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A THEORETICAL METHOD FOR DETERMINING THE CRYSTALLIZED FRACTION AND KINETIC PARAMETERS BY DSC, USING NON-ISOTHERMAL TECHNIQUES

J. VÁZQUEZ[1], C. WAGNER[1], P. VILLARES[2] and R. JIMÉNEZ-GARAY[1]

[1]Departamento de Física de la Materia Condensada and [2]Departamento de Física Aplicada, Facultad de Ciencias, Universidad de Cádiz, Apdo 40, Puerto Real (Cádiz), Spain

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Abstract—A procedure has been developed for determining expressions for the volume fraction crystallized and for the kinetic parameters in non-isothermal reactions in solid systems involving the formation and growth of nuclei. This method makes use of an equation for the evolution with time of the volume fraction crystallized. This equation has been integrated under non-isothermal conditions and assuming an Arrhenian temperature dependence of the nucleation frequency and of the crystal growth rate, thus obtaining a general expression for the volume fraction crystallized for each value of the related parameter with the dimensionality of the crystal. 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 agree very satisfactorily with the published data. This fact shows the reliability of the theoretical method developed. *Copyright © 1996 Acta Metallurgica Inc.*

1. INTRODUCTION

The last decades have seen a strong theoretical and experimental interest in the application of isothermal and non-isothermal experimental analysis techniques to the study of phase transformations. While isothermal experimental analysis techniques are in most cases more definitive, non-isothermal thermoanalytical techniques have several advantages. The rapidity with which non-isothermal experiments can be performed makes these types of experiment attractive. Non-isothermal experiments can be used to extend the temperature range of measurements beyond that accessible to isothermal experiments. Many phase transformations occur too rapidly to be measured under isothermal conditions because of transients inherently associated with the experimental apparatus. Industrial processes often depend on the kinetic behaviour of systems undergoing phase transformations under non-isothermal conditions. In this instance a definitive measurement of non-isothermal transformation kinetics is desirable.

The study of crystallization kinetics in glass-forming liquids has often been limited by the elaborate nature of the experimental procedures that are employed. The increasing use of thermoanalytical techniques such as differential thermal analysis (DTA) or differential scanning calorimetry (DSC) has, however, offered the promise of obtaining useful data with simple methods.

The utilization of thermoanalytical techniques depends in turn on the development of sound method for analysing the experimental data. With this objective, a large number of mathematical treatments have been proposed for analysing DSC and DTA 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 lead to contradictory results. It was suggested by Henderson [1] 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 [2, 3] 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 and DTA have been examined as techniques that are applicable to the study of phase transformations involving nucleation and growth, and in particular to the crystallization kinetics of glass-forming liquids [4–12]; with very few exceptions the analysis of the data obtained has been carried out using the Johnson–Mehl–Avrami transformation rate equation.

In this work a theoretical method has been developed for determining the volume fraction crystallized and the kinetic parameters by DSC, using non-isothermal techniques in solid systems involving formation and growth of nuclei, starting from the formal theory of transformation kinetics.

2. THEORETICAL DEVELOPMENT

2.1. *Deducing the volume fraction crystallized*

The theoretical basis for interpreting DTA or DSC results is provided by the formal theory of transformation kinetics as developed by Johnson and Mehl [13] and Avrami [14–16]. In its basic form the theory describes the evolution with time, t, of the volume fraction crystallized, x, in terms of the nucleation frequency per unit volume, I_v, and the crystal growth rate, u

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

Here g is a geometric factor which depends on the shape of the growing crystal and m is an integer or half integer which depends on the mechanism of growth and the dimensionality of the crystal.

For interface-controlled growth or diffusion-controlled growth with u independent of time, m assumes the values 1, 2 and 3 for one-, two-, and three-dimensional growth, respectively. For diffusion-controlled growth where u decreases as $t^{-1/2}$, m assumes the values 1/2, 1 and 3/2 for the respective dimensionalities of growth. For materials whose growth rates are notably anisotropic (dependent on orientation), the factor $[\int u\,\mathrm{d}\tau]^m$ in equation (1) is replaced by the product $\Pi_i \int u_i\,\mathrm{d}\tau$ where u_i is the growth rate in direction i.

