Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

ELSEVIER

Physica B 336 (2003) 297–307

PHYSICA B

www.elsevier.com/locate/physb

Theoretical study on the glass–crystal transformation and deduction of its kinetic parameters by DSC, using non-isothermal regime

J. Vázquez*, R. González-Palma, P. Villares, R. Jiménez-Garay

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

Received 16 October 2002; received in revised form 5 March 2003

Abstract

A method has been developed for deriving the evolution equation with time of the volume fraction crystallized, for integrating the above-mentioned equation under non-isothermal conditions, and for deriving the kinetic parameters of the glass–crystal transformations in solid systems involving the formation and growth nuclei. By means of this method, and considering the assumptions of extended volume and random nucleation, a general expression of the fraction crystallized has been obtained as a function of the time. This equation has been integrated under continuous-heating regime and assuming an Arrhenian temperature dependence of the nucleation frequency and of the crystal growth rate, thus obtaining the volume fraction transformed as a function of temperature, in terms of the heating rate, and the related exponent with the dimensionality of the crystal growth. The kinetic parameters have been deduced, obtaining the maximum crystallization rate, bearing in mind the fact that, in the non-isothermal processes the reaction rate constant is a time function through its Arrhenian temperature dependence. Finally, the theoretical expressions of the kinetic parameters have been applied to the experimental data corresponding to a set of glassy alloys, quoted in the literature, thus obtaining mean values that agreed very satisfactorily with the published data. This fact shows the reliability of the theoretical procedure developed.

PACS: 61.40; 64.60.Qb; 64.70.Kb; 64.70.Pf

Keywords: Glassy alloy; Nucleation and crystal growth; Glass–crystal transformation; Extended volume; Differential scanning calorimetry; Crystallization rate; Kinetic parameters

1. Introduction

Although glass has been used as an artistic medium and industrial material for centuries it has been only in recent years that "glass science" has emerged as a field of study in its own right. The advances that have been made in the physics and chemistry of these materials have been widely appreciated within the research community. A strong theoretical and practical interest in the application of isothermal and non-isothermal experimental analysis techniques to the study of

---

*Corresponding author. Tel.: +349-56-016323; fax: +349-56-016288.

E-mail address: jose.vazquez@uca.es (J. Vázquez).

doi:10.1016/S0921-4526(03)00296-5

glass–crystal transformations has been developed in the last decades. While isothermal experimental analysis techniques are in most cases more definitive, non-isothermal thermoanalytical techniques have several advantages. These techniques can be used to extend the temperature range of measurement beyond that accessible to isothermal experiments. The non-isothermal thermoanalytical regimes have become particularly prevalent for the research of the processes of nucleation and growth that occur during transformation of the metastable phases in a glassy alloy as it is heated. These regimes provide rapid information on such physical characteristics as glass transition temperature, transformation enthalpy and activation energy over a wide range of temperature [1]. In addition, the high thermal conductivity as well as the temperature at which transformations occur in most amorphous alloys make these transformations particularly suited to analysis in a differential scanning calorimeter (DSC).

The study of crystallization kinetics in amorphous materials by DSC methods has been widely discussed in the literature [2,3]. The increasing use thermoanalytical techniques has, however, offered the promise of obtaining useful data with simple methods. The utilization of the quoted techniques depends in turn on the development of sound methods for analyzing the experimental data. With this objective a large number of mathematical treatments have been proposed for analyzing DSC data. While all of the treatments are based on the formal theory of transformation kinetics, they differ greatly in their assumptions, and in some cases they lead to contradictory results. It was suggested by Henderson [4] in a notable work that many of the treatments are based on an incomplete understanding of the formal theory of transformation kinetics.

Experiments reported in the literature [5,6] indicate that the growth rate of crystallites in glass-forming liquids is not limited (at least in certain glass-forming systems) by the removal of heat from the crystal–liquid interface. The departure in temperature of the interface from that of either bulk phase is negligible. In this light, glass-forming liquids may provide unique systems in which to assess the validity of the theoretical models used to describe the processes of crystal growth. They provide systems in which the temperature of the liquid–crystal interface is well defined by the temperature of the system, and therefore, the time evolution of the crystallization kinetics can meaningfully be measured using thermal analysis techniques. Thus, it is not surprising that recently DSC has been examined as a technique which is applicable to the study of phase transformations involving nucleation and growth and in particular to the crystallization kinetics of the glass-forming liquids [7–15]; with very few exceptions the analysis of the data obtained has been carried out using the Johnson–Mehl–Avrami (JMA) [16–19] transformation rate equation.

In the present work, a theoretical method has been developed for obtaining an evolution equation with time for the volume fraction crystallized and for integrating the quoted equation under non-isothermal conditions by DSC. Besides, through the above-mentioned method, the kinetic parameters of the glass–crystal transformation have been deduced in solid systems involving formation and growth of nuclei, starting from the formal theory of transformation kinetics.

