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A study on the crystallization kinetics by differential scanning calorimetry using non-isothermal techniques in the case of "site saturation"

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Abstract

A procedure has been developed for analyzing the evolution with time of the volume fraction crystallized and for calculating the kinetic parameters at non-isothermal reactions in materials involving growth of nuclei. By means of this method, and considering the assumptions of extended volume and randomly located nuclei, a general expression of the fraction crystallized has been obtained as a function of the temperature in bulk crystallization. The kinetic parameters have been deduced, assuming that the reaction rate constant is a time function through its Arrhenian temperature dependence. The theoretical method described has been applied to the crystallization kinetics of the $Sb_{0.04}As_{0.48}Se_{0.48}$ glassy alloy with and without previous reheating. According to the study carried out, it is possible to state that in the considered alloy, the nuclei were dominant before thermal analysis, and therefore, the reheating did not appreciably change the number of pre-existing nuclei in the material, which constitutes a case of "site saturation".

Keywords: Glassy semiconductor; Crystal growth; Site saturation; Crystallization kinetics; Kinetic parameters; As-quenched glass; Reheated glass

1. Introduction

Knowledge of amorphous solids is one of the most active fields of research in the physics of condensed matter today [1]. The great interest in these materials is largely due to their ever-increasing applications in modern technology. Their possibilities in the immediate future are huge based on characteristic properties such as electronic-excitation phenomena, chemical reactivity and inertia and superconductivity. Therefore, the advances that have been made in physics and chemistry of the quoted materials during the last 30 years of the twentieth century have been very appreciated within the research community. In this respect, the glassy alloys of chalcogen elements were the initial object of study because of their interesting semiconducting properties and more recent importance in optical recording [2]. In addition, the last decades have seen a strong theoretical and practical interest in the application of non-isothermal experimental analysis techniques to the study of phase

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transformations. The non-isothermal 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 a glassy alloy as it is heated 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 [3–5]. Many authors used the so-called Kissinger plot [4] or Ozawa plot [6] directly to examine the kinetics of crystallization of amorphous materials. These methods, however, cannot be directly applied to the crystallization of the quoted materials and the physical meaning of the activation energies thus obtained is obscure because the crystallization is advanced not by the *n*th-order reaction but by the nucleation and growth process. On the other hand, some authors applied the Johnson–Mehl–Avrami (JMA) equation to the non-isothermal crystallization process [7–10]. Although sometimes they appeared to get reasonable activation energies, this procedure is not appropriate because the JMA equation was derived for isothermal crystallization [11].

In this work, an alternative method is proposed for analyzing the non-isothermal crystallization kinetics on the basis of nucleation and crystal growth processes, in the case of an as-quenched glass, which contains a large number of nuclei "site saturation" [12]. In addition, the present paper applies the proposed method to the analysis of the crystallization kinetics of the $Sb_{0.04}As_{0.48}Se_{0.48}$ glassy semiconductor. The material was reheated to research the applicability of the quoted method, obtaining for the kinetic exponent similar values before and after reheating. This result confirms the presence of a sufficient number of nuclei in the as-quenched glass, and therefore, it is a case of "site saturation".

2. Theoretical basis

Crystallization is a particular case of nucleation and grain growth-controlled solid-state transformation processes, the formal theory of which is well known [13–16]. This formal theory is largely independent of the particular models used in detailed descriptions of the mechanisms of transformation, and supposes that the crystal growth rate, in general, is anisotropic. This rate in any direction can be then represented in terms of the principal growth velocities, u_i ($i=1$, 2 and 3), in three mutually perpendicular directions. In these conditions, the one-dimensional growth in an elemental time dt' can be expressed as $u_i(t')dt'$, and this growth for a finite time is $\int_\tau^t u_i(t')dt'$. The volume of a region originating at time $t=\tau$ is then

$$v = g\prod_i \int_\tau^t u_i(t')dt' \qquad (1)$$

where g is a geometric factor which depends on the shape of the growing crystal and the expression $\prod_i \int_\tau^t u_i(t')dt'$ condenses the product of the integrals corresponding to the values of the above quoted subscript i.

