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Application of the single-scan calorimetric technique to the crystallization of the semiconducting $Sb_{0.16}As_{0.29}Se_{0.55}$ alloy

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Abstract

A procedure has been considered for analyzing the change with time of the volume fraction crystallized and for calculating the kinetic parameters (activation energy, kinetic exponent and frequency factor) of non-isothermal reactions in materials involving formation and growth of nuclei. By using the assumptions of extended volume and random nucleation, a particular expression of the fraction crystallized as a function of time has been derived in isothermal crystallization processes. The application of the crystallization rate equation to the non-isothermal processes has been carried out, and the kinetic parameters have been deduced by using the calorimetric techniques of data analysis of single-scan and multiple-scan. The theoretical method considered has been applied to the crystallization kinetics of the semiconducting alloy $Sb_{0.16}As_{0.29}Se_{0.55}$. The agreement between the kinetic parameters obtained according to both techniques confirms the reliability and accuracy of the single-scan technique when calculating the above-mentioned parameters in non-isothermal crystallization processes. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The study of crystallization kinetics in amorphous materials by differential scanning calorimetry (DSC) methods has been discussed in the literature [1,2]. There is a variety of mathematical treatments mostly based in the Johnson–Mehl–Avrami (JMA) transformation rate equation [3–6]. In this work the conditions of applicability of the JMA transformation rate equation to non-isothermal crystallization are established. The kinetic parameters of the above-mentioned crystallization are obtained by using the calorimetric techniques of data analysis of single-scan and multiple-scan. Finally, the present paper applies the JMA techniques to the analysis of the crystallization kinetics of the glassy alloy $Sb_{0.16}As_{0.29}Se_{0.55}$ and the kinetic parameters thus obtained differ by about 8%. This fact shows the reliability and accuracy of the single-scan technique for the calculation of the parameters (activation energy, kinetic exponent, and frequency factor) from a continuous heating treatment.

2. Theoretical basis

The theoretical basis for interpreting DSC results is provided by the formal theory of

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transformation kinetics [3–8]. Defining an extended volume of transformed material and assuming spatially random nucleation [9] it is possible to describe the change with time, t, of the volume fraction transformed, x, in terms of the nucleation frequency, I_V, and the crystal growth rate, u

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

where g is a geometric factor, m is an exponent which depends on the dimensionality of the crystal growth, and where the critical size of each nucleus has been disregarded.

For the important case of isothermal crystallization with nucleation frequency and growth rate independent of time, Eq. (1) can be integrated yielding a expression that can be taken as a detailed case of the JMA [3–6] transformation equation

$$x(t) = 1 - \exp(-Kt^n). \tag{2}$$

Here $K = K_0\exp(-E/RT)$ is a quantity related to the reaction rate constant, where K_0 is a pre-exponential factor, E is the effective activation energy, T is the absolute temperature and R is the gas constant.

The isothermal transformation rate can be determined from Eq. (2) by differentiating with respect to time and substituting in resulting expression the explicit relation between x and t given by Eq. (2) to yield

$$\begin{aligned}\mathrm{d}x/\mathrm{d}t &= nK^{1/n}(1-x)[-\ln(1-x)]^{(n-1)/n}\\ &= nK^{1/n}f(x).\end{aligned} \tag{3}$$

This equation, which is referred to as the JMA transformation rate equation, can be applied under non-isothermal conditions [10], if it can be shown that the transformation rate, depends only on the variables x and T. Under these conditions, defining the heating rate, $\beta = \mathrm{d}T/\mathrm{d}t$, and according to Henderson [10], Eq. (3) is separable in x and T and, therefore, can be directly integrated, if the substitution $y' = E/nRT'$ is used, resulting in

$$\begin{aligned}[-\ln(1-x)]^{1/n} &= \frac{EK_0^{1/n}}{nR\beta}\int_y^\infty \mathrm{e}^{-y'}y'^{-2}\,\mathrm{d}y'\\ &= \frac{EK_0^{1/n}}{nR\beta}\left[\frac{\mathrm{e}^{-y'}}{y'^2}\sum_{k=0}^{\infty}\frac{(-1)^k(k+1)!}{y'^k}\right]_\infty^y,\end{aligned} \tag{4}$$

where the series is defined clearly in the work of Vázquez et al. [8].

