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An alternative theoretical procedure to analyze the non-isothermal glass-crystal transformation kinetics: crystallization of the $Sb_{0.13}As_{0.35}Se_{0.52}$ glassy semiconductor

J.L. Cárdenas-Leal *, D.García-G. Barreda, J. Vázquez, P. Villares

Departamento de Física de la Materia Condensada, Facultad de Ciencias, Universidad de Cádiz, Apartado 40, 11510 Puerto Real, (Cádiz), Spain

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ABSTRACT

A procedure has been developed for analyzing the evolution with temperature of the actual transformed volume fraction and for calculating the kinetic parameters at non-isothermal reactions in materials involving formation and growth of nuclei. By considering the assumptions of extended volume and spatially random nucleation, as well as, assuming that both the nucleation frequency and the crystal growth rate depend on time as a power law, an equation of the extended transformed volume fraction has been obtained as a function of the temperature. From the quoted equation and according to the Jhonson–Mehl–Avrami model, it has been deduced an expression for the actual transformed volume fraction. The theoretical procedure described has been applied to the non-isothermal crystallization kinetics of the $Sb_{0.13}As_{0.35}Se_{0.52}$ glassy alloy, with and without previous reheating, using DSC technique. In accordance with the study carried out, it is possible to state that the reheating did not cause the appearance of nuclei, but that the as-quenched material already contains a sufficient number of them. Likewise, it has been analyzed the variations of the kinetic exponent and the activation energy with the temperature. This analysis suggests that the transformation cannot be described by a mechanism of single-step, which demonstrates a mechanism of complex multi-step. Moreover, the experimental curve of the transformed fraction shows a satisfactory agreement with the theoretical curve corresponding to the considered procedure, confirming the reliability of the same to analyze the transformation kinetics of the studied alloy. The phase at which the alloy crystallizes after the thermal process has been identified by X-ray diffraction. The obtained diffractogram suggests the presence of micro crystallites of Sb_2Se_3, remaining an additional amorphous matrix.

1. Introduction

Solid-state transformations play an important role in the production of many materials and therefore, the glass-crystal transformation has been studied intensively by the researchers of the last decades, especially since Duwez et al. [1] published their introduction to the preparation of glassy alloys by quenching technique. In this sense, a great impulse has been given at the study of a general description of the kinetics of phase transformations [2]. In addition, the interest in these materials has been increasing due to their unique isotropic, structural and chemical properties [3,4]. In this respect, it is understandable the strong theoretical and practical interest that has arisen in the application of calorimetric analysis techniques to the study of the already quoted transformations [5–7]. Thus, the classical formal theory of nucleation and crystal growth has been developed over the last 60 years. A full development of the quoted theory is given by Christian [8] and a noticeable review published by Kelton [9].

The quantitative study of the glass-crystal transformation in different glassy systems by means of differential scanning calorimetry methods has been widely discussed in the literature [9–15] and there is a large variety of theoretical models and theoretical functions proposed to explain the glass-crystal transformation kinetics. The application of each of them depends on the type of amorphous material studied and how it has been made.

In the present article a theoretical procedure has been developed in order to analyze the non-isothermal glass-crystal transformation kinetics and to calculate the corresponding kinetic parameters. By assuming the assumptions of extended volume and spatially random nucleation and considering that, both the nucleation frequency and the crystal growth rate depend on time as a power law [16,17], we have obtained an evolution equation with the temperature for the extended transformed volume fraction. According to the Jhonson–Mehl–Avrami model and from the quoted equation, it has been deduced an expression for the actual transformed volume fraction. In addition, the present work applies the quoted theoretical procedure to the analysis of the crystallization kinetics of the $Sb_{0.13}As_{0.35}Se_{0.52}$ chalcogenide glass. From this analysis it is possible to state that the as-quenched material

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* Corresponding author.
E-mail address: joseluis.cardenas@uca.es (J.L. Cárdenas-Leal).