2. Theoretical procedure

2.1. Nucleation, crystal growth and volume fraction crystallized

The theoretical basis for interpreting DTA or DSC is provided by the formal theory of transformation kinetics [16–23]. 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 [24]. 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 $t = \tau$ (being τ the nucleation period) is then

$$v_\tau = g\prod_i \int_\tau^t u_i(t')\,\mathrm{d}t', \tag{1}$$

where the expression $\prod_i \int_\tau^t u_i(t')\,\mathrm{d}t'$condenses the product of the integrals corresponding to the values of the above-quoted subscript i and g is a geometric factor, which depends on the dimensionality and shape of the crystal growth, and therefore its dimension equation can be expressed as

$[g] = [L]^{3-i}$ ($[L]$ is the length).

Defining an extended volume of transformed material and assuming spatially random nucleation [25,26], the elemental extended volume fraction in terms of nucleation frequency per unit volume, $I_V(\tau)$, is expressed as

$$\begin{aligned}\mathrm{d}x_\mathrm{e} &= v_\tau I_V(\tau)\,\mathrm{d}\tau\\ &= gI_V(\tau)\left(\prod_i \int_\tau^t u_i(t')\,\mathrm{d}t'\right)\mathrm{d}\tau \end{aligned} \tag{2}$$

and bearing in mind the relation $\mathrm{d}x = (1-x)\mathrm{d}x_\mathrm{e}$, one obtains

$$\frac{\mathrm{d}x}{1-x} = gI_V(\tau)\left(\prod_i \int_\tau^t u_i(t')\,\mathrm{d}t'\right)\mathrm{d}\tau, \tag{3}$$

where x is the true volume fraction transformed.

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 [24], Eq. (3) can be written as

$$\frac{\mathrm{d}x}{1-x} = I_V(\tau)v_\tau\,\mathrm{d}\tau = gI_V(\tau)\left(\int_\tau^t u(t')\mathrm{d}t'\right)^m \mathrm{d}\tau, \tag{4}$$

where m is an exponent, which depends on the dimensionality of the crystal growth.

It should be noted that the shape factor, g, must take different values, according to the geometric characteristics of the solid material. When this is a bulk with sufficiently large dimensions to allow a three-dimensional growth, according to Eq. (4) the value $g = 4\pi/3$ is obtained. If the transformation occurs in a thin sheet, it may happen that the average dimension of a transformed region is much greater than the thickness, d, of the sheet. The growth in this direction must soon cease, and thereafter the growth is essentially two-dimensional, therefore, according to Eq. (4) the volume of a transformed region can be expressed as

$$v_\tau = g\left(\int_\tau^t u(t')\,\mathrm{d}t'\right)^m = \pi d\left(\int_\tau^t u(t')\,\mathrm{d}t'\right)^2$$

with $g = \pi d$, measured in meters.

Finally, when the transformation carries out in a wire of diameter d, the growth would be one-dimensional and according to Eq. (4) the transformed volume can be written as

$$v_\tau = g\left(\int_\tau^t u(t')\mathrm{d}t'\right)^m = \frac{\pi d^2}{4}\int_\tau^t u(t')\,\mathrm{d}t',$$

where the geometric factor is $g = \pi d^2/4$, measured in square meters.

For the important case of isothermal crystallization [27] with nucleation frequency and growth rate independent of time, Eq. (4) can be integrated, resulting in

$$\begin{aligned} x &= 1 - \exp\left[-gI_V u^m \int_0^t (t-\tau)^m\,\mathrm{d}\tau\right]\\ &= 1 - \exp(-g' I_V u^m t^n), \end{aligned} \tag{5}$$

where $n = m + 1$ for $I_V \neq 0$ and g' is a new shape factor.

Eq. (5) can be taken as a detailed specific case of the JMA relationship

$$x = 1 - \exp[-(Kt)^n]. \tag{6}$$

Here K is defined as the effective overall reaction rate constant, which is usually assigned an Arrhenian temperature dependence:

$$K = K_0\exp(-E/RT), \tag{7}$$

where E is the effective activation energy, describing the overall crystallization process. By comparing Eqs. (5) and (6), it is seen that K^n is proportional to $I_V u^m$. Hence, assumption of an Arrhenian temperature dependence for K is appropriate when I_V and u vary in an Arrhenian manner with the temperature.

In general, the temperature dependence of the nucleation frequency is far from Arrhenian, and the temperature dependence of the crystal growth rate is also not Arrhenian when a broad range of temperature is considered [27]. Over a sufficiently limited range of temperature (such as the range of crystallization peaks in DTA or DSC experiments), both I_V and u may be described in zeroth-order approximation by

$$I_V \approx I_{V0} \exp(-E_N/RT) \tag{8}$$

and

$$u \approx u_0 \exp(-E_G/RT), \tag{9}$$

where E_N and E_G are the effective activation energies for nucleation and growth, respectively.