From this point, two basic approximations have been used. First one comes from the fact that in the alternating series the error produced is less than the first term neglected, and second one comes from considering that, in most crystallization reactions, $y' \gg 1$ (usually $E/RT' \geqslant 25$). Bearing in mind both approximations, it is possible to use only the two first terms of the quoted series and then the error introduced is not greater than 1%. By using the above-mentioned approximations in Eq. (4) and taking logarithm in the resulting expression, we obtain

$$\ln[-\ln(1-x)] - 2n\ln T = -\frac{E}{RT} + n\ln\frac{nRK_0^{1/n}}{\beta E}, \tag{5}$$

which is linear in $1/T$ and whose slope is the activation energy, assuming [11] that over a temperature range of 100 K the contribution of the term, $2n\ln T$, can be ignored without causing a substantial error in the calculated activation energy.

The logarithmic form of Eq. (3), where the function $f(x)$ has been defined, gives

$$\ln(\mathrm{d}x/\mathrm{d}t) = -\frac{E}{nRT} + \ln[f(x)] + \ln\left(nK_0^{1/n}\right). \tag{6}$$

In addition, $\ln(\mathrm{d}x/\mathrm{d}t)$ is linear in $1/T$, if it is assumed that for $0.25 < x < 0.75$ the function $\ln[f(x)]$ may be considered constant. The slope of this function can then, be used to calculate E/n. The determination of E/n and E through the single-scan technique makes it possible to directly obtain the parameter, n.

On the other hand the crystallization kinetics can be analyzed by means of the multiple-scan technique. When this technique is applied to the case of a JMA transformation rate equation, generalization of Eq. (2) for the treatment of continuous heating experiments is necessary. Assume that the transformation products and mechanism do not change with temperature, then it is reasonable to replace $K^{1/n}t$ with $\int_0^t [K(T(t'))]^{1/n}\,\mathrm{d}t'$, according to literature [12], and Eq. (2) generalizes to

$$x(t) = 1 - \exp\left\{-\left[\int_0^t \left[K\left(T(t')\right)\right]^{1/n}\mathrm{d}t'\right]^n\right\} = 1 - \exp(-I^n), \tag{7}$$

where $K(T(t')) = K_0 \exp(-E/RT)$ and $T(t')$ is the absolute temperature. The maximum transformation rate is found by making $\mathrm{d}^2x/\mathrm{d}t^2 = 0$, and according to Vázquez et al. [12] gives

$$\ln\left(T_\mathrm{p}^2/\beta\right) + \ln\left(nRK_0^{1/n}/E\right) - E/nRT_\mathrm{p} = (2nRT_\mathrm{p}/E)(1 - 1/n^2), \tag{8}$$

where the temperatures which correspond to the maximum crystallization rate are denoted by subscript p. The right-hand-side (RHS) of Eq. (8) is generally negligible in comparison to the individual terms on the left hand side if it is assumed that in most crystallization reactions $ER/T \geqslant 25$. Eq. (8) serves to determine the quotient E/n and the coefficient K_0, related to the frequency factor, from the slope and intercept, respectively, of a $\ln(T_\mathrm{p}^2/\beta)$ versus $1/T_\mathrm{p}$ plot. In addition, as Eq. (8) with RHS = 0 is obtained assuming that $2RT_\mathrm{p}/E \ll 1$, according to literature [13], results in

$$E = RT_\mathrm{p}^2(\mathrm{d}x/\mathrm{d}t)|_\mathrm{p}(0.37\beta)^{-1}, \tag{9}$$

from which we calculate the kinetic parameter, E, in a set of exotherms taken at different heating rates and the corresponding mean represents the overall activation energy of the crystallization process.