In the case of as-quenched glass where a large number of nuclei already exist and no new nuclei are formed during the thermal treatment (site saturation), the integral of Eq. (1) is evaluated between 0 and t since there is no nucleation period $\tau=0$. Defining and extended volume V_e of transformed material and assuming randomly located nuclei [17], it is possible to write the relation between the actual volume V_b and V_e in the form

$$dV_b = (1 - V_b/V)dV_e = (1-x)v\,dN' \qquad (2)$$

where $x=V_b/V$ is the volume fraction transformed with V being the volume of the whole assembly and where dN' is the number of nuclei existing in a volume element of material.

Substituting Eq. (1) into Eq. (2) and integrating the resulting expression, one obtains

$$x = 1 - \exp\left[-gN_0\left(\prod_i \int_0^t u_i(t')dt'\right)\right] \qquad (3)$$

$N_0=N/V$ being the number of pre-existing nuclei per unit volume.

When the crystal growth rate is isotropic, $u_i=u$, an assumption which is in agreement with the experimental evidence since in many transformations the reaction product grows approximately as spherical nodules, Eq. (3) can be written as

$$x = 1 - \exp\left[-gN_0\left(\int_0^t u(t')dt'\right)^m\right] \qquad (4)$$

where m is an exponent which depends on the dimensionality of the crystal growth. In the considered case, “site saturation” [12], the kinetic exponent is $n = m$. Assuming an Arrhenian temperature dependence for u and a heating rate $\beta = \mathrm{d}T/\mathrm{d}t$, Eq. (4) becomes

$$x = 1 - \exp\left[-gN_0 u_0^n \beta^{-n}\left(\int_{T_0}^{T} \mathrm{e}^{-E_G/RT'}\,\mathrm{d}T'\right)^n\right] = 1 - \exp(-qI^n)$$

E_G being the effective activation energy for crystal growth.

By using the substitution $y' = E_G/RT'$, the integral I can be expressed, according to the literature [18], by the sum of the alternating series

$$S(y') = \frac{-\mathrm{e}^{-y'}}{y'^{\,2}} \sum_{k=0}^{\infty} \frac{(-1^k)(k+1)!}{y'^{\,k}}.$$

Considering that in this type of series the error produced is less than the first term neglected and bearing in mind that in most crystallization reactions $y' = E_G/RT' \gg 1$ (usually $E_G/RT' \geq 25$), it is possible to use only the first term of this series, without making any appreciable error, and the above mentioned integral becomes

$$I = (E_G/R)\mathrm{e}^{-y}y^{-2} = RT^2E_G^{-1}\exp(-E_G/RT) \tag{6}$$

if it is assumed that $T_0 \ll T$ (T_0 is the starting temperature), so that y_0 can be taken as infinity. This assumption is justifiable for any thermal treatment that begins at a temperature where crystal growth is negligible, i.e. below the glass transition temperature T_g [19].

Substituting Eq. (6) into Eq. (5), the volume fraction crystallized in a non-isothermal process is expressed as

$$x = 1 - \exp[-P(K_R T^2 \beta^{-1})^n] \tag{7}$$

where $P = gN_0(R/E_G)^n$ and K_R is the reaction rate constant. It should be noted that Eq. (7) is a general expression for all values of the parameter n, which, as it is well known, in the case of “site saturation” depends on the mechanism of the crystal growth.

With the aim of calculating the kinetic parameters, the crystallization rate has been obtained by deriving Eq. (7) with respect to time, yielding

$$\mathrm{d}x/\mathrm{d}t = nP(K_R T^2 \beta^{-1})^{n-1}(1-x) \times (K_R E_G R^{-1} + 2K_R T), \tag{8}$$

where has been assumed that the reaction rate constant is a time function through its Arrhenian temperature dependence.