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already contains a large number of nuclei and, therefore, the reheating of the same does not change the value of the kinetic exponent, a case of "site saturation" [18]. Likewise, it has been studied the variation of the kinetic exponent and the activation energy with the temperature, which suggests a mechanism of complex multi-step for the transformation. Besides, the experimental and theoretical curves of the transformation show a satisfactory agreement, which confirms the validity of the developed procedure to describe the glass-crystal transformation of the $Sb_{0.13}As_{0.35}Se_{0.52}$ glass semiconductor. Finally, the crystalline phases corresponding to the crystallization process were identified by X-ray diffraction (XRD) measurements, using CuK_{α} radiation. The diffractogram of the transformed material suggests the presence of micro crystallites of Sb_2Se_3, remaining a residual amorphous matrix.

2. Theoretical development

2.1. Extended and actual transformed volume fraction

It is well known that the theoretical basis for interpreting differential scanning calorimeter (DSC) results is provided by the formal theory of transformation kinetics [10–13,15,19,20]. From this theory and according to the literature [16], it is possible to define an extended volume of transformed material and to assume spatially random transformed regions [21–26], so that considering an isotropic growth since in many transformations the reaction product grows approximately as spherical nodules [8], the elemental extended volume fraction, $\mathrm{d}x_\mathrm{e}$, in terms of the nucleation frequency per unit volume, $I_\mathrm{v}(\tau)$, and of the crystal growth rate, $u(t')$, can be expressed as

$$\mathrm{d}x_\mathrm{e} = g[\alpha \mathrm{d}N + (1-\alpha)I_\mathrm{V}(\tau)\mathrm{d}\tau]\left[\int_{(1-\alpha)\tau}^{t} u(t')\mathrm{d}t'\right]^m \tag{1}$$

where τ is the nucleation period, α is a parameter equal to zero in the case of continuous nucleation and equal to the unit in the case of "site saturation" [18], g is a geometric factor which depends on the dimensionality and shape of the crystal growth, being its dimension equation $[g] = [\mathrm{L}]^{3-m}$ ([L] is the length), m is an exponent related to the quoted dimensionality and $\mathrm{d}N$ is the elemental number of nuclei existing per unit volume.

Bearing in mind the physical considerations given in our articles [16, 17], the nucleation frequency per unit volume and the crystal growth rate must depend on time as a power law, whose probable physical nature can be explained considering oriented nucleation and oriented growth processes [27–29], which are non-linear and therefore the corresponding rates must depend explicitly on time in accordance with the following expressions

$$I_\mathrm{V}(\tau) = I_\mathrm{V0}\tau^p \exp(-E_\mathrm{N}/RT) \tag{2}$$

and

$$u(t) = u_0 t^q \exp(-E_\mathrm{G}/RT) \tag{3}$$

where E_N and E_G are the effective activation energies for nucleation and growth, respectively, p and q are the exponents for each of the quoted power laws, being $q > -1$ and $p > -1$ [30], and I_V0 and u_0 are the pre-exponential terms, whose dimension equations are given by $[I_\mathrm{V0}] = [\mathrm{L}]^{-3}[\mathrm{T}]^{-(p+1)}$ and $[u_0] = [\mathrm{L}][\mathrm{T}]^{-(q+1)}$ ([T] is the time).

Thus, for non-isothermal crystallization processes with constant heating rate, $\beta = \mathrm{d}T/\mathrm{d}t$, considering Eqs. (2) and (3), Eq. (1) becomes

$$\mathrm{d}x_\mathrm{e} = \frac{gu_0^m}{\beta^{m(q+1)}}\left[\alpha \mathrm{d}N + \frac{(1-\alpha)I_\mathrm{V0}}{\beta^{p+1}}T_\tau^p e^{-E_\mathrm{N}/RT_\tau}\mathrm{d}T_\tau\right]\left(\int_{T_\tau}^{T} T'^q e^{-E_\mathrm{G}/RT'}\mathrm{d}T'\right)^m \tag{4}$$

where T_τ is the temperature corresponding to time $(1-\alpha)\tau$.