3. Experimental

Antimony, arsenic and selenium (all 99.999%) in appropriate atomic percent proportions to form the alloy $Sb_{0.16}As_{0.29}Se_{0.55}$ were weighed into a quartz glass ampoule, which was sealed at a pressure of 10^{-2} N m^{-2} and heated in a rotating furnace at around 1225 K for 24 h, and then quenched in water. The amorphous state of the material was observed by a diffractometric X-ray scan, (Siemens D500). The homogeneity and composition of the sample were verified through scanning electron microscopy (JSM-820). The thermal properties were investigated using a differential scanning calorimeter (Perkin–Elmer DSC7) with an accuracy of ±0.1 K. Powdered samples weighing about 20 mg were crimped in aluminium pans and scanned at different heating rates: 1, 2, 4, 8, 16, 32 and 64 K min^{-1}. The glass transition temperature, T_g, was taken as a temperature corresponding to the inflection of the lambda-like trace on the DSC scan, as shown in Fig. 1.

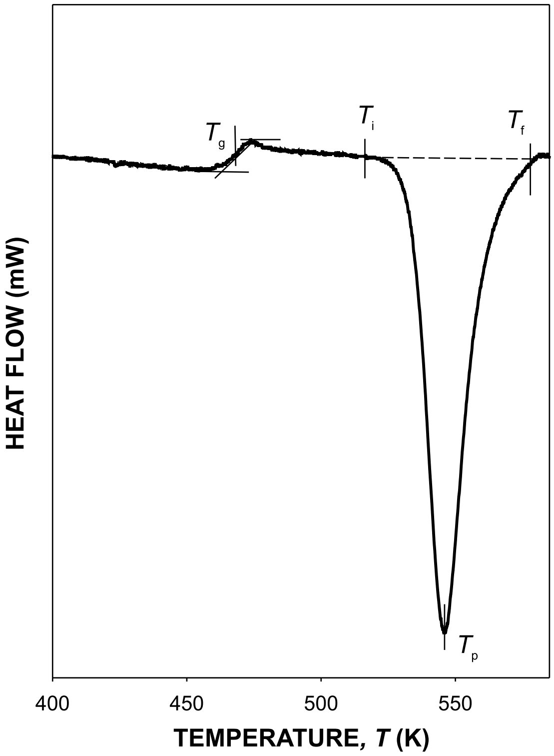

Fig. 1. Typical DSC trace of $Sb_{0.16}As_{0.29}Se_{0.55}$ glassy alloy at a heating rate of 16 K min^{-1}.

4. Results

The crystallization kinetics of the $Sb_{0.16}As_{0.29}Se_{0.55}$ alloy were analyzed by using the calorimetric techniques of single-scan and multiple-scan. With the aim of analyzing the abovementioned 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 rate, respectively, and ΔT is the width of the crystallization maximum. The crystallization enthalpy, ΔH, is also determined for each of the heating rates. The crystallization rates corresponding to the different scans are represented in Fig. 2. We observe that $(dx/dt)|_p$'s increase in the same proportion as the heating rate, a fact according to the literature [14].

The single-scan technique was applied to several sets of experimental data, Table 2, obtained for all heating rates, quoted in Section 3, and results for E from Eq. (5), E/n from Eq. (6), n derived there from, and K_0 are included in Table 2. The means for these parameters are: $\langle E\rangle = 353.3 \pm 12.3$ kJ mol^{-1}, $\langle n\rangle = 2.2 \pm 0.4$ and $\langle K_0\rangle = 1.1 \times 10^{32}$ s^{-n}. To illustrate the above mentioned technique, Fig. 3 shows the plots of $\ln[-\ln(1-x)]$ versus $1/T$ for $\beta = 8$ K min^{-1}, together with the corresponding linear regression plot, while the plots of $\ln(dx/dt)$ versus $1/T$ with the linear regression curve carried out, are shown in Fig. 4. We note that the ranges of $10^3/T$ in each of the figures differ, i.e., 1.86–1.89 K^{-1} in Fig. 3 and 1.870–1.884 K^{-1}, in Fig. 4. The reason for this selection is to get a better fit to a linear function in each case.

