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Journal of Alloys and Compounds 257 (1997) 259–265

Journal of ALLOYS AND COMPOUNDS

A theoretical method for deducing the evolution with time of the fraction crystallized and obtaining the kinetic parameters by DSC, using non-isothermal techniques

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Received 11 October 1996; received in revised form 20 January 1997; accepted 24 January 1997

Abstract

A procedure has been developed for analyzing the evolution with time of the volume fraction crystallized and for calculating the kinetic parameters at non-isothermal reactions in materials involving formation and growth of 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 time. In the quoted expression one considers that the crystal growth rate is anisotropic. In addition, the particular case of isotropic growth rate has been studied, and the obtained equation has been integrated for the important case of nucleation frequency and growth rate independent of time, resulting an expression that may be taken as a detailed specific case of the Johnson–Mehl–Avrami relation. The kinetic parameters have been deduced, fitting a theoretical function, obtained from the JMA model to the experimental data, temperature and volume fraction crystallized. A least-squares method has been used, bearing in mind the fact that, in most non-isothermal processes, the reaction rate constant exhibits an Arrhenian temperature dependence. Finally, the theoretical derivations 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 bibliographical data. This fact shows the reliability of the developed theoretical method.

Keywords: Glassy alloy; Non-isothermal process; Nucleation frequency and crystal growth rate; Heating rate; Kinetic parameters

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 accurate, non-isothermal thermo-analytical techniques have several advantages. The rapidity with which non-isothermal experiments can be performed makes these types of experiments attractive. Non-isothermal experiments can be used to extend the temperature range of measurement 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 an adequate 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 which 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 the thermoanalytical 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 and DTA data [1–4]. 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 [5] in a notable work that many of the treatments are based on an incomplete understanding of the formal theory of transformation kinetics.

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PII S0925-8388(97)00034-0

The experiments reported in the literature [6,7], 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 at the interface from that of either bulk phase is negligible. In this sense, glass forming liquids may provide unique systems for assessing the validity of the theoretical models used to describe 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 which are applicable to the study of phase transformations involving nucleation and growth, and in particular to the crystallization kinetics of glass forming liquids [8–16].

In this work a theoretical method has been developed for deducing a general expression for the evolution with time of the volume fraction crystallized, in terms of the nucleation frequency per unit volume and the crystal growth rate. In addition, by using the Johnson–Mehl–Avrami model and through a least-squares method, theoretical expressions have been obtained for kinetic parameters of crystallization in differential scanning calorimetry, by using non-isothermal techniques.

2. Theoretical development

2.1. Deducing the evolution equation of the volume fraction crystallized

The theoretical basis for interpreting DTA or DSC results is provided by the formal classical theory of transformation kinetics. This formal theory is largely independent of the particular models used in detailed descriptions of the mechanisms of transformation, and therefore it leads to an expression, which can be considered as general, for the equation of evolution of the volume fraction crystallized.

In the development of the formal theory of transformation kinetics is usually adopted an operational definition of the nucleation frequency per unit volume, I_V, which is related to the reciprocal of a mean value of the period τ (the time in which an individual region is formed). Suppose that at time $t=\tau$ the untransformed volume is V_a, and that between times $t=\tau$, $\tau+d\tau$ a number of new regions are nucleated. This number is $I_V V_a \, d\tau$, and defines I_V at time τ; in order to give statistically significant results, the number $I_V V_a$ must be large. As for the crystal growth rate, it must be noted that, in general, it is anisotropic, which happens if the shape of the growing region stays constant. The crystal growth rate in any direction can be then represented in terms of the principal growth velocities, u_i (i=1,2,3), in three mutually perpendicular directions. In these conditions the uni-dimensional growth in an elemental time, dt', can be expressed as $u_i \, dt'$, and this growth for a finite time is $\int_\tau^t u_i \, dt'$. The volume of a region b originating at time $t=\tau$ is then

$$v_\tau = g \prod_i \int_\tau^t u_i \, dt' \qquad (1)$$

where g is a geometric factor which depends on the shape of the growing crystal.