For the important case of isothermal crystallization with nucleation rate and growth rate independent of time, equation (1) can be integrated, resulting in

$$x = 1 - \exp\left[-gI_v u^m \int_0^t (t-t')^m\,\mathrm{d}t'\right]$$
$$= 1 - \exp[-g' I_v u^m t^n] \qquad (2)$$

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

Equation (2) can be taken as a detailed specific case of the Johnson–Mehl–Avrami (JMA) relationship

$$x = 1 - \exp[-(Kt)^n]. \qquad (3)$$

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

$$K = K_0 \exp(-E/RT) \qquad (4)$$

where E is the effective activation energy describing the overall crystallization process. By comparing equations (2) and (3), 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 temperature.

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

$$I_v \simeq I_{v0} \exp(-E_N/RT) \qquad (5)$$

and

$$u \simeq u_0 \exp(-E_G/RT) \qquad (6)$$

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

Combining equations (2)–(6) results in

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

or

$$K_0^n \exp(-nE/RT) \propto I_{v0} u_0^m \exp[-(E_N + mE_G)/RT]$$

and the overall effective activation energy for crystallization is expressed as

$$E \simeq \frac{E_N + mE_G}{n}. \qquad (7)$$

If the nucleation frequency is negligible over the temperature range of concern in the thermoanalytical study, $E \approx E_G$.

Equations (3) and (4) have served as the basis of nearly all treatments of crystallization in DTA or DSC experiments. It should be noted, however, that equation (3) strictly applies only to isothermal experiments, where an integration of the general expression of equation (1) is straghtforward. Nevertheless, equation (3) 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 equation (4) 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 equation (1) under non-isothermal conditions.

In this work a theoretical method has been developed to integrate equation (1) under the above-mentioned conditions and to obtain a general expression for the volume fraction crystallized for each value of parameter m. In this sense, assuming an Arrhenian temperature dependence of the nucleation frequency [equation (5)] and of the crystal growth rate [equation (6)], [equation (1)] becomes

$$x = 1 - \exp\left[-gI_{v0}u_0^m \int_0^t e^{-E_N/RT'} \times \left(\int_{t'}^{t} e^{-E_N/RT_\tau}\,d\tau\right)^m dt'\right] \quad (8)$$

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 and therefore $dt = dT/\beta$, and the volume fraction crystallized can be expressed as

$$x = 1 - \exp\left[-p\int_{T_0}^{T} I_1^m\, e^{-E_N/RT'}\,dT'\right] \quad (9)$$

where p is a parameter equal to $gI_{v0}u_0^m\beta^{-(m+1)}$ and I_1 is an integral defined by

$$I_1 = \int_{T'}^{T} e^{-E_G/RT_\tau}\,dT_\tau. \quad (10)$$

Using the substitution $z_\tau = E_G/RT_\tau$, the integral I_1 is transformed to the relationship

$$I_1 = \frac{E_G}{R}\int_{z}^{z'} \frac{e^{-z_\tau}}{z_\tau^2}\,dz_\tau \quad (11)$$

which can be represented by a series, resulting in

$$I_1 = \frac{E_G}{R}\left[e^{-z_\tau}z_\tau^{-2}\sum_{k=0}^{\infty}\frac{(-1)^k(k+1)!}{z_\tau^k}\right]_{z'}^{z}. \quad (12)$$

Considering that in alternating series the error is less than the first term neglected and 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 this series, without making any appreciable error, and equation (12) becomes

$$I_1 = \frac{E_G}{R}\left[\frac{e^{-z}}{z^2} - \frac{e^{-z'}}{z'^2}\right] = \frac{R}{E_G}[T^2\,e^{-E_G/RT} - T'^2\,e^{-E_G/RT'}]. \quad (13)$$