Table 1
The characteristic temperatures and enthalpies of the crystallization processes of alloy $Sb_{0.16}As_{0.29}Se_{0.55}$

Parameter	Experimental
T_g (K)	450.6–474.5
T_i (K)	495.7–533.4
T_p (K)	509.7–570.4
ΔT (K)	30.5–62.3
ΔH(kJ kg^{-1})	42.1–51.3

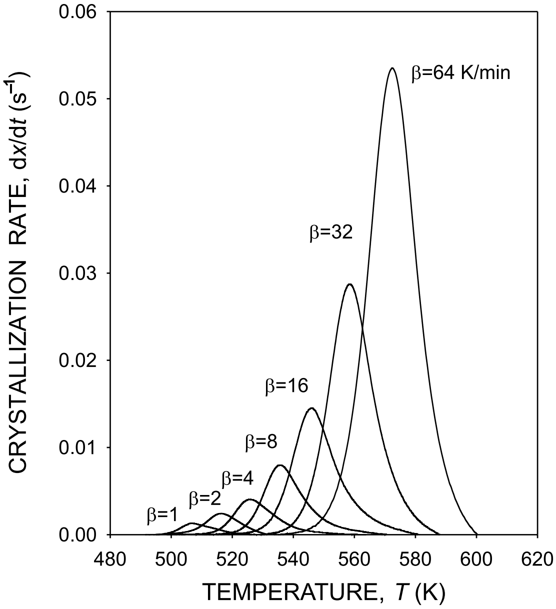

Fig. 2. Crystallization rate versus temperature for different heating rates.

The multiple-scan technique has been also used to analyze the crystallization kinetics of the

Table 2
Kinetic parameters found for the crystallization of the $Sb_{0.16}As_{0.29}Se_{0.55}$ alloy by using the single-scan technique

β (K min^{-1})	Interval		E (kJ mol^{-1})	E/n (kJ mol^{-1})	n	K_0 (s^{-n})
	T(K)	$10^3 dx/dt$(s^{-1})				
1	501.3–509.4	0.54–1.04	381.7 ± 13.3	174.2 ± 5.8	2.2 ± 0.4	7.2×10^{32}
2	513.5–516.2	1.63–1.99	371.7 ± 12.9	166.7 ± 5.8	2.2 ± 0.4	4.2×10^{31}
4	522.2–524.6	2.46–2.92	331.7 ± 11.7	162.9 ± 5.4	2.0 ± 0.3	8.5×10^{27}
8	531.1–534.3	6.12–7.40	369.6 ± 12.9	140.4 ± 5.0	2.6 ± 0.4	2.7×10^{30}
16	540.1–544.2	8.83–11.47	332.9 ± 11.7	155.8 ± 5.4	2.1 ± 0.3	7.3×10^{27}
32	551.8–556.0	19.01–24.93	341.7 ± 11.7	165.4 ± 5.8	2.1 ± 0.4	7.1×10^{28}
64	563.5–570.0	33.76–49.02	344.2 ± 12.1	153.8 ± 5.4	2.2 ± 0.4	4.6×10^{28}

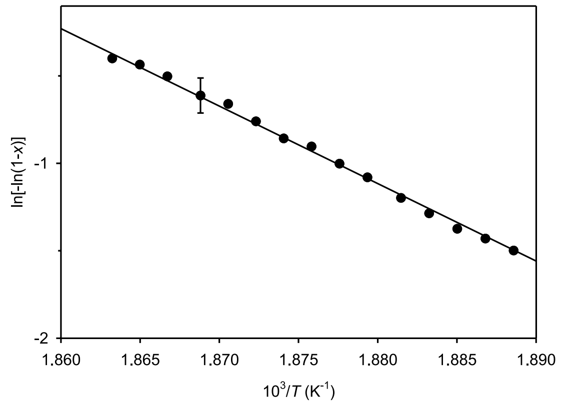

Fig. 3. Variation of $\ln[-\ln(1-x)]$ with $1/T$ for a heating rate of 8 K min^{-1}. The function $\ln[-\ln(1-x)]$ is fitted to the experimental data. The correlation coefficient of the fit is $R = 0.997$.