In the whole assembly, the number of new regions b nucleated in the time interval between τ and $\tau+d\tau$ is $I_V V_a \, d\tau$, as previously mentioned. During the initial stages of transformation, when $V_b \ll V_a$, the nuclei are widely spaced, and the interference of neighbouring nuclei is negligible. Under these conditions, the transformed volume at time t resulting from regions nucleated between times τ and $\tau+d\tau$ is $dV_b = v_\tau \, I_V V_a \, d\tau$. However, in subsequent stages of the process, we must consider the mutual interference of regions growing from separate nuclei. When two such regions impinge on each other, there are several possible consequences. An important possibility is that the two regions develop a common interface, over which growth ceases, although it continues normally elsewhere. This must happen in all solid state transformations, and it is the case of the most crystallization reactions.

During the time $d\tau$, when $I_V V_a \, d\tau$ new transformed regions are nucleated, it may be also considered that $I_V V_b \, d\tau$ regions would have nucleated in the transformed portion of the assembly, had not transformation previously occurred there. It is possible to define [17–19] an extended volume of transformed material, V_e, by the relationship

$$dV_e = v_\tau I_V (V_a + V_b) d\tau = v_\tau I_V V \, d\tau \qquad (2)$$

where V is the volume of the whole assembly.

The extended volume differs from the actual volume, V_b, of transformed material, since some elements of the transformed volume are counted twice, others three times, and so on, in order to obtain the extended volume.

The significance of V_e is that it is simply related to the kinetic law of growth, which may thus be separated from the geometrical problem of impingement. It is possible now to find a relation between V_e and V_b. Consider any small random region, of which a fraction $(1-V_b/V)$ remains untransformed at time t. During a further time dt, the extended volume will increase by dV_e, and the true volume by dV_b. Of the new elements of volume which make up dV_e, a fraction $(1-V_b/V)$ on the average will lie in previously untransformed material, and thus contribute to dV_b, whilst the remainder of dV_e will be in already transformed material. This result clearly follows only if dV_e can be treated as a completely random volume element, and it is for this reason that virtual nuclei have to be included in the definition of V_e.

Bearing in mind the above arguments based on the random nucleation it is possible to write the relation between V_b and V_e in the form

$$dV_b = \left(1 - \frac{V_b}{V}\right) dV_e = (1 - x) dV_e \tag{3}$$

where $x = V_b/V$ is the volume fraction crystallized. Differentiating this expression, substituting the result in Eq. (3), and relating the resulting equation to Eq. (2), where the value for v_τ from Eq. (1) has been included, one obtains

$$\frac{dx}{1-x} = g I_V \left(\Pi_i \int_\tau^t u_i \, dt' \right) d\tau . \tag{4}$$

Integrating this equation and taking the inverse function of the logarithmic form, results in

$$x = 1 - \exp\left[-g \int_0^t I_V \left(\Pi_i \int_\tau^t u_i \, dt' \right) d\tau \right] \tag{5}$$

which is the most general expression for the evolution with time of the volume fraction crystallized, in terms of the nucleation frequency per unit volume, and the crystal growth rate.

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, Eq. (5) can be written as

$$x = 1 - \exp\left[-g \int_0^t I_V \left(\int_\tau^t u \, dt' \right)^m d\tau \right] \tag{6}$$

where m is a numerical exponent which depends on the mechanism of growth and the dimensionality of the crystal.

For the important case of a crystallization reaction with nucleation frequency and crystal growth rate both independent of time, Eq. (6) can be integrated to yield

$$x = 1 - \exp(-g' I_V u^m t^n) , \tag{7}$$

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

If $I_V = 0$, i.e., when the material already contains nuclei but no new nuclei are formed during the thermal process, Eq. (2) can be written

$$dV_e = v_\tau dN = g \left(\int_0^t u \, dt' \right)^m dN \tag{8}$$

dN being the number of nuclei in the elemental extended volume, and where the value for v_τ, given in Eq. (1), has been included, bearing in mind that the growth rate is isotropic. Since there is no nucleation period, $\tau = 0$, the integral has been evaluated between 0 and t.