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

$$P[(K_R)\,|_p\, T_p^2 \beta^{-1}]^n = 1 - (2/n)(1 + E_G/RT_p)(2 + E_G/RT_p)^{-2} \tag{9}$$

where the subscript p denotes the magnitude values corresponding to the maximum crystallization rate. Assuming the above mentioned hypothesis $E_G/RT_p \gg 1$; the logarithmic form of Eq. (9) is written as

$$\ln(T_p^2/\beta) - E_G/RT_p + \ln(P^{1/n}K_{R0}) = 0 \tag{10}$$

equation of a straight line, whose slope and intercept give the activation energy E_G and the pre-exponential factor $p = P^{1/n}K_{R\,0}$, respectively.

On the other hand, the quoted assumption $E_G/RT_p \gg 1$ according to Eqs. (7–9) allows us to express the maximum crystallization rate by the relationship

$$(\mathrm{d}x/\mathrm{d}t)\,|_p = 0.37\beta E_G n(RT_p^2)^{-1}, \tag{11}$$

which makes it possible to obtain, for each heating rate, a value of the kinetic exponent n. The corresponding mean value may be taken as the most probable value of the quoted exponent.

3. Experimental

The $Sb_{0.04}As_{0.48}Se_{0.48}$ glassy alloy was prepared in bulk form by the standard melt quenching method. High purity (99.999%) antimony, arsenic and selenium in appropriate atomic percent proportions were

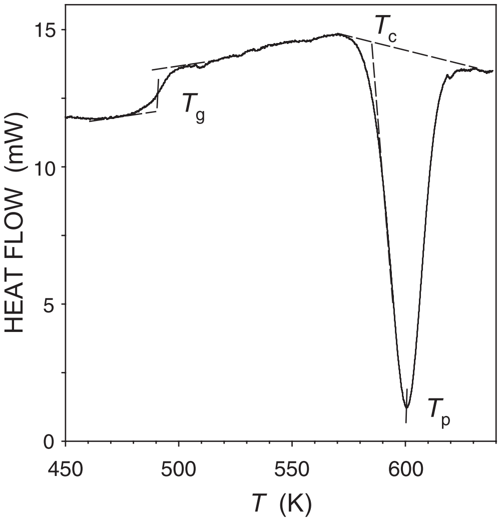

Fig. 1. DSC trace of the $Sb_{0.04}As_{0.48}Se_{0.48}$ glassy alloy at a heating rate of 64 K min^{-1}.

weighed (7 g/batch) into a quartz glass ampoule (6-mm diameter). The content of the quoted ampoule was sealed under a vacuum of 10^{-2} Pa, heated in a rotating furnace at around 1225 K for 24 h and then quenched in water, which supplied the necessary cooling rate for obtaining the glass. The amorphous state 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 scanning electron microscopy (SEM) in a JEOL scanning microscope JSM-820. The calorimetric measurements were carried out in a Perkin-Elmer DSC7 differential scanning calorimeter with an accuracy of ± 0.1 K. 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 indium and zinc supplied with the instrument. Powdered samples weighing about 20 mg (particle size around 40 μm) were crimped in aluminium pans and scanned at room temperature through their 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 60 ml min^{-1} flow of nitrogen was maintained in order to provide a constant thermal blanket within the DSC cell, thus eliminating thermal gradients and ensuring the validity of the applied calibration standard from sample to sample. Moreover, the nitrogen purge allows to expel 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 inflection of the lambda-like trace on the DSC scan, as shown in Fig. 1.

4. Results

The typical DSC trace of $Sb_{0.04}As_{0.48}Se_{0.48}$ semiconductor glass obtained at a heating rate of 64 K min^{-1} and plotted in Fig. 1 shows three characteristic phenomena which are resolved in the temperature region studied. The first one (T = 490.4 K) corresponds to the glass transition temperature T_g, the second (T = 585.0 K) to the extrapolated onset crystallization temperature T_c and the third (T = 600.5 K) to the peak temperature of crystallization T_p of the quoted semiconductor glass. This behaviour is typical for a glass–crystal transformation. It should be noted that the values of T_g, T_c and T_p increase with increasing the heating rate, as often occurs in the literature [20].

