of analyzing DSC and DTA experiments result from different definitions of $g(x)$ and $h(T)$. It should be noted that use of Eq. (1), the separation of variables approximation, introduces an additional assumption into the analysis. Although the uncertainty introduced by this assumption is difficult to evaluate a priori, the method of separation of variables is frequently used in the literature to analyze transformation reactions. Some authors introduce two further requirements: that $g(x)$ is independent of the heating rate (i.e. independent of thermal history) and that the temperature dependence of the reaction rate constant K is exponential. Identifying $h(T)$ as K with an Arrhenius type temperature dependence leads to

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

where K_0 is the frequency factor, E the activation energy of the transformation process, and R the gas constant. Note that neither the order nor even the type of transformation kinetics (i.e. the form of $g(x)$) need be specified. The only constraints imposed on the kinetics by the above requirements are that only one parameter in the rate equation can be temperature dependent and that only a single rate controlling mechanism is operating throughout.

To obtain the required relationships, Eq. (2) must be integrated by separation of variables to obtain

$$G(x') = \int_0^{x'} \frac{dx}{g(x)} = K_0 \int_0^t \exp\left(\frac{-E}{RT}\right) dt \quad (3)$$

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 $\beta = dT/dt$, yielding

$$G(x') = \frac{K_0}{\beta} \int_{T_0}^{T'} \exp\left(\frac{-E}{RT}\right) dt \quad (4)$$

where T_0 is the initial temperature of the heating process. The integral of Eq. (4) may be rewritten by a substitution of variables, $y = E/RT$

$$G(x') = -\frac{K_0 E}{\beta R} \int_{y_0}^{y'} \frac{\exp(-y)}{y^2} dy \quad (5)$$

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 ∞. This assumption is justifiable for any heat treatment which begins at a temperature where nucleation and crystal growth are negligible, i.e. below T_g (glass transition temperature) for most glass-forming systems.

The exponential integral function is not integrable in closed form and the authors have developed the following approximation to evaluate it. Considering the exponential integral function of order p

$$E_p(-y') = \int_{y'}^{\infty} \exp(-y) y^{-p} dy$$

and using the method of integration by parts with substitutions $dv = \exp(-y)dy$ and $u = y^{-p}$ one obtains the relationship

$$E_p(-y') = \exp(-y')y'^{-p} - p \int_{y'}^{\infty} \exp(-y) y^{-p-1} dy$$

reiterating the integration process, the function $E_p(y')$ may be expresed by the series

$$E_p(-y') = \exp(-y')y'^{-p} \sum_{n=0}^{\infty} \frac{(-1)^n (p+n-1)!}{y'^n (p-1)!}$$

When only the first term of this series is used, the exponential integral function can be approximated by

$$E_p(-y') = \int_{y'}^{\infty} \exp(-y) y^{-p} \mathrm{d}y \approx \exp(-y') y'^{-p}$$

In the case of the exponential integral of order two, $E_2(-y')$, used for the thermal analysis studied in this work, considering that in alternate 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 Eq. (5) without making any appreciable error, yielding

$$G(x') = \frac{K_0 R}{E} \frac{T'^2}{\beta} \exp\left(\frac{-E}{RT'}\right)$$

or, in a logarithmic form

$$\ln[G(x')] = \ln\left(\frac{T'^2}{\beta}\right) + \ln\left(\frac{K_0 R}{E}\right) - \frac{E}{R}\frac{1}{T'} \tag{6}$$

Assuming that the function $G(x')$ is independent of the heating rate and therefore a fixed fraction transformed, x', can be identified in a set of exotherms taken at different heating rates, Eq. (6) represents a straight line, whose slope yields a value of E/R which permits us 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.

In contrast, 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 with the volume fraction transformed

$$x = 1 - \exp\left[-Q\left(\frac{KT^2}{\beta}\right)^n\right] \tag{7}$$

deduced by Vázquez et al. [6] from the equation of the evolution with time of the fraction transformed in terms of the nucleation frequency per unit volume I_v and the crystal growth rate u

$$x = 1 - \exp\left[-g\int_0^t I_v\left(\int_{t'}^t u\,\mathrm{d}\tau\right)^m \mathrm{d}t'\right]$$

where g is a geometric factor and m is an integer or half integer which depends on the mechanism of growth and the dimensionality of the crystal.

