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Theoretical study on the mechanism and transformation kinetics under non-isothermal conditions. Application to the crystallization of $Sb_{0.12}As_{0.36}Se_{0.52}$ glassy alloy

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Abstract

A procedure has been developed to determine the reliable form of the glass-crystal transformation function, and to deduce the kinetic parameters by using differential scanning calorimetry data, obtained from experiments performed under non-isothermal conditions. It is an integral method, which is based on a transformation rate independent of the thermal history and expressed as the product of two separable functions of absolute temperature and the fraction transformed. Considering the same temperatures for the different heating rates, one obtains a constant value for temperature integral, and, therefore, a plot of a function of the volume fraction transformed versus the reciprocal of the heating rate leads to a straight line with an intercept of zero, if the reaction mechanism is correctly chosen. Besides, by using the first mean value theorem to approach the temperature integral, one obtains a relationship between a function of the temperature and other function of the volume fraction transformed. The logarithmic form of the quoted relationship leads to a straight line, whose slope and intercept allow to obtain the activation energy and the frequency factor. The method developed has been applied to the crystallization kinetics of the $Sb_{0.12}As_{0.36}Se_{0.52}$ glassy alloy and it has been found that the kinetic model of normal grain growth is the most suitable to describe the crystallization of the quoted alloy. The mean values obtained for the activation energy and the frequency factor have been 27.36 kcal mol^{-1} and 1.5×10^{9} s^{-1}, respectively.

Keywords: A. Amorphous materials; C. Differential scanning calorimetry (DSC); D. Phase transitions; D. Semiconductivity

1. Introduction

Amorphous materials themselves are nothing new, since the man has been making glasses (mainly silica) for centuries. What is relatively recent is the scientific study of the quoted materials. The amorphous alloys have received a great attention in the past four decades due to their unique isotropic structural and chemical properties [1,2]. They are expected to have special conditions and in fact they have been found important practical or potential applications in various fields, such as in powder metallurgy, magnetic recording media, ferrofluids, composite materials and catalysis [3]. Accordingly, a strong theoretical and practical interest in the application of isothermal and non-isothermal experimental analysis techniques to study of phase transformations has arisen in the last times. Thus, the non-isothermal 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, transformation enthalpy and activation energy over a wide range of temperatures [4,5]. The study of crystallization kinetics in the quoted alloys by differential scanning calorimetry (DSC) methods has been widely discussed in the literature [4,6–10]. There is a large variety of theoretical models and theoretical functions proposed to explain the crystallization kinetics. Thus, many authors applied the Johnson–Mehl–Avrami (JMA) [11] equation to the non-isothermal processes [12], though this equation has been deduced under isothermal conditions [13].

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In this work a theoretical method is considered to determine the true form of the transformation function, $f(x)$, and to calculate the kinetic parameters: activation energy and frequency factor, by using DSC data obtained from experiments carried out under various heating rates. The quoted method assumes that the reaction rate depends only on the volume fraction transformed and temperature, and that these variables are independent ones [14,15]. Besides, the present work applies the above-mentioned method to the analysis of the crystallization kinetics of the $Sb_{0.12}As_{0.36}Se_{0.52}$ glassy semiconductor and reveals that the glass-crystal transformation of the quoted semiconductor does not fulfil the JMA model. However, it seems that the kinetic model of normal grain growth, R_n with $n = 1.9$, is the most adequate to describe the crystallization of the glass studied, since the quoted model shows the correlation coefficients closer to the unit.

2. Basic theory

The main purpose of the kinetic study of the glass-crystal transformation under non-isothermal regime is the determination of the corresponding parameters: activation energy, E, kinetic exponent, n, and frequency factor, K_0, in addition to the analytical form of the transformation function $f(x)$, that is, the transformation mechanism. In accordance with the literature [14] the integral methods based on data recorded for various heating rates give results which are more reliable and less affected by errors, since the quoted methods evaluate the whole experimental data set and are based on the primary experimentally acquired data, x and T. The integral method proposed in this work assumes, as in most solid-state reactions, that the glass-crystal transformation rate, $\mathrm{d}x/\mathrm{d}t$, under non-isothermal regime is independent of thermal history and is expressed as the product of two separable functions of absolute temperature, T, and the volume fraction transformed, x [15,16]

$$\mathrm{d}x/\mathrm{d}t = K(T)f(x), \tag{1}$$

where $K(T)$ is the reaction rate constant and $f(x)$ a function of the fraction transformed, which reflects the mechanism of the transformation.

