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Glass transition and crystallization kinetics in $Sb_{0.18}As_{0.34}Se_{0.48}$ glassy alloy by using non-isothermal techniques

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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 the formal theory of transformations for heterogeneous nucleation, case referred to as “site saturation”. The kinetic parameters were deduced, bearing in mind the dependence of the reaction rate constant on time, through temperature. The procedure was applied to the experimental data obtained by differential scanning calorimetry (DSC), 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 postulate the type of 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 indicates the presence of microcrystallites of Sb_2Se_3 and AsSe, remaining an additional amorphous matrix. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

The last decades have seen a strong theoretical and practical 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 glasssy alloy as it is heated. These techniques provide rapid information on such parameters as glass transition temperature, T_g, and transformation enthalpy, temperature and activation energy over a wide range of temperature [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 by differential scanning calorimetry (DSC).

The study of crystallization kinetics in amorphous materials by DSC 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

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was made. For glassy materials obtained in bulk form, which is the case for the $Sb_{0.18}As_{0.34}Se_{0.48}$, submitted to continuous heating experiments, it is usual to consider the formal theory of transformation kinetics for heterogeneous nucleation, case referred to as "site saturation" [6], thus obtaining satisfactory kinetic parameters (activation energy E, kinetic exponent n, and pre-exponential factor, q, related to the frequency factor) describing the crystallization reactions.

The present paper studies the glass transition and the crystallization kinetics of the glassy alloy $Sb_{0.18}As_{0.34}Se_{0.48}$ by using DSC with continuous-heating techniques. Finally, the crystalline phases corresponding to the crystallization process were identified by X-ray diffraction (XRD) measurements, using Cu K_α radiation.

2. Theoretical background

The theoretical basis for interpreting DSC results is provided by the formal theory of transformation kinetics as developed by Johnson and Mehl [7] and Avrami [8]. This theory describes the evolution with time, t, of the volume fraction crystallized, x, in terms of the crystal growth u

$$x = 1 - \exp\left[-g\left(\int_0^t u \,\mathrm{d}t' \right)^n \right]. \tag{1}$$

Here g is a geometric factor and n is an exponent which depends on the mechanism of transformation. In the Eq. (1) is assumed that the nucleation process takes place early in the transformation and the nucleation rate is zero thereafter. This process of heterogeneous nucleation has been quoted as "site saturation" [6].

Assuming an Arrhenian temperature dependence for the crystal growth rate [9] and recalling that the heating rate is $\beta = \mathrm{d}T/\mathrm{d}t$, the Eq. (1) becomes

$$x = 1 - \exp\left[-g(u_0/\beta)^n \left(\int_{T_0}^{T} \exp(-E/\mathrm{R}T')\,\mathrm{d}T' \right)^n \right] = 1 - \exp(-pI^n), \tag{2}$$

where T_0 is the initial temperature of the non-isothermal process and E is the effective activation energy for crystal growth.

By using the substitution $z' = E/\mathrm{R}T'$ the integral I can be represented by an alternating series [10], where it is possible to use only the first term, without making any appreciable error, and to obtain $I = (RT^2/E)\exp(-E/\mathrm{R}T)$, if it is assumed that $T_0 \ll \mathrm{T}$, so that y_0 can be taken as infinity. Substituting the last expression of I in Eq. (2), and introducing the parameter $Q = g(R/E)^n$, the volume fraction crystallized is expressed as

$$x = 1 - \exp\left[-Q\left(\frac{K_V T^2}{\beta} \right)^n \right], \tag{3}$$

K_V being the reaction rate constant.