Substituting this expression in equation (9) one obtains

$$x = 1 - \exp\left[-P\int_{T_0}^{T} e^{-E_N/RT}(T^2\,e^{-E_G/RT} - T^2\,e^{-E_G/RT'})^m\,dT'\right] = 1 - \exp[-PI_2] \quad (14)$$

with $P = p(R/E_G)^m$, and where the integral I_2 is solved using the expansion of the binomial-potential series, yielding

$$I_2 = \int_{T_0}^{T} e^{-E_N/RT'}\sum_{s=0}^{m}(-1)^s\binom{m}{s} \times (T^2\,e^{-E_G/RT'})^{m-s}(T'^2\,e^{-E_G/RT'})^s\,dT' = \sum_{s=0}^{m}(-1)^s\binom{m}{s}(T^2\,e^{-E_G/RT})^{m-s}I_3. \quad (15)$$

Replacing $(E_N + sE_G)/RT'$ with y', the integral I_3 can be written as

$$I_3 = \int_{T_0}^{T} T'^{2s}\,e^{-(E_N+sE_G)/RT'}\,dT' = -M\int_{y_0}^{y}\frac{e^{-y}}{y'^{2s+2}}\,dy'$$

with

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

If this relationship is again represented by a series, the integral in equation (15) becomes

$$I_3 = M\left[e^{-y'}(y')^{-(2s+2)}\sum_{k=0}^{\infty}\frac{(-1)^k(2s+k+1)!}{(2s+1)!}\right]_{y_0}^{y} \quad (16)$$

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

$$I_3 = M[e^{-y}y^{-(2s+2)} - e^{-y_0}y_0^{-(2s+2)}]. \quad (17)$$

This expression is approximated by $I_3 \simeq M\,e^{-y}y^{-(2s+2)}$ 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.

Substituting the last value obtained for I_3 in equation (15) gives

$$I_2 = RT^{2(m+1)}\,e^{-(E_N+mE_G)/RT}\sum_{s=0}^{m}(-1)^s \times \binom{m}{s}(E_N + sE_G)^{-1}$$

and introducing the parameter

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

and defining the reaction rate constant

$$K_V = (I_{v0}u_0^m)^{1/(m+1)}\,e^{-(E_N+mE_G)/(m+1)RT}$$

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

$$x = 1 - \exp\left[-Q\left(\frac{K_V T^2}{\beta}\right)^{(m+1)}\right] \qquad (18)$$

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

The graphical representation of the last equation shows the typical sigmoid curve of the volume fraction transformed as a function of temperature, in crystallization reactions, as it appears in the literature [17, 18]. Figure 1 shows the representation of equation (18) 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 parameter m, deduced above, enables us to evaluate the above-mentioned magnitude, x, in non-isothermal reactions with very different mechanisms of nucleation and crystal growth. This fact is very useful when analysing the kinetic parameters of crystallization reactions in alloys studied using differential scanning calorimetery, with continuous-heating methods.

The logarithmic form of equation (18) may be written as

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

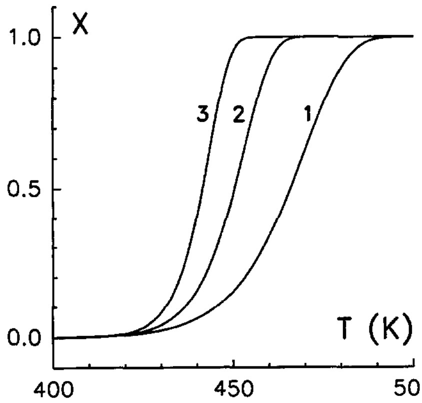

Fig. 1. Crystallized fraction as function of temperature calculated from equation (18), with $I_{v0} = 10^7\,s^{-1}$, $E_N = 20$ kcal/mole, $u_0 = 10^5\,s^{-1}$, $E_G = 14$ kcal/mole, $\beta = 0.07$ K/s and for crystal growth in one (1), two (2) and three (3) dimensions.