Combining Eqs. (5)–(9) results in

$$K^n \propto I_V u^m$$

or

$$K_0^n \exp(-nE/RT) \propto I_{V0} u_0^m \exp[-(E_N + mE_G)/RT] \tag{10}$$

and the overall effective activation energy for crystallization is expressed as

$$E \approx (E_N + mE_G)/n. \tag{11}$$

Eqs. (6) and (7) have served as the basis of nearly all treatment of crystallization in DTA or DSC experiments. It should be noted, however, that Eq. (6) strictly applies only to isothermal experiments, where an integration of the general expression of Eq. (4) is straightforward. Nevertheless, Eq. (6) has been extensively used to derive expressions describing non-isothermal crystallization. Experimental studies interpreted on the basis of such expressions have often indicated good agreement between the overall effective activation energy, E, of Eq. (7) and activation energies obtained by other methods, most notably activation energies for viscosity or crystal growth. In spite of this, it is more accurate to integrate Eq. (4) under non-isothermal conditions, according to the literature [22,27,28].

In the present work, a theoretical method has been developed to integrate Eq. (4) under the above-mentioned conditions and to obtain a general expression for the volume fraction crystallized for each value of the m exponent. In this sense, the case when nucleation and crystal growth occur simultaneously has been considered. Both the nucleation frequency Eq. (8), and crystal growth rate, Eq. (9), may still be approximately described by Arrhenius-type laws at temperatures lower than the peak temperatures for both quantities. In the quoted case, the temperature dependence of volume fraction transformed, x, involves a range of particles that are nucleated at different temperatures and, thus, grow to different final sizes when the sample is subjected to continuous heating. By considering the quoted fact of nucleation and crystal growth simultaneous, which agrees with literature [22], Eq. (4) becomes

$$\frac{\mathrm{d}x}{1-x} = g I_{V0} u_0^m \mathrm{e}^{-E_N/RT_\tau} \left(\int_\tau^t \mathrm{e}^{-E_G/RT'} \, \mathrm{d}t' \right)^m \mathrm{d}\tau, \tag{12}$$

where T_τ is the temperature at time τ.

Bearing in mind that a linear heating rate, β, is usually employed in non-isothermal experiments, then $T = T_0 + \beta t$, where T_0 is the initial temperature of the thermal treatment and therefore $\mathrm{d}t = \mathrm{d}T/\beta$, and the preceding relationship can be rewritten as

$$\frac{\mathrm{d}x}{1-x} = p I_1^m \mathrm{e}^{-E_N/RT_\tau} \, \mathrm{d}\tau, \tag{13}$$

where p is a parameter equal to $g I_{V0} u_0^m \beta^{-m}$ and I_1 is an integral defined by

$$I_1 = \int_{T_\tau}^{T} \mathrm{e}^{-E_G/RT'} \mathrm{d}T'. \tag{14}$$

Using the substitution $z' = E_G/RT'$, the integral I_1 is transformed to the expression

$$I_1 = \frac{E_G}{R} \int_z^{z_\tau} \frac{\mathrm{e}^{-z'}}{z'^2} \mathrm{d}z'. \tag{15}$$

This exponential integral of order two is a particular case of that of order r, which we have evaluated by means of a set of consecutive integrations by parts, obtaining the sum of the alternating series

$$S_r(z_\tau, z) = \left[\frac{-\mathrm{e}^{-z'}}{z'^r} \sum_{k=0}^{\infty} \frac{(-1)^k (k+r-1)!}{(r-1)! z'^k} \right]_z^{z_\tau}. \tag{16}$$

Accordingly, taking $r = 2$ in Eq. (16) and considering that in this type of series the error produced is less than the first term neglected, Eq. (15) becomes

$$I_1 = \frac{E_G}{R}\left[\frac{e^{-z}}{z^2} - \frac{e^{-z_\tau}}{z_\tau^2}\right] = \frac{R}{E_G}\left[T^2 e^{-E_G/RT} - T_\tau^2 e^{-E_G/RT_\tau}\right] \qquad (17)$$

bearing in mind that in most crystallization reactions $z' = E/RT' \gg 1$, usually $E/RT' \geqslant 25$, it is possible to use only the first term of the above-mentioned series without making any appreciable error.

Substituting Eq. (17) into Eq. (13), by using the expansion of the binomial-potential series and integrating the resulting expression one obtains

$$x = 1 - \exp\left[-P\sum_{s=0}^{m}(-1)^s \binom{m}{s}\left(T^2 e^{-E_G/RT}\right)^{m-s} I_2(s)\right] \qquad (18)$$

with $P = (p/\beta)(R/E_G)^m$ and where $I_2(s)$ is an integral defined by

$$I_2(s) = \int_{T_0}^{T} T_\tau^{2s} e^{-(E_N+sE_G)/RT_\tau}\,dT_\tau. \qquad (19)$$

Replacing $(E_N + sE_G)/RT_\tau$ with y_τ the integral $I_2(s)$ can be written as

$$I_2(s) = -M\int_{y_0}^{y} \frac{e^{-y_\tau}}{y_\tau^{2s+2}}\,dy_\tau \qquad (20)$$

with $M = [(E_N + sE_G)/R]^{2s+1}$.