Deriving the Eq. (3) with respect to time, the crystallization rate is obtained as

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{Qn}{\beta}(1-x)\left(\frac{K_V T^2}{\beta} \right)^{n-1}\left(2\beta T K_V + T^2 \frac{\mathrm{d}K_V}{\mathrm{d}t} \right) \tag{4}$$

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

$$y_p = -\ln(1-x_p) = Q\left(\frac{(K_V)_p T_p^2}{\beta} \right)^n = 1 - \frac{2}{n}\left(1 + \frac{E}{\mathrm{R}T_p} \right)\left(2 + \frac{E}{\mathrm{R}T_p} \right)^{-2}, \tag{5}$$

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

Bearing in mind that in most crystallization reactions $E/\mathrm{R}T_p \gg 1$ (usually $E/\mathrm{R}T_p \geqslant 25$), the Eq. (5) can be rewritten as $Q((K_V)_p T_p^2/\beta)^n = 1$; whose logarithmic form is

$$\ln(T_p^2/\beta) = E/\mathrm{R}T_p - \ln q, \quad q = Q^{1/n} K_{V0} \tag{6}$$

a linear relationship which makes it possible to calculate the kinetic parameters E and q. At the same time, if the expression $Q^{1/n}(K_V)_p T_p^2/\beta = 1$ is introduced into Eq. (4), one obtains

$$n = (\mathrm{d}x/\mathrm{d}t)_p \mathrm{R}T_p^2 (0.37\beta E)^{-1}, \tag{7}$$

which makes it possible to calculate the kinetic exponent n .

3. Experimental

The glassy alloy $Sb_{0.18}As_{0.34}Se_{0.48}$ was made in bulk form, from their components of 99.999% purity which were pulverized, mixed in adequate proportions, and introduced into a quartz ampoule. The content was sealed under a vacuum of 10^{-2} N m^{-2}, heated at 950°C for 24 h and then quenched in a water bath. The glassy nature of the material was confirmed through a diffractometric X-ray scan, in a Siemens D500 diffractometer.

The calorimetric measurements were carried out in a Perkin-Elmer DSC7 calorimeter with an accuracy of ±0.1°C. For non-isothermal experiments, glass samples were sealed in aluminium pans and scanned from room temperature through their T_g at different heating rates of 1, 2, 4, 8, 16, 32 and 64 K min^{-1}. 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.

Finally, 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 ($\lambda = 1.542$ Å) at 40 kV and 40 mA, with a scanning speed of 0.1° s^{-1}.

4. Results

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 [11]. This approach was originally suggested based on results for $Ge_{0.15}Te_{0.85}$ glass. For the $Sb_{0.18}As_{0.34}Se_{0.48}$ glassy alloy, the empirical relationship can be written as $T_g = 476.0 + 4.4 \ln \beta$, where a straight regression line has been fitted to the experimental data.

The other approach is the use of the Eq. (6) for the evaluation of the activation energy for glass transition, E_g, of the glass transition. For crystallization processes with spherical nuclei, it has been suggested [12] that the dependence of the glass transition temperature on β may be written as

$$\ln\left(T_g^2/\beta\right) = E_g/RT_g + \text{constant},$$

an expression that, though originally deduced for the crystallization kinetics, has often been used [12,13] to calculate E_g. In addition, if it is assumed that, usually, the change in ln T_g^2 with β is negligibly small compared with the change in ln β [14], one obtains

$$\ln \beta = -E_g/RT_g + \text{constant},$$

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

Fig. 1 shows the plots of $\ln(T_g^2/\beta)$ (curve a) and ln β (curve b) vs. $1/T_g$ for the $Sb_{0.18}As_{0.34}Se_{0.48}$ glassy alloy, displaying the linearity of the equations used. The values of the activation energy obtained for the glass transition are 96 ± 2 Kcal mol^{-1} (plot a) and 98 ± 2 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].

As for the crystallization process of the alloy in question has been studied according to the approximation described in the preceding theory. With the aim of analyzing the kinetics of the above mentioned process, the variation intervals of the