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

$$-\ln(1-x) = gI_{v0}\left(\frac{u_0}{E_G}\right)^m\left(\frac{RT^2}{\beta}\right)^{m+1} \times e^{-(E_N+mE_G)/RT}\sum_{s=0}^{m}(-1)^s\binom{m}{s}(E_N+sE_G)^{-1} \qquad (19)$$

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

$$-\ln(1-x) = g\frac{I_{v0}}{E_N}\frac{u_0}{E_G}\left(\frac{RT^2}{\beta}\right)^2 \times\left(1-\frac{E_N}{E_N+E_G}\right)e^{-(E_N+E_G)/RT} \qquad (20)$$

$$-\ln(1-x) = g\frac{I_{v0}}{E_N}\left(\frac{u_0}{E_G}\right)^2\left(\frac{RT^2}{\beta}\right)^3 \times\left(1-\frac{2E_N}{E_N+E_G}+\frac{\mathrm{E}_N}{E_N+2E_G}\right)e^{-(E_N+2E_G)/RT} \qquad (21)$$

and

$$-\ln(1-x) = g\frac{I_{v0}}{E_N}\left(\frac{u_0}{E_G}\right)^3\left(\frac{RT^2}{\beta}\right)^4 \times\left(1-\frac{3E_N}{E_N+E_G} +\frac{3E_N}{E_N+2E_G}-\frac{E_N}{E_N+3E_G}\right)e^{-(E_N+3E_G)/RT} \qquad (22)$$

which are functions of the volume fraction crystallized for growth in one, two and three dimensions, as they are quoted in the literature [19].

2.2. *Calculating the kinetic parameters*

The usual analytical methods, proposed in the literature for analysing the crystallization kinetics in glass-forming liquids, assume that the reaction rate constant can be defined by an 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 rate is negligible (i.e. the condition of site saturation).

(ii) Both the crystal growth and the 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 equation (7). From this point of view, the crystallization rate is obtained by deriving the volume fraction crystallized [equation (18)] with respect to time, bearing in mind the fact that, in the non-isothermal processes, the reaction rate constant is a time function through its above-mentioned Arrhenian temperature dependence, resulting in

$$\frac{\mathrm{d}x}{\mathrm{d}t}=\frac{Q(m+1)}{\beta}\left(\frac{K_{\mathrm{V}}T^2}{\beta}\right)^m\left[T^2\frac{\mathrm{d}K_{\mathrm{V}}}{\mathrm{d}t}+2\beta TK_{\mathrm{V}}\right]\times\exp\left[-Q\left(\frac{K_{\mathrm{V}}T^2}{\beta}\right)^{m+1}\right]. \quad (23)$$

Substituting the exponential function by its given value in equation (18), one obtains

$$\frac{\mathrm{d}x}{\mathrm{d}t}=\frac{Q(m+1)}{\beta}\left(\frac{K_{\mathrm{V}}T^2}{\beta}\right)^m(1-x)\times\left[T^2\frac{\mathrm{d}K_{\mathrm{V}}}{\mathrm{d}t}+2\beta TK_{\mathrm{V}}\right]. \quad (24)$$

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

$$Q\left(\frac{T_p^2(K_{\mathrm{V}})_p}{\beta}\right)^{m+1}=1-\frac{1}{m+1}\left(1-T_p^2(K_{\mathrm{V}})_p\times\left[2\beta^2(K_{\mathrm{V}})_p+4\beta T_p\left.\frac{\mathrm{d}K_{\mathrm{V}}}{\mathrm{d}t}\right|_p+T_p^2\left.\frac{\mathrm{d}^2K_{\mathrm{V}}}{\mathrm{d}t^2}\right|_p\right]\left[2\beta T_p(K_{\mathrm{V}})_p+T_p^2\left.\frac{\mathrm{d}K_{\mathrm{V}}}{\mathrm{d}t}\right|_p\right]^{-2}\right) \quad (25)$$

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

Taking the first and the second derivative of the reaction rate constant, K_{V}, with respect to t, gives

$$\left.\frac{\mathrm{d}K_{\mathrm{V}}}{\mathrm{d}t}\right|_p=\beta(K_{\mathrm{V}})_p\frac{E_{\mathrm{N}}+mE_{\mathrm{G}}}{(m+1)RT_p^2} \quad (26)$$

and

$$\left.\frac{\mathrm{d}^2K_{\mathrm{V}}}{\mathrm{d}t^2}\right|_p=\beta^2(K_{\mathrm{V}})_p\frac{E_{\mathrm{N}}+mE_{\mathrm{G}}}{(m+1)RT_p^3}\left(\frac{E_{\mathrm{N}}+mE_{\mathrm{G}}}{(m+1)RT_p}-2\right). \quad (27)$$