In this sense, the crystallization rate is obtained by deriving the volume fraction transformed (Eq. (7)) with respect to time, bearing in mind the fact that, in non-isothermal processes, the reaction rate constant is a time function through its Arrhenius type temperature dependence, resulting in

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{Qn}{\beta}\left(\frac{KT^2}{\beta}\right)^{n-1}\left[T^2\frac{\mathrm{d}K}{\mathrm{d}t} + 2\beta KT\right]\exp\left[-Q\left(\frac{KT^2}{\beta}\right)^n\right]$$

Substituting the exponential function by its given value in Eq. (7), one obtains

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{Qn}{\beta}\left(\frac{KT^2}{\beta}\right)^{n-1}(1-x)\left[T^2\frac{\mathrm{d}K}{\mathrm{d}t} + 2\beta KT\right] \tag{8}$$

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

$$\begin{aligned} Q\left(\frac{K_pT_p^2}{\beta}\right) = 1 &- \frac{1}{n}\left\{\left[T_p^4\left(\left.\frac{\mathrm{d}K}{\mathrm{d}t}\right|_p\right)^2 + 2\beta^2K_p^2T_p^2\right.\right. \\ &\left.- K_pT_p^4\left.\frac{\mathrm{d}^2K}{\mathrm{d}t^2}\right|_p\right]\left[T_p^2\left.\frac{\mathrm{d}K}{\mathrm{d}t}\right|_p \right. \\ &\left.\left. + 2\beta K_pT_p\right]^{-2}\right\} \end{aligned} \tag{9}$$

where subscript p now denotes the magnitude values corresponding to the maximum crystallization rate.

Taking the first and second derivative of the reaction rate constant with respect to time results in

$$\left.\frac{\mathrm{d}K}{\mathrm{d}t}\right|_p = \frac{\beta K_pE}{RT_p^2} \quad \text{and} \quad \left.\frac{\mathrm{d}^2K}{\mathrm{d}t^2}\right|_p = \frac{\beta^2K_pE}{RT_p^3}\left(\frac{E}{RT_p} - 2\right)$$

Substituting these expressions into Eq. (9) yields

$$Q\left(\frac{K_pT_p^2}{\beta}\right)^n = 1 - \frac{2}{n}\left(1 + \frac{E}{RT_p}\right)\left(2 + \frac{E}{RT_p}\right)^{-2} \tag{10}$$

which relates the kinetic parameters E and n with the magnitude values that can be experimentally determined, and which correspond to the maximum transformation rate.

Bearing in mind the above mentioned fact that in most transformation reactions $E \gg RT_p$, it is possible to express Eq. (8) by the following relationship

$$\begin{aligned} \left.\frac{\mathrm{d}x}{\mathrm{d}t}\right|_p &= n\beta Q\left(\frac{K_pT_p^2}{\beta}\right)^n(1-x_p)\frac{E}{RT_p^2} \\ &= 0.37\frac{\beta E}{RT_p^2}n \end{aligned} \tag{11}$$

which makes it possible to calculate the reaction order for each heating rate. The corresponding mean value may be considered as the most probable value of the reaction order of the transformation reaction.

Finally, the pre-exponential factor $q = Q^{1/n}K_0$ in Eq. (7), which measures the probability of effective molecular collisions for the formation of the activated complex, can be obtained from the expression (10), which can be approximated by

$$\frac{T_p^2}{\beta} q \exp\left(\frac{-E}{RT_p}\right) = 1 \qquad (12)$$

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 (K s)$^{-1}$). The corresponding mean value may be taken as the most probable value of the pre-exponential factor, related to the frequency factor of the transformation reaction.