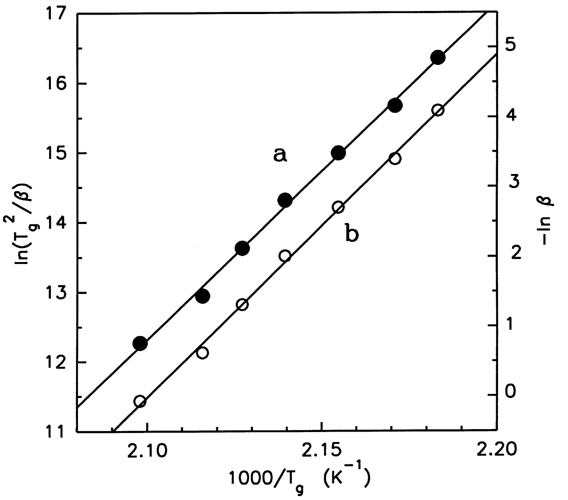

Fig. 1. (a) Plot of $\ln(T_g^2/\beta)$ vs. $1000/T_g$ of the analyzed material. (b) Plot of $\ln(\beta)$ vs. $1000/T_g$ of the studied glass (β in K s^{-1}).

Table 1
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

magnitudes described by the thermograms for the different heating rates, quoted in Section 3, are obtained and given in Table 1, where T_i is the temperature at which crystallization begins, and ΔT is the width of the crystallization peak. The crystallization enthalpy, ΔH, is also determined for each of the above mentioned heating rates. The ratio between the ordinates of the DSC curve 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. 2. 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. 3. From the slope of this experimental straight line it is possible to deduce the value of the activation energy, $E = 44 \pm 1$ Kcal mol^{-1} , for the crystallization process, and the origin ordinate gives the value corresponding to the logarithm of the pre-exponential factor, $\ln q = 24.3 \pm 0.4$ (q in (K s)$^{-1}$). Finally, the experimental data T_p and $(dx/dt)_p$, shown in Table 2, and the above mentioned value of the activation energy, make it possible to determine, through relationship (7), the kinetic exponent n for each of the experimental heating rates, whose values are also given in Table 2, the mean value being $\langle n \rangle = 1.73 \pm 0.20$.

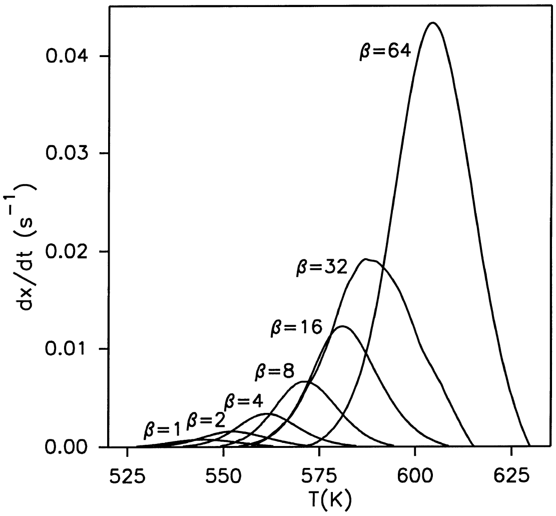

Fig. 2. Crystallization rate, vs. temperature of the exothermal peaks at different heating rates.

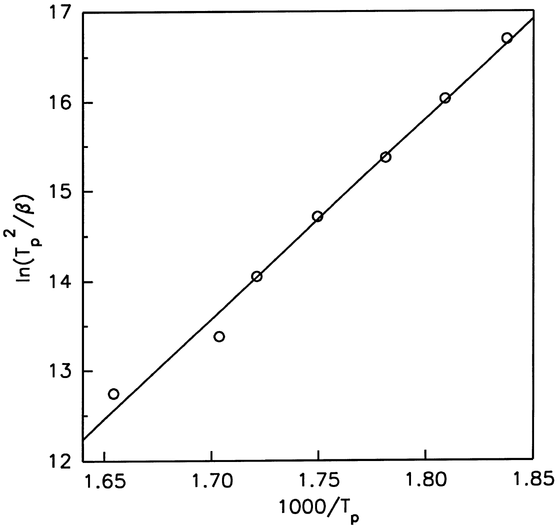

Fig. 3. Experimental plot of $\ln(T_p^2/\beta)$ vs. $1000/T_p$ straight regression line of $Sb_{0.18}As_{0.34}Se_{0.48}$ alloy (β in K s^{-1}).