Some author [16] introduce two further requirements: that $f(x)$ is independent of the heating rate, β, and that the temperature dependence of $K(T)$ is exponential, Arrhenius type, which allows to calculate the activation energy.

In accordance with the literature [14], by integrating Eq. (1) with the usual change of the variable time into temperature, one obtains

$$F_{\mathrm{rs}} = \int_{x_\mathrm{r}}^{x_\mathrm{s}} \frac{\mathrm{d}x}{f(x)} = \frac{1}{\beta}\int_{T_\mathrm{r}}^{T_\mathrm{s}} K(T)\,\mathrm{d}T = \frac{1}{\beta} I_{\mathrm{rs}}, \tag{2}$$

where x_r, x_s are two different degrees of conversion and T_r, T_s are their corresponding temperatures.

For two selected temperatures T_r and T_s, one can determine pairs of values of x, i.e. ($x_{\mathrm{r}1}$, $x_{\mathrm{s}1}$), ($x_{\mathrm{r}2}$, $x_{\mathrm{s}2}$), … for the experimental data at different heating rates. From these pairs and using various kinetic model functions such as those given in Table 1, the values of $F_{\mathrm{rs}1}$, $F_{\mathrm{rs}2}$, … can be calculated according to Eq. (2). As the temperatures T_r and T_s are the same for all the experiments, considering again Eq. (2), it follows that I_{rs} is constant, and, therefore, a plot of the values of F_{rs} versus $1/\beta$ has to lead to a straight line with an intercept of zero, if the analytical form of $f(x)$ is correctly chosen. The procedure may be repeated for other pairs of temperatures and, consequently, other straight lines will be obtained for the correct form of $f(x)$, by using the best correlation coefficient to choose the suitable kinetic model function. Nevertheless, it is well-known that for the crystallization of glassy alloys, the experimental DSC data are generally analyzed with the framework of formal theory of nucleation and growth, and then the mostly used expression of $f(x)$ is the JMA equation (Table 1) with n called kinetic exponent.

2.1. How to test the applicability of the JMA model

The JMA equation was originally developed to analyse isothermal DSC data. Henderson [4] and Shepilov [17] have shown that the validity of the quoted equation can be extended in non-isothermal regime if the entire nucleation process takes place during the early stages of the transformation, and it becomes negligible afterward. Thus, it seems necessary to develop a simple and reliable method to test the applicability of the quoted equation. In this sense, we define the functions $y(x)$ and $z(x)$ [18] that can be easily obtained by a simple transformation of experimental data. The quoted functions are proportional to the $f(x)$ and $f(x)F(x) = f(x)\int_0^x \mathrm{d}x'/f(x')$ functions, respectively, which are invariant with respect to the experimental variables.

When the continuous heating regime is used, it is necessary to define $y(x) = (\Delta H_\mathrm{c})(\mathrm{d}x/\mathrm{d}t)\exp(E/RT)$, with ΔH_c the total enthalpy change associated with the

Table 1
Theoretical kinetic model equations considered

Model	$f(x)$	$F(x)$	Label
Johnson–Mehl–Avrami (JMA)	$n(1-x)[-\ln(1-x)]^{(n-1)/n}$	$[-\ln(1-x)]^{1/n}$	A_n
Three-dimensional diffusion	$(3/2)[(1-x)^{-1/3}-1]^{-1}$	$1-(2/3)x-(1-x)^{2/3}$	D
Mampel unimolecular law, $n = 1$	$1-x$	$-\ln(1-x)$	R_1
Normal grain growth	$(1-x)^n$	$[1-(1-x)^{1-n}]/(1-n)$	R_n

transformation, and considering Eq. (1), in accordance with the literature [18], one obtains

$$y(x) = A_1 f(x), \tag{3}$$

where $A_1 = (\Delta H_c)\, K_0$ is a constant.