3. Experimental details

High purity (99.999%) antimony, arsenic and selenium in appropriate atomic per cent 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 rev min^{-1} in order to ensure the homogeneity of the molten material. It was then immersed in a recepticle containing water in order to solidify the material quickly, avoiding crystallization of the compound. The amorphous nature of the material was checked through a diffractometric X-ray scan, in a Siemens D500 diffractometer. The homogeneity and composition of the sample were verified through SEM in a Jeol, scanning microscope JSM-820. The thermal behaviour was investigated using a Perkin–Elmer DSC 7 differential scanning calorimeter. 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 (particles size around 40 μm) were crimped in an aluminium pan and scanned at room temperature through their glass transition temperature T_g at different heating rates: 1, 2, 4, 8, 1, 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 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 is just beginning and the temperature T_f where the crystallization is complete 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 into which the samples crystallize, diffractograms of the material crystallized during DSC 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 (λ =

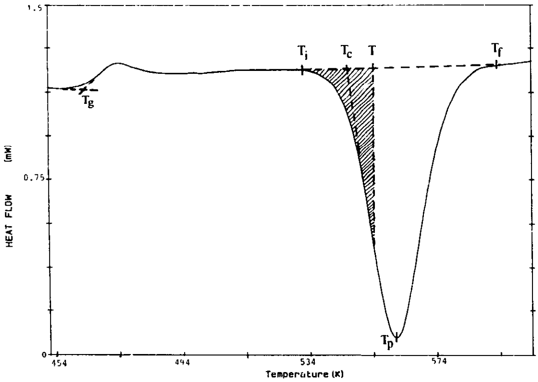

Fig. 1. Typical DSC trace of $Sb_{0.18}As_{0.34}Se_{0.48}$ glassy alloy at a heating rate 4 K min^{-1}. The hatched area shows A_T, the area between T_i and T.

1.542 Å) at 40 kV and 40 mA, with a scanning speed of 0.1° s^{-1}.

4. Results and discussion

The typical DSC trace of $Sb_{0.18}As_{0.34}Se_{0.48}$ chalcogenide glass obtained at a heating rate of 4 K min^{-1} and plotted in Fig. 1 shows three characteristic phenomena which are resolved in the temperature region studied. The first ($T = 464.1$ K) corresponds to the glass transition temperature T_g, the second ($T = 546.0$ K) to the extrapolated onset crystallization temperature T_c, and the third ($T = 561.3$ 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 temperature values T_g, T_c and T_p increase with increasing 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 [7]. This was 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 $Sb_{0.18}As_{0.34}Se_{0.48}$ chalcogenide glass. For this glass, the empirical relationship can be written in the form

$$T_g = 47.6 + 4.6262\ln\beta \qquad (13)$$

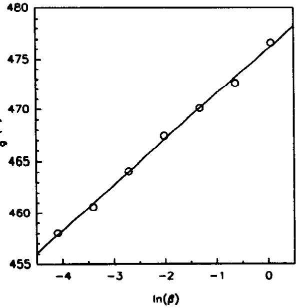

Fig. 2. Glass transition temperature versus ln β (β in K s^{-1}) of $Sb_{0.18}As_{0.34}Se_{0.48}$ alloy.

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

The other approach is the use of Eq. (6) for the evaluation of the activation energy E_g of the glass transition. For homogeneous crystallization with spherical nuclei, it has been shown [8,9] that the dependence of the crystallization temperature on β is given by

$$\ln\left(\frac{T_c^2}{\beta}\right) = \frac{E}{R}\frac{1}{T_c} + \text{constant} \qquad (14)$$

Though originally deduced for the crystallization process, it is suggested that this expression is valid in a very general sense [10], and it has often been used [8–11] to calculate E_g.

The activation energy for glass transition can also be evaluated from Eq. (10), bearing in mind that in most transformation reactions $E_g \gg RT_g$. It is therefore possible to write Eq. (10) as

$$Q\left(\frac{K_g T_g^2}{\beta}\right)^n = 1 \qquad (15)$$

where subscript g denotes magnitude values corresponding to the glass transition temperature. Taking the logarithm of Eq. (15) and assuming that, usually, the change in $\ln T_g^2$ with β is negligibly small compared with the change in $\ln\beta$ [12–14], one obtains

$$\ln\beta = \frac{E_g}{R}\frac{1}{T_g} + \text{constant} \qquad (16)$$

a straight line, whose slope yields a value of E_g.