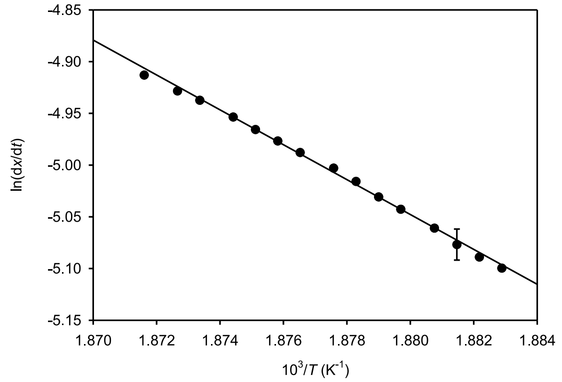

Fig. 4. Experimental plots of $\ln(dx/dt)$ versus $1/T$ and straight regression line of the $Sb_{0.16}As_{0.29}Se_{0.55}$ alloy, for $\beta = 8$ K min^{-1}. The function $\ln(dx/dt)$ is fitted to the experimental data. The correlation coefficient of the fit is $R = 0.998$.

semiconducting $Sb_{0.16}As_{0.29}Se_{0.55}$ alloy. The plots of $\ln(T_p^2/\beta)$ versus $1/T_p$ at each heating rate, can be fit with a linear function. According to Eq. (8) with RHS $= 0$, from the slope and the intercept of the above function, the quotient $E/n = 156.3 \pm 5.4$ kJ mol^{-1} and $K_0 = (5.0 \pm 0.4) \times 10^{28}$ s^{-n} have been calculated. By using the maximum crystallization rate, and the temperatures, which correspond to the quoted maxima, given in Table 3, it is possible to obtain, through the Eq. (9), the activation energy of the process corresponding to each of the experimental heating rates. The parameters, E, are also shown in Table 3, and the corresponding mean, $\langle E \rangle = 342.5 \pm 11.9$ kJ mol^{-1}, has been calculated. Once the E/n and E were known, the kinetic exponent, $n = 2.2 \pm 0.4$, was immediately obtained.

Table 3
The maximum crystallization rate, corresponding temperature and activation energy for the different heating rates

β (K min^{-1})	T_p (K)	$10^3(dx/dt)\vert_p$ (s^{-1})	E (kJ mol^{-1})
1	509.7	1.05	370.0 ± 12.9
2	516.8	2.00	360.4 ± 12.5
4	525.2	3.43	320.0 ± 11.3
8	534.9	7.43	359.2 ± 12.5
16	545.1	12.82	321.7 ± 11.3
32	557.0	25.11	329.2 ± 11.3
64	570.4	48.95	336.3 ± 11.7

The parameters E, n and $\ln K_0$, calculated by means techniques of single-scan and multiple-scan, were compared, finding that the error between them is less than 8.5%, in agreement with the literature [11].

5. Conclusions

The considered theoretical procedure enable us to study the changes with time of the volume fraction transformed in materials involving nucleation and crystal growth processes. In the case of isothermal transformation, the quoted fraction is expressed by means of the JMA transformation equation. The application of this equation in non-isothermal transformations implies that the transformation rate depends only on the fraction transformed and the temperature, and under these conditions the kinetic parameters have been deduced by using the techniques of single-scan and multiple-scan. These techniques have been applied to the crystallization kinetics of the semiconducting $Sb_{0.16}As_{0.29}Se_{0.55}$ alloy. The agreement between the parameters obtained by means of both techniques shows the reliability of the single-scan technique for the analysis of the crystallization kinetics.

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