The obtained values for the kinetic parameters make it possible to suppose that in the glassy alloy $Sb_{0.18}As_{0.34}Se_{0.48}$ there is a relatively stable crystallization phase ($E = 44 \pm 1$ Kcal mol^{-1}), and according to the literature [16] the mentioned phase may exhibit all shapes growing from small dimensions with zero nucleation rate.

Table 2
Maximum crystallization rate, corresponding temperature, and kinetic exponent for the different heating rates

β (K min^{-1})	$10^3(dx/dt)_p$ (s^{-1})	T_p (K)	n
1	0.76	544.1	1.65
2	1.20	553.8	1.35
4	3.33	561.3	1.92
8	6.61	571.6	1.98
16	12.27	581.0	1.90
32	23.14	587.0	1.82
64	35.58	605.1	1.49

5. Identification of the crystalline phases

The identification of the possible phases, that crystallize during the thermal treatment, has been carried out by means of adequate XRD measurements. For this purpose in Fig. 4 are shown the most relevant portions of the diffractometer tracings for the as-quenched glass and for the material submitted to the thermal process. The diffractogram of the transformed material after the

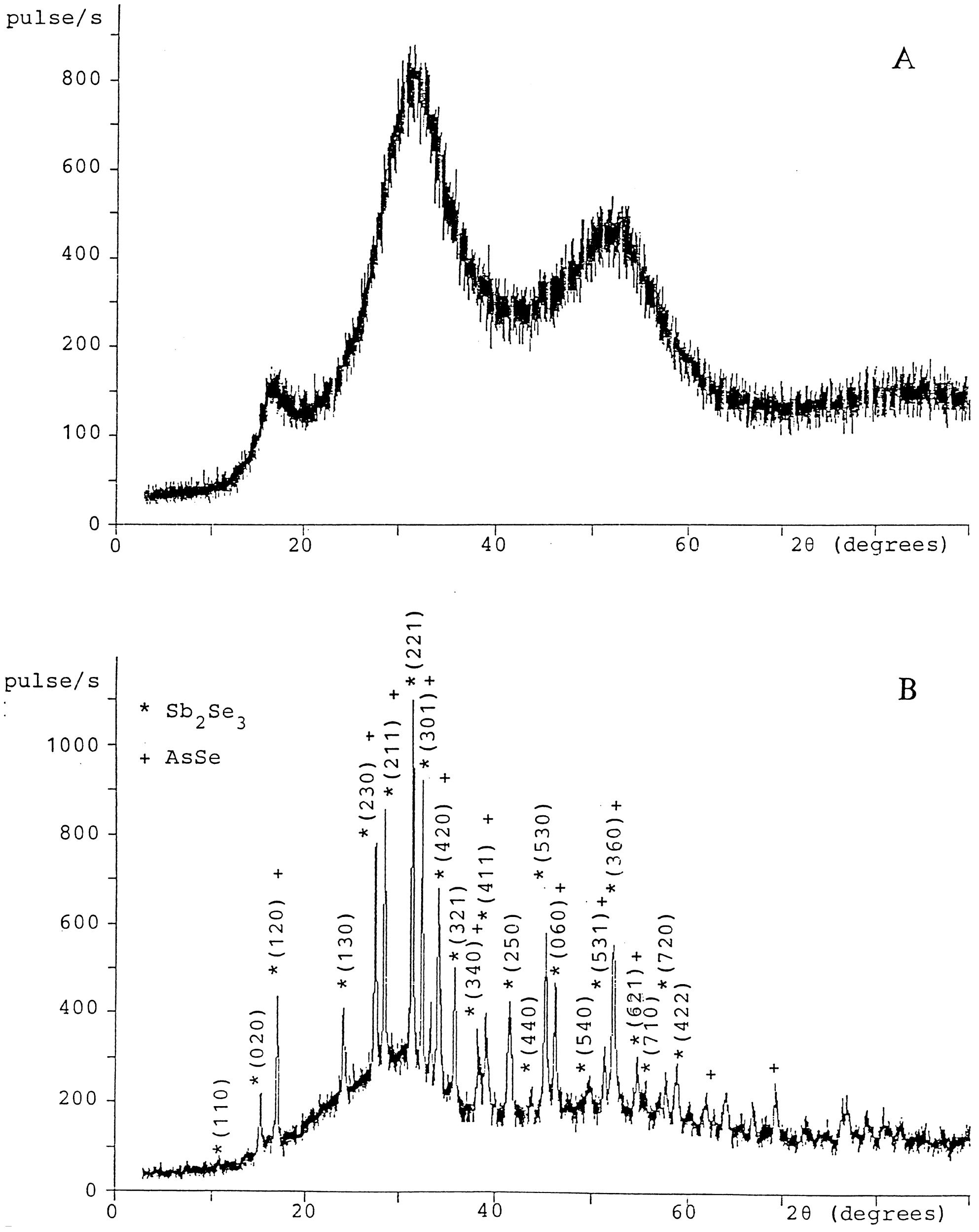

Fig. 4. (A) Diffractogram of amorphous alloy $Sb_{0.18}As_{0.34}Se_{0.48}$. (B) Diffraction peaks of alloy crystallized in DSC.

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 crystallizes in the orthorhombic system [17] with a unit cell defined by $a = 11.633$ Å, $b = 11.78$ Å 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 doublet at $2\theta = 27.43°$ and $2\theta = 27.55°$, which corresponds to the highest intensity line in the crystalline AsSe diffraction pattern (marked +) [18]. 