4.1. Crystallization

The crystallization kinetics of the $Sb_{0.04}As_{0.48}Se_{0.48}$ alloy was analyzed according to the theory developed in Section 2. With the aim of analyzing the quoted kinetics, 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

Table 1
Characteristic temperatures and enthalpies of the crystallization process of the alloy $Sb_{0.04}As_{0.48}Se_{0.48}$

Parameter	Experimental value	
	As-quenched	Reheated
T_g (K)	458.7–490.4	461.5–474.2
T_i (K)	528.1–568.5	524.5–570.2
T_p (K)	545.7–600.5	555.6–605.0
ΔT (K)	24.7–65.7	21.3–44.8
ΔH (mcal mg^{-1})	4.0–4.9	7.7–8.6

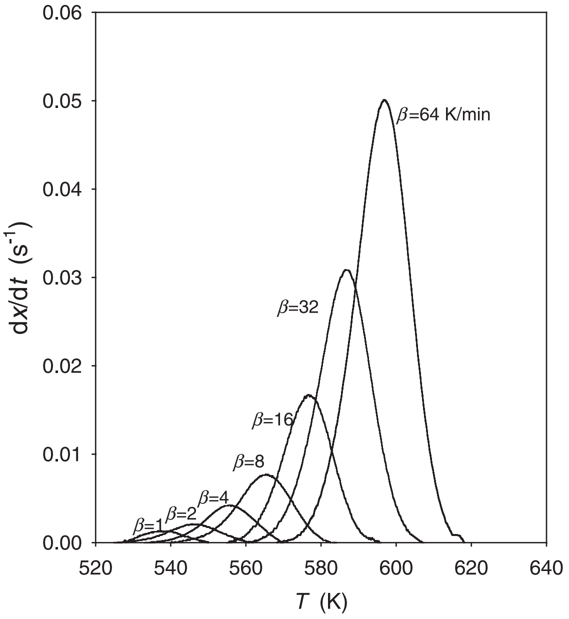

Fig. 2. Crystallization rate versus temperature for the as-quenched glass at different heating rates.

rate, respectively, and ΔT is the width of the crystallization peak. The crystallization enthalpy ΔH is also determined for each of the heating rates. The crystallization rates d*x*/d*t* corresponding to the different scans are represented in Fig. 2. It may be observed that the $(dx/dt)|_p$ values increase in the same proportion as the heating rate, a property that has been widely discussed in the literature [21].

To research the applicability of the preceding theory, the material was reheated up to 503 K (a temperature slightly higher than T_g) for 1 h in order to form a large number of nuclei and subjected to the same calorimetric scans for the as-quenched glass. The data of $\ln(T_p^2/\beta)$ and $1/T_p$, both for the as-quenched and for reheated glass, are fitted to linear functions by least squares fitting and shown in Fig. 3. From the slope and intercept of these fits, according to Eq. (10), the activation energy E_G and pre-exponential factor p are obtained. The results are the following: $E_G = 39.7$ kcal mol^{-1} and $p = 6.8 \times 10^8$ K s^{-1} for the as-quenched glass, and $E_G = 44.4$ kcal mol^{-1} and $p = 2.4 \times 10^{10}$ K s^{-1} for the reheated glass. In addition, the experimental data $(dx/dt)|_p$, given in Table 2 together with T_p values and the quoted results of the activation energy, make it possible to determine, by using Eq. (11), the kinetic exponent n shown in Table 2 for each β both for the as-quenched and for the reheated glass. The mean values of the above mentioned exponent are the following: $\langle n \rangle = 2.7$ for the as-quenched glass, and $\langle n \rangle = 2.6$ for the reheated glass. Allowing for experimental error, both values are