Relating Eq. (8) with dV_e as a function of the volume fraction crystallized, and integrating the resulting expression, one obtains

$$\ln(1 - x) = -g'' \left(\int_0^t u dt' \right)^m , \; g'' \text{ is a constant.} \tag{9}$$

Eq. (9), may be written in exponential form

$$x = 1 - \exp\left[-g'' \left(\int_0^t u dt' \right)^m \right] \tag{10}$$

and if the growth rate is independent of time,

$$x = 1 - \exp(-g'' u^m t^n) \tag{11}$$

where $n = m$, as it happens in the case of a glass containing a sufficiently large number of nuclei.

Eqs. (7) and (11) can be taken as detailed specific cases of the Johnson–Mehl–Avrami (JMA) isothermal relationship

$$x = 1 - \exp[-(Kt)^n] . \tag{12}$$

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

$$K = K_0 \exp(-E/RT) \tag{13}$$

where R is the gas constant, K_0 is the frequency factor and E is the effective activation energy describing the overall crystallization process. By comparing Eq. (7), volume fraction crystallized for a quenched glass containing no nuclei, with Eq. (12), 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, nucleation frequency and crystal growth rate exhibit far from Arrhenius-type behaviour [20]; however, for a sufficiently limited temperature range, such as the range of crystallization peaks in DTA or DSC experiments, both quantities can be considered to exhibit the said behaviour [21].

It is a well-known fact that Eqs. (12) and (13) are used as the basis of nearly all treatments of crystallization in DTA or DSC experiments, but it must be noted that expression Eq. (12) can be applied strictly only in experiments carried out under isothermal conditions, for which it was deduced. However, this expression is often used for deducing relationships describing non-isothermal crystallization processes, taking the suitable restrictions into account. Henderson [5] gives a clear description of the above mentioned restrictions governing the use of the Avrami formalism to non-isothermal processes. One of the specific cases where it is justified to apply the Avrami formalism to non-isothermal crystallization, is the 'site saturation' case [22,23], that is, when the nucleation process takes place early in the transformation and the nucleation rate is zero thereafter.

2.2. Calculating 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 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 frequency is negligible (i.e., the condition of site saturation).

(ii) Both the crystal growth rate and the nucleation frequency have Arrhenian temperature dependences.

In the present work is assumed the first condition, and therefore u may be described in a zero-order approximation by

$$u \simeq u_0 \exp(-E_G/RT) \tag{14}$$

where E_G is the effective activation energy for crystal growth.

The analysis of the crystallization kinetics, when non-isothermal techniques are used, can be performed from the Eq. (10) bearing in mind the above-mentioned assumption of an Arrhenian temperature dependence for crystal growth rate. Hence the volume fraction crystallized can be expressed as

$$\begin{aligned} x &= 1 - \exp\left[- g'' u_0^n \beta^{-n} \left(\int_{T_0}^{T} \exp(-E/RT')\mathrm{d}T' \right)^n \right] \\ &= 1 - \exp[-g'' u_0^n \beta^{-n} I_1^n] \end{aligned} \tag{15}$$

where E may be written as E_G, the activation energy for growth solely, and $\beta = \mathrm{d}T/\mathrm{d}t$ is a linear heating rate, usually employed in non-isothermal experiments.

Using the substitution $y' = E/RT'$ the integral I_1 is transformed to the relationship

$$I_1 = \frac{E}{R}\int_{y}^{y_0} \frac{e^{-y'}}{y'^2}\,\mathrm{d}y' = \frac{E}{R}\frac{e^{-y}}{y} \tag{16}$$

where 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 which begins at a temperature where nucleation and crystal growth are negligible, i.e., below T_g (glass transition temperature) for most glass-forming systems.