In the case of continuous nucleation, $\alpha = 0$, according to Eq. (4), one obtains

$$\begin{aligned}\mathrm{d}x_\mathrm{e} &= \frac{gu_0^m I_\mathrm{V0}}{\beta^{m(q+1)+p+1}}T_\tau^p e^{-E_\mathrm{N}/RT_\tau}\left(\int_{T_\tau}^{T} T'^q e^{-E_\mathrm{G}/RT'}\mathrm{d}T'\right)^m \mathrm{d}T_\tau \\ &= \frac{gu_0^m I_\mathrm{V0}}{\beta^{m(q+1)+p+1}}T_\tau^p e^{-E_\mathrm{N}/RT_\tau}I_1^m \mathrm{d}T_\tau.\end{aligned} \tag{5}$$

Following the literature [16], by means of substitution $y' = E_\mathrm{G}/RT'$, the I_1 integral of the Eq. (5) is transformed in an exponential integral of order $2 + q$, which is a particular case of the order r, and that in accordance with the quoted reference can be expressed by the alternating series

$$S_r(y, y_\tau) = \left[-\frac{\mathrm{e}^{-y'}}{y'^r}\sum_{k=0}^{\infty}\frac{(-1)^k(k+r-1)!}{(r-1)!y'^k}\right]_{y_\tau}^{y} \tag{6}$$

and bearing in mind that in this type of series the error produced is less than the first term neglected and that in most glass-crystal transformations $y' = E_\mathrm{G}/RT' >> 1$, usually $E_\mathrm{G}/RT' \geq 25$ [26], it is possible to use only the first term of the quoted series, without making any appreciable error, so that the I_1 integral can be written as

$$I_1 = \left(\frac{E_\mathrm{G}}{R}\right)^{q+1}\left(\frac{e^{-y}}{y^{q+2}} - \frac{e^{-y_\tau}}{y_\tau^{q+2}}\right). \tag{7}$$

Furthermore, since $T > T_\tau$, it is deduced that $y < y_\tau$, and therefore $y_\tau = Ay$ with $A > 1$, so that the I_1 integral can be expressed as

$$I_1 = \left(\frac{E_\mathrm{G}}{R}\right)^{q+1}\frac{e^{-y}}{y^{q+2}}\left(1 - \frac{e^{-(A-1)y}}{A^{q+2}}\right) \tag{8}$$

and bearing in mind that $q > -1$, $y >> 1$ and $A > 1$, it is obtained, on the one hand that $A^{q+2} > 1$ and on the other hand that $e^{-(A-1)y} << 1$, for which the expression $e^{-(A-1)y}/A^{q+2}$ is negligible in comparison with the unit and Eq. (8) becomes

$$I_1 = \left(\frac{E_\mathrm{G}}{R}\right)^{q+1}\frac{e^{-y}}{y^{q+2}}. \tag{9}$$

Substituting Eq. (9) into Eq. (5) and integrating the resulting expression, one obtains

$$\begin{aligned}x_e &= \frac{gu_0^m I_\mathrm{V0}}{\beta^{m(q+1)+p+1}}\left(\frac{E_\mathrm{G}}{R}\right)^{m(q+1)}\left(\frac{e^{-y}}{y^{q+2}}\right)^m \int_{T_0}^{T} T_\tau^p e^{-E_\mathrm{N}/RT_\tau}\mathrm{d}T_\tau \\ &= \frac{gu_0^m I_\mathrm{V0}}{\beta^{m(q+1)+p+1}}\left(\frac{E_\mathrm{G}}{R}\right)^{m(q+1)}\left(\frac{e^{-y}}{y^{q+2}}\right)^m I_2.\end{aligned} \tag{10}$$

T_0 being the temperature corresponding to time $t = 0$.

By the substitution $z' = E_\mathrm{N}/RT$, the I_2 integral of Eq. (10) is transformed in an exponential integral of order $2 + p$, which is evaluated as the I_1 integral, yielding

$$I_2 = \left(\frac{E_\mathrm{N}}{R}\right)^{p+1}\left(\frac{e^{-z}}{z^{p+2}} - \frac{e^{-z_0}}{z_0^{p+2}}\right) = \left(\frac{E_\mathrm{N}}{R}\right)^{p+1}\frac{e^{-z}}{z^{p+2}} \tag{11}$$

if it is assumed that $T_0 << T$, so that $z_0 >> z$ (even, z_0 can be taken as infinity). This hypothesis is justifiable for any thermal process that begins at a temperature where the nucleation and the growth are negligible, i.e., below the glass transition temperature, T_g [26].