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 a $Sb_{0.18}As_{0.34}Se_{0.48}$ glass sample has been studied using calorimetric and X-ray powder diffraction techniques. The study of crystallization kinetics was made using the formal theory of transformations for heterogeneous nucleation, case referred to as “site saturation”. The kinetic parameters have been deduced bearing in mind the dependence of the reaction rate constant on time. This form of 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 crystalline growth process, according to the value found for the kinetic exponent. 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.

Acknowledgements

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References

[1] Z. Altounian, J.O. Strom-Olsen, in: R.D. Shull, A. Joshi (Eds.), Thermal Analysis in Metallurgy, The Minerals, Metals and Materials Society, Warrendale, PA, 1992, p. 155.
[2] D.W. Henderson, J. Non-Cryst. Solids 30 (1979) 301.
[3] H.E. Kissinger, Anal. Chem. 29 (1957) 1702.
[4] D.J. Sarrach, J.P. De Neufville, J. Non-Cryst. Solids 22 (1976) 245.
[5] S. Surinach, M.D. Baró, M.T. Clavaguera-Mora, N. Clavaguera, J. Non-Cryst. Solids 58 (1983) 209.
[6] J.W. Cahn, Acta Metall. 4 (1956) 449; 573.
[7] W.A. Johnson, K.F. Mehl, Trans. Amer. Inst. Mining Eng. 135 (1981) 315.
[8] M. Avrami, J. Chem. Phys. 7 (1939) 1103; 8 (1940) 212; 9 (1941) 177.
[9] H. Yinnon, D.R. Uhlmann, J. Non-Cryst. Solids 54 (1983) 253.
[10] J. Vázquez, C. Wagner, P. Villares, R. Jiménez-Garay, Acta Mater. 44 (1996) 4807.
[11] M. Lasocka, Mater. Sci. Eng. 23 (1976) 173.
[12] J. Colmenero, J.M. Barandiaran, J. Non-Cryst. Solids 30 (1978) 263.
[13] J.A. Macmillan, J. Phys. Chem. 42 (1965) 3497.
[14] J. Sestak, Phys. Chem. Glasses 15 (1974) 137.
[15] C.Y. Zahara, A.M. Zahara, J. Non-Cryst. Solids 190 (1995) 251.
[16] J.W. Christian, The Theory of Transformations in Metals and Alloys, 2nd ed., Pergamon, New York, 1975.
[17] Natl. Bur. Stand. (U.S.), Monogr. 25 (1964) 3.
[18] S.A. Dembovskii, Russian J. Inorg. Chem. 8 (1963) 798.