Replacing y with E/RT in the Eq. (16) and substituting the resulting expression in the Eq. (15), one obtains

$$x = 1 - \exp\left[-\left(K\frac{T}{\beta} \right)^n \right] \tag{17}$$

K being the above-mentioned reaction rate constant with an Arrhenius-type temperature dependence.

Eq. (17) can be used to describe the volume fraction crystallized in non-isothermal reactions, taking Henderson [5] restrictions into account, specially the 'site saturation' case previously quoted.

In order to obtain the kinetic parameters the logarithm has been taken twice in Eq. (17), yielding

$$\begin{aligned} y = \ln[-\ln(1-x)] &= n\left[\ln\frac{K_0}{\beta} + \ln T - \frac{E}{R}\frac{1}{T} \right] \\ &= \mathrm{h}(T) \end{aligned} \tag{18}$$

that establishes a relatively simple relation between a function of the volume fraction crystallized and another of the temperature.

In Fig. 1 the representation of Eq. (18) is shown for the $(\mathrm{GeSe_2})_{60}(\mathrm{GeTe})_{40}$ glass quoted in the literature [24], at heating rates of 2.5, 5, 10 and 20 K min^{-1} and kinetic parameters: $E = 54\,960$ cal mol^{-1}, $n = 2.4$ and $\ln K_0 = 33.4$, together with plots of the experimental values.

The procedure, which is developed in this work, consists to calculate the kinetic parameters E, n and K_0, fitting the theoretical function $\mathrm{h}(T)$ to the experimental data T_i and $y_i = \ln[-\ln(1-x_i)]$ through a least-squares method, defining the function $S(E, n, K_0)$ as

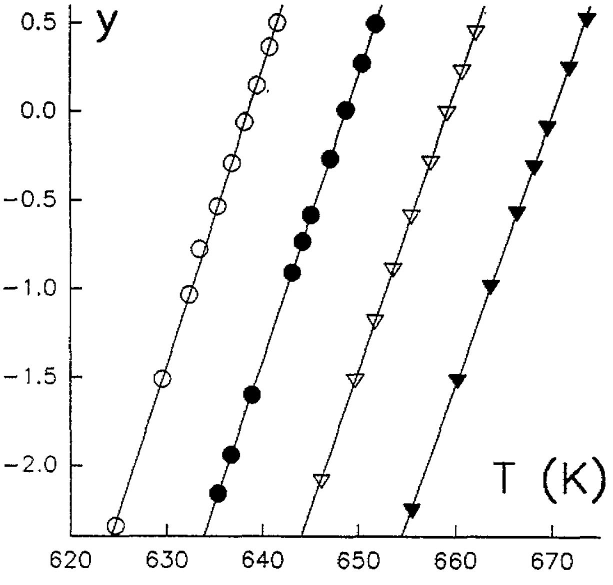

Fig. 1. Volume fraction crystallized versus temperature, obtained from Eq. (18) for the $(\mathrm{GeSe_2})_{60}$ $(\mathrm{GeTe})_{40}$ glass [24], with $E = 54\,960$ cal mol^{-1}, $n = 2.4$ and $\ln K_0 = 33.4$, together with the plots of the experimental values at heating rates of 2.5(○), 5(•), 10 (▽) and 20 (▼) K min^{-1}.

$$S=\sum_{i=1}^{k}\left[y_i-h(T_i)\right]^2 =\sum_{i=1}^{k}\left[y_i-n\left(\ln\frac{K_0}{\beta}+\ln T_i-\frac{E}{R}\frac{1}{T_i}\right)\right]^2 \qquad (19)$$

expression that, when minimized, supplies the most adequate kinetic parameters, k being the number of data used in the fitting.