Substituting equations (26) and (27) in equation (25) yields

$$Q\left(\frac{T_p^2(K_{\mathrm{V}})_p}{\beta}\right)^{m+1}=1-\frac{2}{m+1}\left[1+\frac{E_{\mathrm{N}}+mE_{\mathrm{G}}}{(m+1)RT_p}\right]\times\left[2+\frac{E_{\mathrm{N}}+mE_{\mathrm{G}}}{(m+1)RT_p}\right]^{-2} \quad (28)$$

and assuming that the overall effective activation energy, E, is given by equation (7), as already stated, and taking $n=m+1$, the preceding equation can be rewritten as

$$Q\left(\frac{T_p^2(K_{\mathrm{V}})_p}{\beta}\right)^n=1-\frac{2}{n}\left(1+\frac{E}{RT_p}\right)\left(2+\frac{E}{RT_p}\right)^{-2} \quad (29)$$

which relates the kinetic crystallization parameters E and n to the magnitude values that can be determined experimentally, and which correspond to the maximum crystallization rate. Relating the last expression to equation (18) verifies that

$$y_p=-\ln(1-x_p)=Q\left(\frac{T_p^2(K_{\mathrm{V}})_p}{\beta}\right)^n=1-\frac{2}{n}\frac{1+z_p}{(2+z_p)^2} \quad (30)$$

with $z_p=E/RT_p$; this makes it possible to write the reaction order, n, as a function of the overall activation energy through the variable z_p, resulting in

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

If the fraction $(1+z_p)/(2+z_p)^2$ is expanded as a series, one obtains

$$n=\frac{2}{1-y_p}\left(\frac{1}{z_p}-\frac{3}{z_p^2}+\frac{8}{z_p^3}-\cdots\right)=\frac{2}{1-y_p}\sum_{\alpha=1}^{\infty}\frac{(-1)^{\alpha+1}(\alpha+1)2^{\alpha-2}}{z_p^\alpha}$$

and considering the $z_p\geqslant 25$, it is possible to use only the first term of this series, without making any noticeable error; hence the reaction order may be expressed as

$$n=\frac{2RT_p}{(1-y_p)E}. \quad (31)$$

On the other hand, the value of the maximum crystallization rate is obtained by substituting equations (26) and (18) in equation (24), yielding

$$\left.\frac{\mathrm{d}x}{\mathrm{d}t}\right|_p=n\beta T_p^{-1}y_p(1-x_p)\left(2+\frac{E}{RT_p}\right)$$

a relationship which, by inserting the value of the parameter n, given in equation (31), allows us to express the activation energy as a function of the volume fraction crystallized, x_p corresponding to the maximum crystallization rate. Hence

$$E=\frac{4\beta RT_py_p(1-x_p)}{T_p(1-y_p)\left.\frac{\mathrm{d}x}{\mathrm{d}t}\right|_p-2\beta y_p(1-x_p)}. \quad (32)$$

This expression permits the kinetic parameter, E, to be calculated in a set of exotherms taken at

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

Alloy	β (K/min)	T_p (K)	x_p	$10^3\,\mathrm{d}x/\mathrm{d}t\,\vert_p$ (s^{-1})	E (cal/mol)	n	Ref.
$Cu_{0.10}As_{0.40}Se_{0.50}$ (M1)	2	552	0.62680	3.21	60600	2.60	[9]
	4	559	0.62700	6.58			
	8	566	0.62715	13.39			
	16	573	0.62735	27.58			
	32	580	0.62754	56.78			
$Cu_{0.20}As_{0.30}Se_{0.50}$ (M2)	2	506	0.61745	1.28	59800	1.20	[9]
	4	512	0.61779	2.59			
	8	518	0.61798	5.19			
	16	524	0.61816	10.40			
	32	530	0.61838	20.90			
$Cu_{0.10}As_{0.45}Te_{0.45}$ (M3)	2	469	0.61816	1.45	53880	0.91	[12]
	4	476	0.61877	2.99			
	8	479	0.61882	5.97			
	16	485	0.61956	12.49			
	32	493	0.61968	24.83			
$As_{0.20}Se_{0.40}Te_{0.40}$ (M4)	2	459	0.61638	1.34	34210	1.94	[20]
	4	465	0.61692	2.74			
	8	472	0.61740	5.58			
	16	478	0.61788	11.40			
	32	485	0.61844	23.40			
$As_{0.30}Se_{0.25}Te_{0.45}$ (M5)	2	450	0.62960	8.17	74000	4.16	[17]
	4	460	0.62962	16.13			
	8	471	0.62965	31.91			
	16	483	0.62970	63.56			
	32	496	0.62978	128.10			

different heating rates and the corresponding mean value, represents the overall effective activation energy of the crystallization process.