In the case of $z(x)$ function, by using the substitution $u' = E/RT'$, the temperature integral $\int_{T_0}^{T} K(T')\,\mathrm{d}T'$is transformed in an exponential integral of order two, which can be expressed, in accordance with the literature [19], by an alternating series, and Eq. (2) becomes

$$\begin{aligned} F(x) &= \frac{K_0 E}{\beta R}\frac{\mathrm{e}^{-u}}{u^2}\sum_{k=0}^{\infty}\frac{(-1)^k (k+1)!}{u^k} \\ &= \frac{K_0 T}{\beta}\left[\exp(-E/RT)\right] S(E/RT), \end{aligned} \tag{4}$$

if it is assumed that $T_0 \ll T$, so that u_0 can be taken as infinity [20].

Next, we define the $z(x) = (\Delta H_c) T^2 (\mathrm{d}x/\mathrm{d}t)$ function [18] and considering Eqs. (1) and (4), one obtains

$$z(x) = A_2 f(x) F(x) \tag{5}$$

bearing in mind that in most glass-crystal transformations $E/RT \gg 1$,usually $E/RT \geqslant 25$ [20], it is possible to use only the first term of the series of Eq. (4) and the approximation $S(E/RT) \approx RT/E$ is sufficiently accurate. It should be noted that $A_2 = (\Delta H_c)\beta E/R$ is a constant.

From Eqs. (3) and (5) invariant with respect to the experimental variables it can be obtained a reliable test of applicability of the JMA model. Thus, taking the derivative of Eq. (3) with respect to x and equalling to zero the resulting expression leads to

$$\left.\frac{\mathrm{d}[f(x)]}{\mathrm{d}x}\right|_{x_q} = \left[-\ln(1-x_q)\right]^{(n-1)/n} - \frac{n-1}{n}\left[-\ln(1-x_q)\right]^{-1/n} = 0. \tag{6}$$

This equation allows to obtain an expression of x_q, which depends on the kinetic exponent:

$$\begin{aligned} &x_q = 0 \quad \text{for } n \leqslant 1, \\ &x_q = 1 - \exp\left(-\frac{n-1}{n}\right) \quad \text{for } n > 1, \end{aligned} \tag{7}$$

and gives an maximum value for the $y(x)$ function.

In the case of the $z(x)$ function, taking the derivative of Eq. (5) with respect to x and setting the resulting expression equal to zero yields

$$\left.\frac{\mathrm{d}[f(x)]}{\mathrm{d}x}\right|_{x_p} F(x_p) + 1 = 0, \tag{8}$$

the condition that must be fulfilled by x_p at the maximum of the $z(x)$ function.

Introducing the functions $f(x)$, taken from the JMA model and $F(x) = \int_0^x \mathrm{d}x'/f(x')$ into Eq. (8), one obtains

$$\ln(1 - x_p) = -1, \text{ i.e., } x_p = 0.632, \tag{9}$$

the value of the volume fraction transformed, which gives a maximum value for the $z(x)$ function. This value is a characteristic of the quoted model, and, accordingly, it can be used as a simple test of its applicability [18]. Both $y(x)$ and $z(x)$ functions are usually normalized within the (0,1) range, as it is shown in Fig. 1 for the JMA model with kinetic exponent $n = 2.3$.

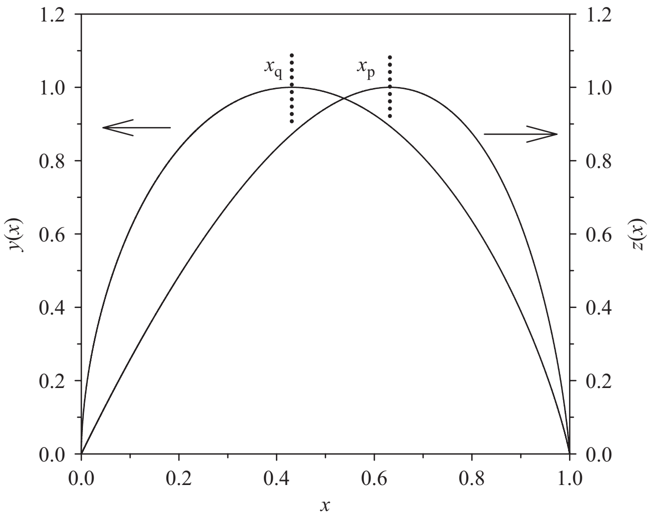

Fig. 1. Normalized $y(x)$ and $z(x)$ functions obtained from the theoretical JMA model with kinetic exponent, $n = 2.3$. The broken lines show the theoretical x_q and x_p values corresponding to the quoted model.