In order to minimize the function S, it is derived which respect to each variable E, n, K_0, and equalled to zero the partial derivatives

$$\frac{\partial S}{\partial E}=\left\{\sum_{i=1}^{k}\left[y_i-n\left(\ln\frac{K_0}{\beta}+\ln T_i-\frac{E}{R}\frac{1}{T_i}\right)\right]\right\}\frac{1}{T_i}=0$$

$$\frac{\partial S}{\partial n}=\left\{\sum_{i=1}^{k}\left[y_i-n\left(\ln\frac{K_0}{\beta}+\ln T_i-\frac{E}{R}\frac{1}{T_i}\right)\right]\right\} \times\left(\ln\frac{K_0}{\beta}+\ln T_i-\frac{E}{R}\frac{1}{T_i}\right)=0 \qquad (20)$$

$$\frac{\partial S}{\partial K_0}=\sum_{i=1}^{k}\left[y_i-n\left(\ln\frac{K_0}{\beta}+\ln T_i-\frac{E}{R}\frac{1}{T_i}\right)\right]=0$$

a system of linear equations, which has been resolved through a equalization method and whose solution gives the kinetic parameters of the crystallization reaction:(i) The activation energy

$$E=R\frac{A\sum\limits_{i=1}^{k}\ln T_i+B\sum\limits_{i=1}^{k}y_i+Ck}{A\sum\limits_{i=1}^{k}\frac{1}{T_i}+D\sum\limits_{i=1}^{k}y_i+Fk}. \qquad (21)$$

where A, B, C, D and F are intermediate parameters given by the expressions, which appear in the Appendix. It should be noted that above-mentioned parameters only depend on experimental data such as temperature and volume fraction crystallized(ii) The frequency factor

$$\ln K_0=\ln\beta+\frac{M\frac{E}{R}+N}{\left(\sum\limits_{i=1}^{k}y_i\right)\left(\sum\limits_{i=1}^{k}\frac{1}{T_i}\right)-k\sum\limits_{i=1}^{k}\frac{y_i}{T_i}} \qquad (22)$$

as a function of the previously calculated value for activation energy and the parameters M and N (see Appendix).(iii) The reaction order or kinetic exponent

$$n=\left(\sum_{i=1}^{k}y_i\right)\left[k\ln\frac{K_0}{\beta}+\sum_{i=1}^{k}\ln T_i-\frac{E}{R}\sum_{i=1}^{k}\frac{1}{T_i}\right]^{-1} \qquad (23)$$

expression, which depends on before obtains values for E and K_0, and the above mentioned experimental data.

It should be noted that the expression for the activation energy is independent of the heating rate, is in agreement with the literature [24], often suggesting that the activation energy does not depend on the thermal history of the material.

The theoretical method developed supplies a good approximation for the values of the kinetic parameters in crystallization reactions, since the method uses all the experimental data supplied by each exotherm. This fact is very useful when analysing the crystallization kinetics in alloys studied using differential scanning calorimetry, with continuous-heating techniques.

3. Application to some practical cases

The theoretical procedure described for calculating the kinetic parameters of crystallization reactions, using non-isothermal techniques in DSC, was applied to a set of glassy alloys whose experimental data, T_i and x_i, 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 literature [24–26], showing the goodness of the theoretical method developed. This work shows the theoretical calculation of the kinetic parameters of three glassy alloys whose bibliographical data are shown in Table 1. In this table, the temperature and volume fraction crystallized ranges where the method is applied, for different heating rates, are given.

Using the theoretical expressions given in the Appendix for the intermediate parameters, the values of the quoted parameters shown in Table 2 were calculated, corresponding to each alloy and for different heating rates. Finally, by using the set of results given in Table 2 and through the expressions already deduced for the kinetic parameters in crystallization reactions, the values of the above mentioned parameters, summarized in Table 3, were obtained. Bearing in mind that the calorimetric analysis is an indirect method which only makes it possible to obtain mean values for the parameters which control the kinetics of a reaction, the mentioned mean values, given in Table 3 were calculated. In order to check the goodness of the theoretical method of fit, the deduced values for the kinetic parameters have been compared to supplied data on the literature. It should be noted that, although the treatments used for the analysis of the above-mentioned data were based on different derivations of the Avrami equation, the agreement between the fitted values and the parameters supplied by the literature can be considered acceptable. This affirmation can be carried out since all fitted values for the activation energy and the Avrami exponent differ less than 2% and 8% respectively, from those previously reported. This fact confirms that the theoretical method developed is adequate to describe the crystallization kinetics of the glassy alloys.