This integral is again evaluated according to Eq. (16) with $r = 2s+2$, yielding

$$I_2(s) = M\left[e^{-y_\tau} y_\tau^{-(2s+2)} \sum_{k=0}^{\infty} \frac{(-1)^k (2s+k+1)!}{(2s+1)!\,y_\tau^k}\right]_{y_0}^{y} \qquad (21)$$

and with the above-mentioned assumptions for alternating series and for most crystallization reactions, the preceding equation can be rewritten as

$$I_2(s) = M\left[e^{-y} y^{-(2s+2)} - e^{-y_0} y_0^{-(2s+2)}\right]. \qquad (22)$$

This expression is approximated by $I_2(s) \approx M e^{-y} y^{-(2s+2)}$ if it is assumed that $T_0 \ll T$, so that y_0 can be taken as infinity. This assumption is justifiable for any heating treatment that begins at a temperature where nucleation and crystal growth are negligible, i.e. below T_g (glass transition temperature) for most glass-forming systems [27].

Substituting the last value obtained for $I_2(s)$ in Eq. (18), introducing the parameter

$$Q = R\left(\frac{R}{E_G}\right)^m \sum_{s=0}^{m}(-1)^s \binom{m}{s}(E_N + sE_G)^{-1}$$

and defining the reaction rate constant

$$K_V = (K_{V0})^{1/(m+1)} e^{-(E_N+mE_G)/(m+1)RT} \quad (K_{V0}^{m+1} = g I_{V0} u_0^m) \qquad (23)$$

with an Arrhenian temperature dependence, the volume fraction crystallized, in non-isothermal reactions, is expressed as

$$x = 1 - \exp\left[-Q\left(\frac{K_V T^2}{\beta}\right)^{m+1}\right] \qquad (24)$$

which, as can be observed, is a general expression for all possible values of the m exponent, which, as is well known, depends on the dimensionality of the crystal growth.

It should be noted that the frequency factor, $K_{V0} = (g I_{V0} u_0^m)^{1/(m+1)}$, of Eq. (23) can be expressed by the relationship $K_{V0} = (I'_{V0} u_0'^{\,m})^{1/(m+1)}$, which include the shape factor, g, and where the dimension equation of each of the quantities I'_{V0} and u'_0 is $[T]^{-1}$.

The graphical representation of Eq. (24) shows the typical sigmoid curve of the volume fraction transformed as a function of temperature in crystallization reactions, as it appears in the literature [29,30]. Fig. 1 shows the representation of the quoted equation for some selected kinetic parameters and for crystal growth in one, two or three dimensions.

The expression for the theoretical volume fraction crystallized as a function of the exponent m, deduced above, enables us to evaluate the above-mentioned quantity, x, in non-isothermal reactions with very different mechanisms of nucleation and crystal growth. This fact is very useful when analyzing the kinetic parameters of crystallization reactions in alloys studied using differential scanning calorimetry, with continuous-heating regimes.

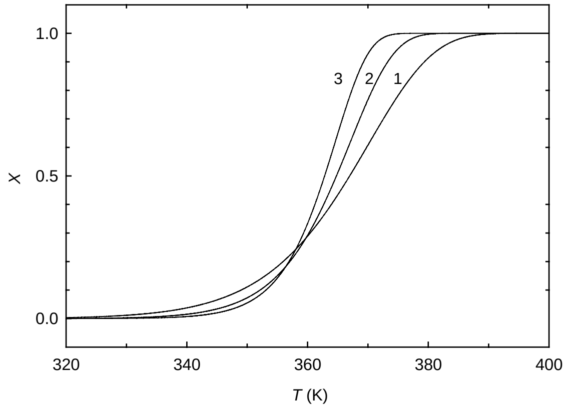

Fig. 1. Crystallized fraction as a function of temperature calculated from Eq. (24), with $I'_{V0} = 10^6\ \mathrm{s}^{-1}$, $E_\mathrm{N} = 14\ \mathrm{K\,cal\,mol^{-1}}$, $u'_0 = 10^4\ \mathrm{s}^{-1}$, $E_\mathrm{G} = 10\ \mathrm{K\,cal\,mol^{-1}}$, $\beta = 0.14\ \mathrm{K\,s^{-1}}$ and for crystal growth in one (1), two (2) and three (3) dimensions.