2.2. *Deducing the kinetic parameters*

Once by means of Eq. (2) it is possible to find the most probable kinetic mechanism of the studied transformation, it is necessary to calculate the values of the kinetic parameters E and K_0 [14]. Assuming an Arrhenian temperature dependence for $K(T)$ in Eq. (2), the simplest approach of I_{rs} is to use the first mean value theorem for definite integrals and thus to write

$$\begin{aligned} I_{rs} &= K_0 \int_{T_r}^{T_s} \left[\exp(-E/RT)\right] \mathrm{d}T \\ &= K_0 (T_s - T_r) \exp(-E/R\overline{T}), \end{aligned} \tag{10}$$

where $\overline{T}$ belongs to the (T_r, T_s) range, and, accordingly, the logarithmic form of Eq. (2) can be expressed as

$$\ln\frac{\beta}{T_s - T_r} = \ln\frac{K_0}{F_{rs}} - \frac{E}{R\overline{T}}. \tag{11}$$

For two selected volume fraction transformed x_r and x_s, one can determine a pair of values of T, i.e., (T_{ri}, T_{si}) corresponding to each β_i value. The plot of $\ln[\beta/(T_s–T_r)]$ vs. $1/\overline{T}$ leads to a straight line whose slope, $-E/R$, and intercept, $\ln(K_0/F_{rs})$, allow the calculation of E and K_0, respectively. The procedure may be repeated for other pairs of transformed fraction and, consequently, other straight lines are obtained.

3. Experimental procedure

The $Sb_{0.12}As_{0.36}Se_{0.52}$ glassy alloy was obtained in our laboratory in bulk form, by the standard melt quenching method. High purity (99.999%) antimony, arsenic and selenium in appropriate atomic percentage proportions were weighed into a quartz glass ampoule (6 mm diameter). The content of the ampoule (7 g total) was sealed at a pressure of 10^{-2} Pa, heated in a rotating furnace at 1223 K for 24 h and quenched in water in order to avoid the crystallization of the compound. The amorphous state of the material was checked through a diffractometric X-ray scan, in a Siemens D500 diffractometer. The thermal behaviour was investigated using a Perking-Elmer DSC7 differential scanning calorimeter with an accuracy of ± 0.1 K. The samples weighing about 20 mg were crimped in aluminium pans and scanned from room temperature through their glass transition temperatures, T_g, at different heating rates of 2, 4, 8, 16, 32 and 64 K min^{-1}, by using an empty aluminium pan as reference. The glass transition temperature was considered as a temperature corresponding to the inflection of the lambda-like trace on the DSC scan.

4. Results

The typical DSC traces of $Sb_{0.12}As_{0.36}Se_{0.52}$ chalcogenide glass obtained at the heating rates quoted in Section 3 are plotted in Fig. 2. It should be noted that DSC data for the different heating rates, quoted in Section 3, show values of the quantities T_g, T_c and T_p which increase with increasing β, a property which has been reported in the literature [21]. The quotient between the ordinates of the any thermogram and the total area of its peak gives the corresponding crystallization rates, which allow to plot the curves of the exothermal peaks represented in Fig. 3. The $(dx/dt)|_p$ values increase in the same proportion that the heating rate, a property which has been widely discussed in the literature [22].

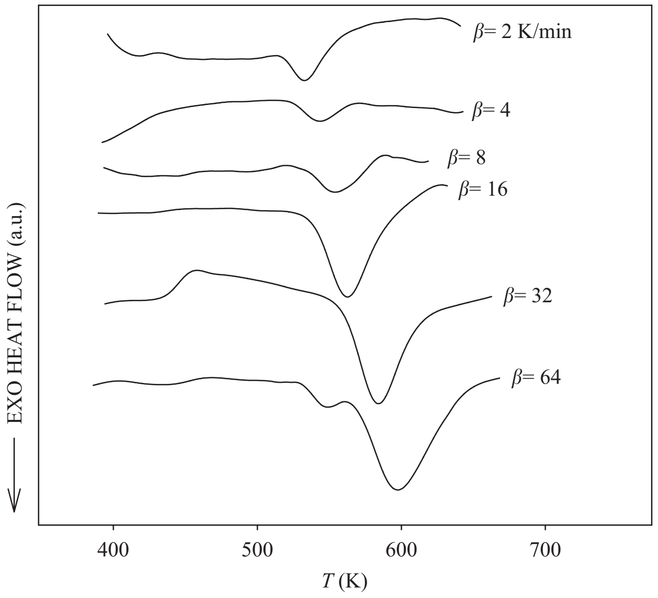

Fig. 2. Continuous heating DSC plots of $Sb_{0.12}As_{0.36}Se_{0.52}$ glassy alloy.