Table 1
Experimental data and kinetic parameters E, K_0 and n, supplied by literature for three glassy alloys

Alloy	β (K min^{-1})	k	T (K)	x	E (cal mol^{-1})	ln K_0	n	Ref.
$(GeSe_2)_{60}(GeTe)_{40}$	2.5	10	624.67–641.57	0.0912–0.8087	54 960	33.4	2.4	[24]
(M1)	5	10	635.54–651.84	0.1090–0.8068				
	10	9	646.14–662.21	0.1175–0.7934				
	20	8	655.54–673.70	0.1004–0.8177				
$Sn_8As_{26}Se_{66}$	4	14	583.80–603.63	0.1982–0.6796	38 600	27.2	1.2	[25]
(M2)	8	10	581.82–609.35	0.1857–0.6644				
	16	9	596.99–621.27	0.1707–0.6564				
	32	9	606.75–631.68	0.1564–0.6686				
$Sb_{18}As_{34}Se_{48}$	4	43	554.82–564.94	0.1967–0.6581	44 300	24.1	1.8	[26]
(M3)	8	43	564.80–574.92	0.1981–0.6589				
	16	52	574.36–585.29	0.1988–0.6586				

Table 2
Intermediate parameters in the analysis of the crystallization kinetics for three glassy alloys, obtained by using the developed theoretical method

Alloy	β (K min^{-1})	10^3 A (K^{-1})	10^3 B (K^{-1})	10^3 C (K^{-1})	10^6 D (K^{-2})	10^6 F (K^{-2})	10^6 M (K^{-2})	10^3 N (K^{-1})
M1	2.5	−7.9093	−0.3716	50.8381	−0.1241	12.3831	1.6620	−6.8570
	5	−8.4005	0.2279	54.5038	−0.12382	12.9497	1.7347	−7.2864
	10	−5.6797	2.1876	38.2583	−0.6138	8.2735	1.1510	−4.9251
	20	−5.3991	0.5086	35.4169	−0.0727	8.0613	1.0747	−4.6857
M2	4	−12.7148	0.2980	81.3846	−0.4364	21.1506	2.8625	−11.0111
	8	−9.7560	0.1786	62.4620	−0.4486	16.06396	2.1733	−8.4591
	16	−7.0993	0.0226	45.5357	−0.2654	11.4587	1.5457	−6.1566
	32	−7.5593	0.1603	48.7179	−0.2638	12.0056	1.6177	−6.5650
M3	4	−60.6119	−5.2518	380.0391	−1.2277	107.4477	14.6638	−52.4042
	8	−58.3695	9.3362	376.5186	−1.1402	101.6846	13.8381	−50.4619
	16	−88.4830	18.9	575.38	−1.8320	151.4138	20.5716	−76.5850

Table 3
Kinetic parameters of crystallization for three glassy alloys, deduced from the developed theoretical method

Alloy	β (K min^{-1})	E (cal mol^{-1})	$<E>$ (cal mol^{-1})	ln K_0	$<\ln K_0>$	n	$<n>$
M1	2.5	54 500	54 623.9	33.0	33.2	2.3	2.4
	5	54 000		32.7		2.4	
	10	54 904.76		33.4		2.5	
	20	55 090.91		33.5		2.5	
M2	4	39 666.67	39 363.1	23.9	24.0	1.4	1.3
	8	39 500		24.1		1.1	
	16	38 285.71		23.2		1.4	
	32	40 000		24.7		1.4	
M3	4	44 232.84	44 183.6	30.2	30.1	1.7	1.9
	8	44 309.62		30.2		1.9	
	16	44 008.46		30.0		2.1	

4. Conclusions

The described theoretical method enables study of the evolution with time of the volume fraction crystallized in materials whose growth rates are notably anisotropic. This procedure assumes the concept of the extended volume of transformed material and the condition of random nucleation. Using these assumptions a general expression of the volume fraction crystallized has been obtained, as a function of time, in terms of the nucleation frequency per unit volume, and the crystal growth rate.