The logarithmic form of Eq. (24) may be written as

$$-\ln(1-x) = Q(K_V \beta^{-1} T^2)^{m+1}$$

and substituting the parameter Q and reaction rate constant, K_V, by their corresponding values, one obtains

$$-\ln(1-x) = g I_{V0}\left(\frac{u_0}{E_\mathrm{G}}\right)^m \left(\frac{RT^2}{\beta}\right)^{m+1} \times \mathrm{e}^{-(E_\mathrm{N}+mE_\mathrm{G})/RT} \sum_{s=0}^{m} (-1)^s \binom{m}{s} \times (E_\mathrm{N}+sE_\mathrm{G})^{-1}, \tag{25}$$

where making the m exponent equal to 1, 2 and 3 results, respectively, in

$$-\ln(1-x) = g\frac{I_{V0}\,u_0}{E_\mathrm{N}E_\mathrm{G}}\left(1-\frac{E_\mathrm{N}}{E_\mathrm{N}+E_\mathrm{G}}\right)\left(\frac{RT^2}{\beta}\right)^2 \times \exp\left[-(E_\mathrm{N}+E_\mathrm{G})/RT\right], \tag{26}$$

$$-\ln(1-x) = g\frac{I_{V0}}{E_\mathrm{N}}\left(\frac{u_0}{E_\mathrm{G}}\right)^2\left(1-\frac{2E_\mathrm{N}}{E_\mathrm{N}+E_\mathrm{G}}+\frac{E_\mathrm{N}}{E_\mathrm{N}+2E_\mathrm{G}}\right) \times \left(\frac{RT^2}{\beta}\right)^3 \exp\left[-(E_\mathrm{N}+2E_\mathrm{G})/RT\right] \tag{27}$$

and

$$-\ln(1-x) = g\frac{I_{V0}}{E_\mathrm{N}}\left(\frac{u_0}{E_\mathrm{G}}\right)^3 \times \left(1-\frac{3E_\mathrm{N}}{E_\mathrm{N}+E_\mathrm{G}}+\frac{3E_\mathrm{N}}{E_\mathrm{N}+2E_\mathrm{G}}-\frac{E_\mathrm{N}}{E_\mathrm{N}+3E_\mathrm{G}}\right) \times \left(\frac{RT^2}{\beta}\right)^4 \exp\left[-(E_\mathrm{N}+3E_\mathrm{G})/RT\right] \tag{28}$$

which are functions of the volume fraction crystallized for growth in one, two and three dimensions, as they are quoted in the literature [28].

2.2. Deducing the kinetic parameters

The usual analytical methods, proposed in the literature for analyzing the crystallization kinetics in glass-forming liquids, assume that the reaction rate constant can be defined by Arrhenian temperature dependence. In order for this assumption to hold, one of the following two sets of conditions should apply:

(i) The crystal growth rate, u, has an Arrhenian temperature dependence, and over the temperature range where the thermoanalytical measurements are carried out, the nucleation frequency is negligible (i.e., the condition of site saturation).
(ii) Both the crystal growth rate and nucleation frequency have Arrhenian temperature dependences.

In the present work, the second condition is assumed, and therefore, the overall effective activation energy for crystallization, E, is given by Eq. (11). From this point of view, the crystallization rate is obtained by deriving the volume fraction crystallized [Eq. (24)] with respect to time, bearing in mind the fact that, in non-isothermal processes, the reaction rate constant is a time function through its above-mentioned Arrhenian temperature dependence. Moreover, if in the resulting expression, the exponential function is substituted by its given value in Eq. (24), one obtains

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{Q(m+1)}{\beta}\left(\frac{K_V T^2}{\beta}\right)^m \times (1-x)\left(T^2\frac{\mathrm{d}K_V}{\mathrm{d}t} + 2\beta T K_V\right). \quad (29)$$

The maximum crystallization rate is found by making $\mathrm{d}^2x/\mathrm{d}t^2 = 0$, resulting in

$$Q\left[\frac{K_V|_p T_p^2}{\beta}\right]^{(m+1)} = 1 - \frac{1}{m+1}\left[T_p^2\left(\left.\frac{\mathrm{d}K_V}{\mathrm{d}t}\right|_p\right)^2 + 2\beta^2(K_V|_p)^2 - T_p^2(K_V)_p\left.\frac{\mathrm{d}^2K_V}{\mathrm{d}t^2}\right|_p\right] \times \left[T_p\left.\frac{\mathrm{d}K_V}{\mathrm{d}t}\right|_p + 2\beta K_V|_p\right]^{-2}, \quad (30)$$

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

Taking the first and the second derivative of the reaction rate constant, K_V, with respect to time, one obtains for the maximum crystallization rate the following expressions for quoted derivatives

$$\left.\frac{\mathrm{d}K_V}{\mathrm{d}t}\right|_p = \beta K_V|_p \frac{E_\mathrm{N} + mE_\mathrm{G}}{(m+1)RT_p^2} \quad (31)$$

and

$$\left.\frac{\mathrm{d}^2K_V}{\mathrm{d}t^2}\right|_p = \beta^2 K_V|_p \frac{E_\mathrm{N} + mE_\mathrm{G}}{(m+1)RT_p^3} \times \left(\frac{E_\mathrm{N} + mE_\mathrm{G}}{(m+1)RT_p} - 2\right). \quad (32)$$