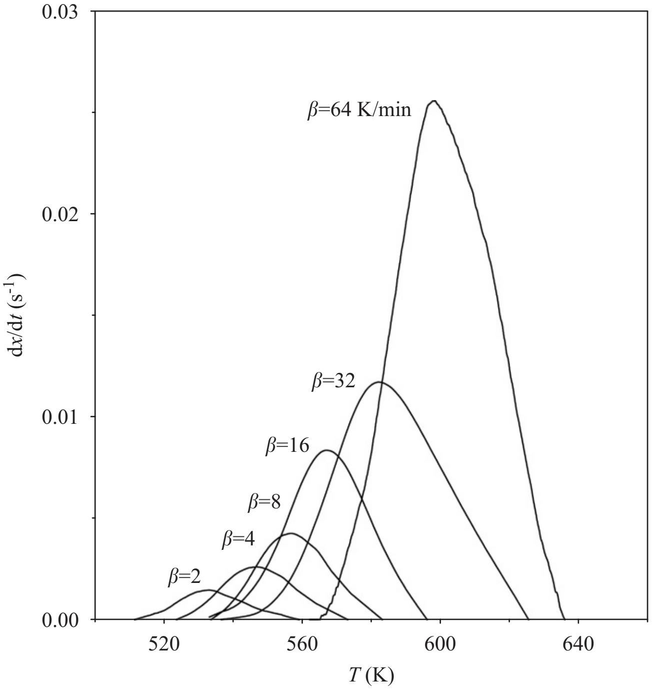

Fig. 3. Crystallization rate versus temperature of the exothermal peaks at different heating rates.

Table 2
Volume fraction transformed, x, corresponding to various temperatures T_r, T_s at different heating rates

T (K)	x					
	β(K min^{-1})					
	2	4	8	16	32	64
541	0.79117	0.38522	0.15868	0.04	—	—
550	0.96229	0.72310	0.38278	0.14	0.04	—
563	—	0.97650	0.80332	0.52	0.18	0.1
571	—	—	0.96385	0.76	0.32	0.14

4.1. Glass-crystal transformation

With the aim of correctly applying the preceding theory to choose the most suitable kinetic mechanism for the crystallization of the material studied, the temperatures T_r, T_s, and the corresponding volume fractions transformed for each of them, at different β, are given in Table 2. With the help of the functions of Table 1, by using Eq. 2 and the least-squares method, Table 3 was obtained, wherein the correlation coefficients for each plot of F_{rs} vs. $1/\beta$ are given. The quoted coefficients are calculated for the straight lines, which pass through the computed points $(1/\beta, F_{rs})$ and the origin of the axes, because as mentioned, the intercept of

Table 3
Correlation coefficients, r, corresponding to kinetic mechanisms of Table 1 for $Sb_{0.12}As_{0.36}Se_{0.52}$ glassy alloy

Mechanism label	r		
	$T_r = 541$ K $T_s = 550$ K	$T_r = 550$ K $T_s = 563$ K	$T_r = 563$ K $T_s = 571$ K
A_2	0.9391	0.9400	0.9905
A_3	0.8106	0.8094	0.9647
D	0.9844	0.9856	0.9811
R_1	0.9241	0.9239	0.9236
$R_{1.9}$	0.9973	0.9981	0.9898

Table 4
Temperatures corresponding, T (K), to various volume fraction transformed x at different heating rates

x	T (K)					
	β(K min^{-1})					
	2	4	8	16	32	64
0.1	522.7	532.0	537.6	547.5	557.5	560.2
0.4	531.0	541.5	550.4	559.6	574.2	593.7
0.8	541.2	552.5	563.0	572.3	594.4	612.1
0.9	545.5	557.0	567.2	577.4	602.6	618.6