The above mentioned expression has been particularized for the case in which the crystal growth rate is isotropic, assumption in agreement with the experimental evidence in many transformation reactions. For the important case of a crystallization reaction with nucleation frequency and crystal growth rate independent of time, the quoted expression has been integrated, yielding an equation that may be taken as a detailed specific case of Johnson–Mehl–Avrami relation.

The kinetic parameters E, n and K_0 have been obtained by fitting a theoretical function, deduced from the JMA model, to the experimental data (expressed as temperature and a function of the fraction crystallized), by means of the least-squares method. 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 developed theoretical method has been applied to a set of glassy alloys, whose experimental data are quoted in the literature. The theoretical results obtained for kinetic parameters agree very satisfactorily with the corresponding values given in literature, confirming the reliability of the described method.

Acknowledgments

The authors are grateful to the Junta de Andalucia for their financial support.

Appendix 1

The fit of the theoretical function h(T) to the experimental data T_i and y_i through a least-squares method supplies the intermediate parameters, which appear in the equations of the activation energy, kinetic exponent and frequency factor. The above-mentioned parameters are given by the following expressions

$$A=\left(\sum_{i=1}^{k}\frac{y_i}{T_i}\right)\left(\sum_{i=1}^{k}\ln T_i\right)-\left(\sum_{i=1}^{k}\frac{1}{T_i}\right)\left(\sum_{i=1}^{k}y_i\ln T_i\right),$$

$$B=\left(\sum_{i=1}^{k}\frac{1}{T_i}\right)\left(\sum_{i=1}^{k}(\ln T_i)^2\right)-\left(\sum_{i=1}^{k}\ln T_i\right)\left(\sum_{i=1}^{k}\frac{1}{T_i}\ln T_i\right)$$

$$C=\left(\sum_{i=1}^{k}\frac{1}{T_i}\ln T_i\right)\left(\sum_{i=1}^{k}y_i\ln T_i\right)-\left(\sum_{i=1}^{k}\frac{y_i}{T_i}\right)\left(\sum_{i=1}^{k}(\ln T_i)^2\right),$$

$$D=\left(\sum_{i=1}^{k}\frac{1}{T_i}\right)\left(\sum_{i=1}^{k}\frac{1}{T_i}\ln T_i\right)-\left(\sum_{i=1}^{k}\frac{1}{T_i^2}\right)\left(\sum_{i=1}^{k}\ln T_i\right)$$

$$F=\left(\sum_{i=1}^{k}\frac{1}{T_i^2}\right)\left(\sum_{i=1}^{k}y_i\ln T_i\right)-\left(\sum_{i=1}^{k}\frac{y_i}{T_i}\right)\left(\sum_{i=1}^{k}\frac{1}{T_i}\ln T_i\right),$$

$$M=\left(\sum_{i=1}^{k}y_i\right)\left(\sum_{i=1}^{k}\frac{1}{T_i^2}\right)-\left(\sum_{i=1}^{k}\frac{y_i}{T_i}\right)\left(\sum_{i=1}^{k}\frac{1}{T_i}\right)$$

$$N=\left(\sum_{i=1}^{k}\frac{y_i}{T_i}\right)\left(\sum_{i=1}^{k}\ln T_i\right)-\left(\sum_{i=1}^{k}y_i\right)\left(\sum_{i=1}^{k}\frac{1}{T_i}\ln T_i\right)$$

which, as may be observed, only depend on experimental data such as temperature and volume fraction crystallized.

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