Once the E-values have been obtained for each heating rate, the n-values can be calculated by equation (31). The corresponding mean value may be considered as the most probable value of the reaction order of the transformation kinetics.

Finally, the pre-exponential factor $q = Q^{1/n}K_{V0}$ [equation (18)], which measures the probability of effective molecular collisions for the formation of the activated complex, can be obtained from expression (30), which is also written as

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

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 K/s). The corresponding mean value may be taken as the most probable value of the pre-exponential factor related to the frequency factor of the crystallization reaction.

3. APPLICATION TO SOME PRACTICAL CASES

The theoretical method described for determining the kinetic parameters of crystallization reactions, using non-isothermal techniques 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 above-mentioned parameters agree with the corresponding values given in the literature, showing the accuracy of the theoretical method developed. This work shows 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 kinetic parameters of crystallization reactions, the values of the quoted parameters shown in Table 2 were calculated, corresponding to each alloy and for different heating rates. Bearing in mind that the calorimetric analysis is an indirect method which only 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 integrate the evolution equation with time for the volume fraction crystallized under non-isothermal conditions. This procedure assumes an Arrhenian temperature dependence of the nucleation frequency and the crystal growth rate and therefore the overall reaction rate constant has an Arrhenian temperature dependence. Using these assumptions a general expression has been obtained for the volume fraction crystallized for each value of the parameter related to the dimensionality of the crystal. The above-mentioned expression permits the quoted fraction to be evaluated in non-isothermal reactions with very

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

Alloy	β (K/min)	E (cal/mol)	$\langle E \rangle$ (cal/mol)	n	$\langle n \rangle$	q (K/s)	$\langle q \rangle$ (K/s)
M1	2	61 225	60696	2.51	2.80	1.32×10^{17}	0.86×10^{17}
	4	60 977		2.65		1.03×10^{17}	
	8	60 704		2.78		0.81×10^{17}	
	16	60 426		2.94		0.64×10^{17}	
	32	60 147		3.12		0.52×10^{17}	
M2	2	60 433	59928	0.86	0.92	1.07×10^{19}	0.73×10^{19}
	4	60 392		0.89		1.00×10^{19}	
	8	60 253		0.91		0.86×10^{19}	
	16	59 432		0.95		0.40×10^{19}	
	32	59 130		0.98		0.31×10^{19}	
M3	2	54 782	53291	0.92	1.03	3.36×10^{18}	1.27×10^{18}
	4	54 381		0.98		1.82×10^{18}	
	8	53 275		1.01		0.79×10^{18}	
	16	52 220		1.11		0.26×10^{18}	
	32	51 797		1.14		0.14×10^{18}	
M4	2	35 534	34868	1.23	1.38	9.88×10^{9}	7.05×10^{9}
	4	35 373		1.30		9.85×10^{9}	
	8	34 846		1.38		6.25×10^{9}	
	16	34 391		1.46		4.77×10^{9}	
	32	34 191		1.55		4.52×10^{9}	
M5	2	76 208	74405	3.46	3.83	9.77×10^{29}	2.05×10^{29}
	4	74 341		3.65		3.90×10^{28}	
	8	73 996		3.80		7.81×10^{27}	
	16	73 811		3.99		1.74×10^{27}	
	32	73 668		4.25		3.86×10^{26}	

different mechanisms of nucleation and crystal growth. This fact is very useful when analysing the kinetic parameters of crystallization reactions in studied alloys using differential scanning calorimetry, with continuous-heating techniques.

The kinetic parameters E, n and K_V have been obtained by using the following considerations: the condition of the maximum crystallization rate, the above-mentioned 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.

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