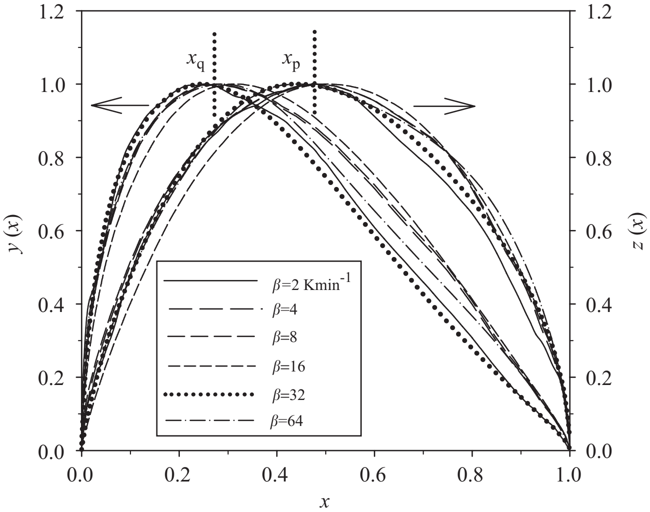

Fig. 4. Plots of normalized $y(x)$ and $z(x)$ functions obtained from experimental data corresponding to the non-isothermal glass-crystal transformation of the $Sb_{0.12}As_{0.36}Se_{0.52}$ alloy.

the plot has to be zero. It should be noted that the correlation coefficients closer to the unit are obtained for the kinetic model R_n with $n = 1.9$ in accordance with Table 3. The same result was obtained for all cases which, for the sake of simplicity, are not listed in this work. Next, to calculate the kinetic parameters E and K_0, we have chosen the volume fractions transformed and the corresponding temperatures for each β, which are given in Table 4. According to Eq. (11) the plots of ln $[\beta/(T_s–T_r)]$ vs. $1/\overline{T}$ leads to straight lines whose slopes and intercepts provide the mean values: $E = 27.36\,\mathrm{kcal\,mol^{-1}}$ and $\ln K_0 = 20.92$ (K_0 in s^{-1}), respectively.

On the other hand, we have used the applicability test of the JMA model considering the functions: $y(x) \propto (\mathrm{d}x/\mathrm{d}t)\exp(E/RT)$ and $z(x) \propto T^2(\mathrm{d}x/\mathrm{d}t)$ [18]. The quoted normalized functions corresponding to the experimental data of the $Sb_{0.12}As_{0.36}Se_{0.52}$ alloy are shown in Fig. 4, which reveals that the quoted model is not fulfilled by the glass-crystal transformation of the above-mentioned alloy. It should be noted that the quoted functions show maximum values $x_q = 0.2711$ and $x_p = 0.4805$, according to Fig. 4. These x-values are notably different from the corresponding to the JMA model, $x_p = 0.6321$ and $x_q = 0.3773$, in accordance with $x_q = 1-\exp[-(n-1)/n]$, quoted in Section 2, and $n = 1.9$. These results seem to confirm again that the kinetic model R_n is the most suitable to describe the crystallization of the alloy studied.

5. Conclusions

An integral method has been considered to determine the suitable form of the glass-crystal transformation function and to deduce the kinetic parameters by using DSC data, obtained from experiments carried out under non-isothermal regime. The assumptions and approximations on which the quoted method is based are the following:

(i) It is assumed that the glass-crystal transformation rate depends on two independent variables: the volume fraction transformed, x, and the temperature, T.
(ii) It is supposed that over adequate ranges of x and β values the analytical forms of $f(x)$ and $K(T)$ do not change, and consequently the transformation kinetics does not change.
(iii) The temperature dependence of the reaction rate constant obeys the Arrhenius relationship.
(iv) It is performed the approximation of taking $\overline{T}$, used to calculate the temperature integral, as the average of the considered temperature interval.

The analysis of the kinetic mechanism is based on assumptions (i) and (ii), whilst the calculation of the kinetic parameters may be performed only if the three assumptions and the approximation quoted before are used together.

The theoretical method considered has been applied to the crystallization kinetics of the $Sb_{0.12}As_{0.36}Se_{0.52}$ glassy alloy. According to the study carried out, it is possible to establish that the kinetic model of normal grain growth with $n = 1.9$ is the most suitable to describe the crystallization of the material analysed. Since the quoted model shows the correlation coefficients closer to the unit. The results obtained for the kinetic parameters: $E = 27.36\,\mathrm{kcal\,mol^{-1}}$ and $\ln K_0 = 20.92$ are in good agreement with the corresponding values given in the literature for similar alloys. This fact confirms the reliability of the method considered.

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