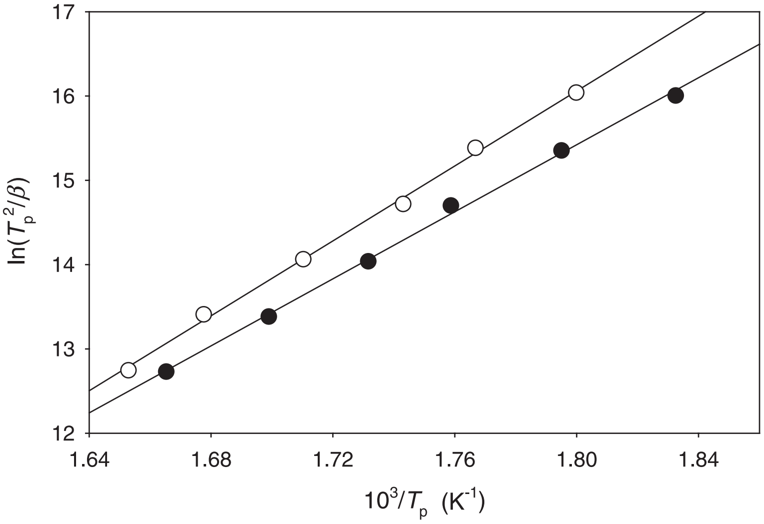

Fig. 3. Experimental plots of $\ln(T_p^2/\beta)$ versus $10^3/T_p$ and straight regression lines of the $Sb_{0.04}As_{0.48}Se_{0.48}$ alloy (β in K s^{-1}): (●) as-quenched glass; (○) reheated glass.

Table 2
Maximum crystallization rate and kinetic exponent of the glass–crystal transformation of the alloy $Sb_{0.04}As_{0.48}Se_{0.48}$

β (K min^{-1})	As-quenched		Reheated	
	$10^3(dx/dt)\|_p$ (s^{-1})	n	$10^3(dx/dt)\|_p$ (s^{-1})	n
2	2.1	2.55	2.3	2.59
4	4.4	2.79	4.5	2.63
8	7.9	2.61	8.7	2.61
16	17.3	2.95	17.1	2.67
32	30.5	2.70	32.8	2.66
64	50.1	2.31	63.1	2.64

very similar. This indicates, according to literature [22], that a large number of nuclei already exist in the as-quenched material by representing a case of "site saturation".

From the mean value of the kinetic exponent n, it is possible to postulate a crystallization reaction mechanism. Mahadevan et al. [23] have shown that n may be 4, 3, 2 or 1, which are related to different crystallization mechanisms: $n=4$, volume nucleation, three-dimensional growth; $n=3$, volume nucleation, two-dimensional growth; $n=2$, volume nucleation, one-dimensional growth; $n=1$, surface nucleation, one-dimensional growth from surface to the inside. Given that in the studied alloy the "site saturation" $n=m$ is presented, the mean values obtained for the kinetic exponent are relatively consistent with a three-dimensional growth mechanism.

5. Conclusions

The described theoretical method enables us to study the evolution with the time of the volume fraction crystallized in materials involving crystal growth processes. This procedure assumes the concept of the extended volume of transformed material and the condition of randomly located nuclei. Using these assumptions, we have obtained a general expression of the volume fraction crystallized as a function of the temperature in bulk crystallization processes. In the quoted expression, the kinetic exponent only depends on the dimensionality of the crystal growth, since an as-quenched glass containing a sufficiently large number of nuclei has been considered. The kinetic parameters have been deduced by using the following considerations: the condition of the maximum crystallization rate and the quoted maximum rate. The theoretical method developed has been applied to the crystallization kinetics of the $Sb_{0.04}As_{0.48}Se_{0.48}$ glassy alloy with and without previous reheating. According to the study carried out, it is possible to establish that the reheating did not cause the appearance of nuclei in this glass, but that the as-quenched material already contains a sufficient number of them. The method for thermal analysis of the quoted alloy has given results in good agreement with the nature of the material under study and representative of a crystal growth process.

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