Substituting Eqs. (31) and (32) into Eq. (30) yields

$$Q\left[\frac{K_V|_p T_p^2}{\beta}\right]^{m+1} = 1 - \frac{2}{m+1}\left[1 + \frac{E_\mathrm{N} + mE_\mathrm{G}}{(m+1)RT_p}\right] \times \left[2 + \frac{E_\mathrm{N} + mE_\mathrm{G}}{(m+1)RT_p}\right]^{-2} \quad (33)$$

and assuming that the overall effective activation energy, E, is given by Eq. (11), as already stated, and taking $n = m + 1$, the preceding equation can be rewritten as

$$Q\left[\frac{K_V|_p T_p^2}{\beta}\right]^n = 1 - \frac{2}{n}\left(1 + \frac{E}{RT_p}\right)\left(2 + \frac{E}{RT_p}\right)^{-2} \quad (34)$$

which relates the crystallization kinetic parameters E and n to the quantity values that can be determined experimentally, and which correspond to the maximum crystallization rate. By relating the last expression to Eq. (24) it is verified that

$$y_p = -\ln(1 - x_p) = Q\left[\frac{K_V|_p T_p^2}{\beta}\right]^n = 1 - \frac{2}{n}\frac{1 + z_p}{(2 + z_p)^2} \quad (35)$$

with $z_p = E/RT_p$. This fact makes possible to write the kinetic exponent, n, as a function of the overall activation energy through the variable z_p, resulting in

$$n = \frac{2}{1 - y_p}\frac{1 + z_p}{(2 + z_p)^2}. \quad (36)$$

On the other hand, by relating Eq. (29) to Eq. (24) for the maximum crystallization rate, and substituting in the resulting expression the value of the n parameter, given in Eq. (36), allow us to express the activation energy through the variable z_p by relationship

$$\frac{1 + z_p}{2 + z_p} = \frac{(1 - y_p)T_p(\mathrm{d}x/\mathrm{d}t)|_p}{2y_p\beta(1 - x_p)} = A \quad (37)$$

which solely depends on the experimental data. Moreover, if Eqs. (36) and (37) are related, the kinetic exponent is obtain as

$$n = \frac{2A(1 - A)}{1 - y_p}. \quad (38)$$

Eqs. (37) and (38) permit the kinetic parameters, E and n to be calculated in a set of exotherms taken at different heating rates. The corresponding mean values of both quantities may be considered as the most probable values of the overall activation energy and the kinetic exponent for the crystallization process.

Finally, the factor $q = Q^{1/n}K_{V0}$ [Eq. (24)], which is related to the probability of effective molecular

Table 1
Experimental data and kinetic parameters E and n, supplied by literature for five glassy alloys

Alloy	β (K min^{-1})	T_p (K)	x_p	10^3 $(\mathrm{d}x/\mathrm{d}t)\vert_p$ (s^{-1})	E (cal mol^{-1})	n	Ref.
$Cu_{0.05}As_{0.45}Se_{0.50}$ (S1)	2	563	0.61816	1.13	30,700	1.70	[11]
	4	566	0.61825	2.26			
	8	570	0.61827	4.49			
	16	572	0.61829	8.95			
	32	575	0.61833	17.84			
$As_{0.20}Se_{0.30}Te_{0.50}$(S2)	2	424	0.62225	2.12	27,210	2.10	[31]
	4	432	0.62228	4.17			
	8	441	0.62234	8.21			
	16	450	0.62238	16.14			
	32	458	0.62242	31.81			
$As_{0.35}Se_{0.30}Te_{0.35}$(S3)	2	478	0.61899	1.41	25,010	1.91	[31]
	4	490	0.61905	2.76			
	8	503	0.61910	5.39			
	16	515	0.61914	10.55			
	32	528	0.61918	20.62			
$Sb_{0.12}As_{0.36}Se_{0.52}$(S4)	2	533	0.62198	1.64	32,700	1.91	[32]
	4	543	0.62202	3.23			
	8	552	0.62207	6.38			
	16	564	0.62210	12.51			
	32	582	0.62214	24.31			
$Sb_{0.16}As_{0.29}Se_{0.55}$(S5)	2	519	0.62491	2.39	54,300	2.10	[33]
	4	530	0.62496	4.71			
	8	539	0.62500	9.31			
	16	550	0.62504	18.34			
	32	561	0.62508	36.14			

collisions for the formation of the activated complex, can be obtained from Eq. (35), which is also written as

$$y_p = \left[\frac{T_p^2}{\beta}\, q \exp\left(-E/RT_p\right)\right]^n, \tag{39}$$

where using the values of y_p, T_p, E and n for each heating rate it is possible to find different values of the above-mentioned factor q [in $(\mathrm{K\,s})^{-1}$]. The corresponding mean value may be taken as the most probable value of the quoted factor related to the frequency factor of the crystallization reaction.