Fig. 3 shows plots of $\ln(T_g^2/\beta)$ (curve a) and $\ln\beta$ (curve b) vs. $1/T_g$ for the $Sb_{0.18}As_{0.34}Se_{0.48}$ chalcogenide glass, displaying the linearity of the equations used. The values of the activation energy obtained for the glass transition are 95.8 Kcal mol^{-1} (plot

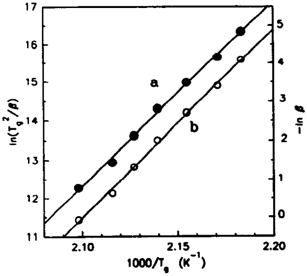

Fig. 3. (a) Plot of $\ln(T_g^2/\beta)$ vs. $1000/T_g$ of the analyzed material. (b) Plot of ln β vs. $1000/T_g$ of the studied glass (β in K s^{-1}).

a) and 97.7 Kcal mol^{-1} (plot b) respectively. It is observed that the obtained values agree with the data quoted in the literature for similar compounds [15,16].

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 Arrhenius type temperature dependence. In order for this assumption to hold, one of the following two sets of conditions should apply.

(i) The crystal growth rate u has an Arrhenius type temperature dependence and, over the temperature range where the thermoanalytical measurements are carried out, the nucleation rate is negligible (i.e. the condition of site saturation).

(ii) Both the crystal growth and the nucleation frequency have Arrhenius type temperature dependences.

In the present work it is assumed that the second condition holds, and therefore the overall effective activation energy for crystallization, E_c, is given by the relationship [6]

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

where E_N and E_G are the effective activation energies for nucleation and growth respectively, and m is an integer or half integer which depends on the mechanism of growth and the dimensionality of the crystal. From this point of view, and bearing in mind the above mentioned fact that in most crystallization processes the overall activation energy is much larger than the product RT, the crystallization kinetics of the alloy $Sb_{0.18}As_{0.34}Se_{0.48}$ may be studied according to the appropriate approximation described in the preceding theory section.

With the aim of analyzing the crystallization kinetics of the above mentioned alloy, the variation intervals of 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, and ΔT is the width of the peak. The crystallization enthalpy ΔH is also determined for each of the above mentioned heating rates.

Table 1
The characteristic temperatures and enthalpies of the crystallization process of alloy $Sb_{0.18}As_{0.34}Se_{0.48}$

Parameter	Experimental value
T_g (K)	458.0–476.7
T_i (K)	514.4–570.3
T_p (K)	544.1–605.1
ΔT (K)	54.2–62.1
ΔH (mcal mg^{-1})	7.6–8.5

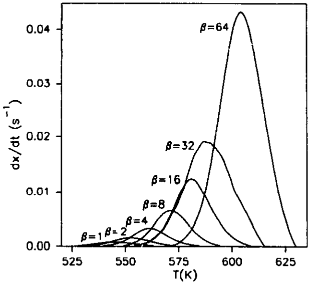

Fig. 4. Crystallization rate versus temperature of the exothermal peaks at different heating rates.

The area under the 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. It may be observed that the $(dx/dt)_p$ values increase in the same proportion as the heating rate, a property which has been widely discussed in the literature [17].

From the experimental data a plot of $\ln(T_p^2/\beta)$ vs. $1/T_p$ has been drawn at each heating rate, and also the straight regression line shown in Fig. 5. From the slope of this experimental straight line it is possible to deduce the value of the activation energy, $E =$

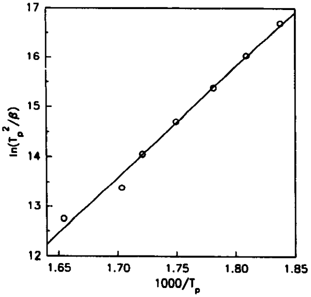

Fig. 5. Experimental plot of $\ln(T_p^2/\beta)$ vs. $1000/T_p$ and straight regression lines of $Sb_{0.18}As_{0.34}Se_{0.48}$ alloy (β in K s^{-1}).

Table 2
The maximum crystallization rate, corresponding temperature, reaction order and pre-exponential factor for the different heating rates

β (K min^{-1})	$(dx/dt)_p$ (s^{-1})	T_p (K)	n	$\langle n \rangle$	$q = Q^{1-1/n}K_0$ ((K s)$^{-1}$)	$\langle q \rangle$ ((K s)$^{-1}$)
1	0.00076	544.1	1.65		2.69×10^{10}	
2	0.00120	553.8	1.35		2.55×10^{10}	
4	0.00333	561.3	1.92		2.91×10^{10}	
8	0.00661	571.6	1.98	1.73	2.75×10^{10}	2.83×10^{10}
16	0.01227	581.0	1.90		2.85×10^{10}	
32	0.02314	587.0	1.82		3.78×10^{10}	
64	0.03558	605.1	1.49		2.30×10^{10}	

44.3 Kcal mol^{-1}, for the crystallization process studied. The experimental data T_p and $dx/dt|_p$ shown in Table 2, 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 (11), the reaction order n for each of the experimental heating rates, whose values are also given in Table 2.