It should be highlighted that Eq. (39) is original, since from Eq. (35), $1-x_p$ can be written as

$$1 - x_p = \exp\left\{-\left[1 - \frac{2}{n}\frac{1+z_p}{(2+z_p)^2}\right]\right\} \tag{40}$$

an expression which depends on the temperature, T_p, corresponding to the maximum crystallization rate, through z_p. This fact agrees with the experimental evidence, since in many glass–crystal transformations the obtained values for x_p vary with the heating rate. From the theoretical point of view, the known constant value of $1-x_p$ in the existing models results only when in Eq. (40) the approximation $z_p = E/RT_p \gg 1$ is taken, thus obtaining $1 - x_p = 0.37$. In this work, the quoted approximation has been not carried out, a fact that can justify the originality of Eq. (39).

3. Application to practical cases

The theoretical method described for analyzing the crystallization kinetics of glass–crystal trans-

Table 2
Kinetic parameters of crystallization for the five glassy alloys, obtained by using the developed theoretical method

Alloy	β (K min^{-1})	E (cal mol^{-1})	$\langle E\rangle$ (cal mol^{-1})	n	$\langle n\rangle$	q (K s)$^{-1}$	$\langle q\rangle$ (K s)$^{-1}$
S1	2	31,730	30,096	1.72	1.84	1.78×10^5	1.27×10^5
	4	30,890		1.78		1.45×10^5	
	8	30,158		1.83		1.24×10^5	
	16	29,173		1.90		0.95×10^5	
	32	28,530		1.95		0.94×10^5	
S2	2	27,316	26,483	2.14	2.31	1.79×10^7	0.92×10^7
	4	26,917		2.22		1.20×10^7	
	8	26,452		2.31		0.72×10^7	
	16	26,089		2.39		0.51×10^7	
	32	25,639		2.48		0.36×10^7	
S3	2	24,924	24,469	1.96	2.10	3.01×10^4	2.06×10^4
	4	24,672		2.03		2.34×10^4	
	8	24,348		2.11		1.68×10^4	
	16	24,254		2.17		1.67×10^4	
	32	24,145		2.23		1.60×10^4	
S4	2	32,847	32,190	2.17	2.32	2.79×10^6	1.95×10^6
	4	32,713		2.23		2.70×10^6	
	8	32,267		2.30		2.13×10^6	
	16	31,704		2.39		1.33×10^6	
	32	31,419		2.49		0.82×10^6	
S5	2	55,331	54,059	1.83	1.97	1.73×10^{16}	5.28×10^{15}
	4	54,435		1.91		4.72×10^{15}	
	8	54,014		1.96		2.62×10^{15}	
	16	53,602		2.03		1.27×10^{15}	
	32	52,912		2.10		0.51×10^{15}	

formations, by using non-isothermal regime in DSC, was applied to a relatively wide set of glassy alloys whose experimental data $[T_p, x_p, (\mathrm{d}x/\mathrm{d}t)|_p]$ corresponding to the maximum crystallization rate for each heating rate, are quoted in the literature. The theoretical results obtained for the kinetic parameters of the quoted crystallizations agree with the corresponding values given in the literature, showing the accuracy of the theoretical method developed. The present work shows the results of the theoretical calculation of the kinetic parameters of the five alloys considered most representative of the set studied, whose bibliographical data are shown in Table 1. Using the theoretical expressions above deduced for the kinetic parameters of crystallization reactions, and taking the experimental data $[T_p, x_p, (\mathrm{d}x/\mathrm{d}t)|_p]$ provided by the literature and collected in Table 1, the values of the quoted parameters shown in Table 2 were calculated, corresponding to each alloy and for different heating rates. As it can be verified the procedure to obtain the value of the above-mentioned kinetic parameters is very simple. By substituting in Eq. (37) the experimental data for the quantities β, T_p, x_p and $(\mathrm{d}x/\mathrm{d}t)|_p$one obtains the value of the A parameter and, immediately, the activation energy, E, of the process from z_p. The kinetic exponent, n, is calculated by substituting the values of the parameters A and y_p in Eq. (38). Finally, the factor $q = Q^{1/n}K_{V0}$ is deduced from Eq. (39), by using the values of y_p, T_p, E and n for each heating rate. Bearing in mind that the calorimetric analysis is a technique which makes it possible to obtain mean values for the parameters that control the kinetics of a reaction, the above-mentioned mean values, shown in Table 2, were obtained. It is observed that the deduced values agree with data supplied in the literature and shown in Table 1, confirming the fact that the theoretical method developed is adequate to describe the crystallization kinetics of the glassy alloys.

4. Conclusions

The described theoretical method enables us to study the evolution with time of the volume fraction crystallized in materials involving nucleation and crystal growth processes. This procedure assumes the concept of extended volume of transformed material and the condition of random nucleation. Using these assumptions we have obtained an evolution equation with time for the volume fraction crystallized, which has been integrated under non-isothermal conditions. The above-mentioned method considers an Arrhenian temperature dependence of the nucleation frequency and crystal growth rate and therefore the overall reaction rate constant has an Arrhenian temperature dependence. It should be emphasized that the value and dimension of the geometric factor depend on the dimensionality and shape of the crystal growth. Bearing in mind the above-assumed hypotheses a general expression has been obtained for the volume fraction crystallized for each value of the m exponent related to the dimensionality of the crystal. The quoted expression permits the above-mentioned fraction to be evaluated in non-isothermal reactions with different mechanisms of nucleation and crystal growth. This fact is very useful when analyzing the kinetic parameters of crystallization reactions in studied alloys using differential scanning calorimetry, with continuous-heating regimes.

The kinetic parameters E, n and q have been obtained by using the following considerations: the condition of the maximum crystallization rate, the above-quoted maximum rate and the volume fraction crystallized corresponding to the maximum crystallization rate. By this method the kinetic parameters are calculated in a set of exotherms taken at different heating rates and the corresponding mean values may be taken as the most probable values of the above-mentioned parameters.

Finally, the theoretical method developed has been applied to a set of glassy alloys, whose experimental data are quoted in the literature. The theoretical results obtained for the kinetic parameters agreed very satisfactorily with the corresponding values given in the literature, confirming the reliability of the method described.

Acknowledgements

The authors are grateful to the Junta de Andalucia and the CICYT (Comisión Interministerial de Ciencia y Tecnología) (project no. MAT 2001–3333) for their financial supports.

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] K.F. Kelton, in: Crystal Nucleation in Liquids and Glasses Solid State Physics, Vol. 45, Academic Press, New York, 1991.
[3] N. Clavaguera, J. Non-Cryst. Solids 162 (1993) 40.
[4] D.W. Henderson, J. Non-Cryst. Solids 30 (1979) 301.
[5] G.S. Melling, D.R. Uhlmann, Phys. Chem. Glasses 2 (1967) 62.
[6] P.J. Vergano, D.R. Uhlmann, Phys. Chem. Glasses 2 (1970) 30.
[7] J. Sestak, Phys. Chem. Glasses 6 (1974) 137.
[8] D.D. Thornburg, R.I. Johnson, J. Non-Cryst. Solids 17 (1975) 2.
[9] N. Clavaguera, J. Non-Cryst. Solids 22 (1976) 23.
[10] H.S. Chen, J. Non-Cryst. Solids 27 (1978) 257.
[11] J. Vázquez, R.A. Ligero, P. Villares, R. Jiménez-Garay, Thermochim. Acta 157 (1990) 181.
[12] R.A. Ligero, M. Casas-Ruiz, J. Vázquez, R. Jiménez-Garay, Phys. Chem. Glasses 34 (1993) 12.
[13] C. Wagner, J. Vázquez, P. Villares, R. Jiménez-Garay, Mater. Chem. Phys. 38 (1994) 74.
[14] P.L. López-Alemany, J. Vázquez, P. Villares, R. Jiménez-Garay, J. Non-Cryst. Solids 274 (2000) 249.
[15] P.L. López-Alemany, J. Vázquez, P. Villares, R. Jiménez-Garay, Thermochim. Acta 374 (2001) 73.
[16] W.A. Johnson, K.F. Mehl, Trans. Am. Inst. Min. Metall. Eng. 135 (1981) 315.
[17] M. Avrami, J. Chem. Phys. 7 (1939) 1103.

[18] M. Avrami, J. Chem. Phys. 8 (1940) 212.
[19] M. Avrami, J. Chem. Phys. 9 (1941) 177.
[20] A.N. Kolmogorov, Bull. Acad. Sci. USSR (Sci. Mater. Nat.) 3 (1937) 3551.
[21] M.C. Weinberg, R. Kapral, J. Chem. Phys. 91 (1989) 7146.
[22] J.R. Frade, J. Am. Ceram. Soc. 81 (1998) 2654.
[23] C.S. Ray, X. Fang, D.E. Day, J. Am. Ceram. Soc. 83 (2000) 865.
[24] J.W. Christian, The Theory of Transformations in Metals and Alloys, Pergamon Press, Oxford, 1975.
[25] J. Vázquez, P. Villares, R. Jiménez-Garay, J. Alloys Compounds 257 (1997) 259.
[26] V.A. Shneidman, D.R. Uhlmann, J. Chem. Phys. 109 (1998) 186.
[27] H. Yinnon, D.R. Uhlmann, J. Non-Cryst. Solids 54 (1983) 253.
[28] T.J.W. De Bruijn, W.A. De Jong, P.J. Van der Berg, Thermochim. Acta 15 (1981) 315.
[29] R.A. Ligero, J. Vázquez, M. Casas-Ruiz, R. Jiménez-Garay, Thermochim. Acta 197 (1992) 319.
[30] C. Wagner, P. Villares, J. Vázquez, R. Jiménez-Garay, Mater. Lett. 15 (1993) 370.
[31] R.A. Ligero, J. Vázquez, P. Villares, R. Jiménez-Garay, Thermochim. Acta 162 (1990) 427.
[32] J. Vázquez, P.L. López-Alemany, P. Villares, R. Jiménez-Garay, Mater. Chem. Phys. 57 (1998) 162.
[33] P.L. López-Alemany, J. Vázquez, P. Villares, R. Jiménez-Garay, Phys. Scripta 63 (2001) 409.