Finally, the values of the pre-exponential factor q shown in Table 2 have been obtained from the expression (12) using the above deduced value of the activation energy and the value of T_p (see Table 2) for each heating rate.

Bearing in mind that the calorimetric analysis is an indirect method which only makes it possible to obtain mean values for the parameters which control the kinetics of a reaction, the mentioned mean values were obtained and are also given in Table 2. From these mean values and according to the Avrami theory of nucleation, the relatively high value found for the pre-exponential factor (related to the probability of molecular collisions) seems to confirm the fact that in the crystallization reaction mechanism there is a diffusion controlled growth, coherent with the basic formalism used.

Unambiguous conclusions on the crystalline growth morphology can only be deduced if, together with the thermal analysis carried out, direct techniques of electron microscopy are applied. However, in the absence of these and using the usual criteria for the interpretation of reaction order [18–20], some observations relating to the morphology of the growth can be worked out. In the glassy alloy $Sb_{0.18}As_{0.34}Se_{0.48}$ there is a relatively stable crystallization phase ($E = 44.3$ Kcal mol^{-1}), exhibiting a bulk nucleation mechanism, and according to the literature [16] the crystalline phase may exhibit all shapes growing from small dimensions with decreasing nucleation rate, since the mean value of the reaction order, $\langle n \rangle \geq 1.73$, is included in the interval 1.5–2.5.

5. Identification of the crystalline phases

Taking into account the crystallization exothermal peaks shown by the glassy alloy $Sb_{0.18}As_{0.34}Se_{0.48}$, it is recommended to try to identify the possible phases that crystallize during the thermal treatment applied to the samples by means of adequate XRD measurements. For this purpose, in Fig. 6 we show the most relevant portions of the diffractometer tracings for an as-quenched glass and for the material submitted to the thermal process. 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, indexed with * in the pattern, while there remains also an additional amorphous phase. The Sb_2Se_3 phase found crystallizes in the orthorhombic system [21] with a unit cell defined by $a = 11.633$, $b = 11.78$ and $c = 3.895$ Å.

All the peaks in the diffractogram of the transformed material can be identified as those of crystalline Sb_2Se_3, except one of the doubles at $2\theta = 27.43°$

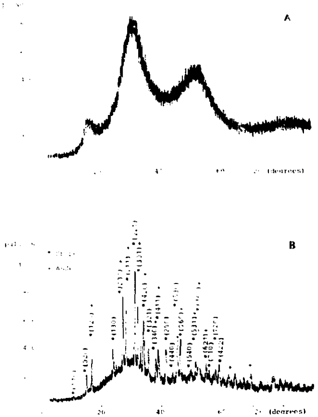

Fig. 6. (A) Diffractogram of amorphous alloy $Sb_{0.18}As_{0.34}Se_{0.48}$. (B) Diffraction peaks of alloy crystallized in DSC.

and $2\theta = 27.55°$, which corresponds to the highest intensity line in the crystalline AsSe diffraction pattern (marked +) [22]. This assumption would also explain the high intensity of some lines, like $2\theta = 16.92°$, 34.22°, 35.87°, 39.05°, 46.28°, which correspond to lines appearing in the c-AsSe diffraction pattern. Furthermore, the composition of the amorphous material is close to the line Sb_2Se_3–AsSe, within the margin of error.

6. Conclusions

Crystallization of bulk $Sb_{0.18}As_{0.34}Se_{0.48}$ 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 in good agreement with the nature of the alloy under study and 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 is the linear dependence of the glass transition temperature on the logarithm of the heating rate. The other is the linear relationship between the logarithm of the quotient T_g^2/β and the reciprocal of the glass transition temperature. Finally, identification of the crystalline phases was made by recording the X-ray diffraction pattern of the transformed material. This pattern shows the existence of microcrystallites of Sb_2Se_3 and AsSe in an amorphous matrix.

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