Journal of Thermal Analysis, Vol. 37 (1991) 1261-1268

Dedicated to Professor Dr. H. J. Seifert on the occasion of his 60^{th} birthday

CRYSTALLIZATION KINETIC STUDIES: A MEANS TO EVALUATE TIME–TEMPERATURE–TRANSFORMATION CURVES. APPLICATION TO METALLIC GLASSES

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(Received December 11, 1990)

It is shown that the study of the kinetics of crystallization of an amorphous alloy may be used to obtain the correct form of the low temperature part of the time-temperature-transformation (*T–T–T*) curves. A unified review of the current kinetics of crystallization studies is presented and the general kinetic equation which gives the reaction rate as a function of temperature and crystalline fraction is shown to contain information related to the *T–T–T* curves. Finally examples of application to two metallic glasses, $Nd_3Fe_{77}B_{20}$ and $Fe_{67.5}Co_{15}Nb_{1.5}B_{16}$, obtained by rapid solidification techniques are presented. The comparison between theory and experiment is satisfactory.

In the past several attempts have been directed towards the determination of the time-temperature-transformation *(T–T–T)* curves. Some of them have a theoretical basis [1, 2] which comes from the assumption of homogeneous nucleation and three dimensional crystal growth, phase boundary limited, in congruently melting alloys [3-8]. Another approach consists in the experimental determination of some points of a *T–T–T* curve [9-11], generally those corresponding to the maximum of the heat evolution per unit time. Some attempts have also been done to relate the *T–T–T* curves to the so called continuous heating (CHT) and continuous cooling (CT) curves [12-14]. More recently a new temperature-heating rate-transformation curve has been proposed to be used when the sample is submitted to a continuous heating treatment [15, 16].

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More generally, the study of the kinetics of the crystallization of an amorphous or glassy sample under isothermal or continuous heating conditions has been, and continues to be, the subject of numerous publications [17-21]. The interpretation of the results obtained follows the following general scheme: the equation giving the relationship between the reaction rate, dx / dt, temperature, T, and crystalline fraction already present, x, has the general form

$$dx / dt = K(T) f(x) \tag{1}$$

where $K(T)$ is the rate constant and $f(x)$ a function which reflects the mechanism of crystallization. It is expected that $K(T)$ could exhibit a simple Arrhenius behaviour with respect to temperature, at least in the small temperature interval in which the rate of reaction due to the crystallization of glasses on heating can be measured experimentally, that is

$$K(T) = K_o \exp(-E / RT) \tag{2}$$

where E is the apparent activation energy and K_o the pre–exponential factor.

There are many types of glasses (oxide, chalcogenide, halide, metallic, polymer, etc.) whose crystallization behavior can be described by the general kinetic equations (1) and (2) in certain temperature range. This is the main reason of the common use of the peak method [22, 23] for the determination of the apparent activation energy of the crystallization process.

In general kinetic processes the simplest way of the analytical formulation of the function $f(x)$ is to assume a reaction of order n, that is

$$f(x) = (1-x)^n \tag{3}$$

However, in the case of crystallization of a glass as a result of nucleation and crystal growth the form most often found for $f(x)$ is that which is called the Johnson-Mehl–Avrami–Erofe'ev (JMAE) expression [24]

$$f(x) = n(1-x)[-\ln(1-x)]^{(n-1)/n} \tag{4}$$

where n is the kinetic exponent. In a more general and empirical way there are other analytical expressions used such as that proposed by Sestak and Berggren [25]

$$f(x) = x^m(1-x)^n \tag{5}$$

where n and m are empirical parameters.

Theoretical considerations

The most widely used theory in crystallization kinetic studies is that presented by Uhlmann [2]. It can be applied to single-component materials or congruently melting compounds, neglecting transient time effects. Assuming isothermal transformation conditions, spatially random nucleation rate, I, and growth rate, u, dependent only on temperature and not on time, the volume fraction x crystallized at time t may be related to I and u by

$$x = 1- \exp[-\pi \mathrm{I} \mathrm{u}^3 t^4/3)] \tag{6}$$

Furthermore, the following equations are deduced

$$I = \frac{N_v^0 kT}{3\pi a_0^3 \eta} \cdot \exp\left[-\frac{16\pi}{3}\frac{\sigma^3 T_m^4}{(\Delta H_m)^2 (\Delta T)^2 R T^3}\right] \tag{7}$$

$$u = \frac{f kT}{3\pi a_0^2 \eta}\left[1 - \exp\left(-\frac{\Delta H_m \Delta T}{R T T_m}\right)\right] \tag{8}$$

where N_v^0 is the number of atoms per unit volume, a_0 is the atomic diameter, η is the viscosity, σ is the molar free interface enthalpy between nucleus and liquid, ΔH_m is the molar enthalpy of fusion, $\Delta T = T_m - T$ is the undercooling and f is the fraction of sites at the crystal–liquid interface where atoms may preferentially be added and removed. Equations (6) to (8) have been used to construct the T–T–T curves [3-8]. More generally, differentiating Eq. (6), under isothermal conditions and expressing the result as a function of temperature and crystalline fraction, one obtains

$$\mathrm{d}x / \mathrm{d}t = 4\,(\pi \mathrm{I} \mathrm{u}^3/3)^{1/4}(1-x)[-\ln(1-x)]^{3/4} \tag{9}$$

This expression is a particular form of the general kinetic Eq. (1) with $f(x)$ given by the JMAE expression with $n = 4$ and

$$K(T) = (\pi I u^3/3)^{1/4} \tag{10}$$

Values of n in the interval 0.5-4 can be obtained from theoretical considerations by assuming other possibilities as zero nucleation rate (pre-existing nuclei), two- or one-dimensional growth, and diffusion controlled growth [19].

As indicated by Eqs (7), (8) and (10) it is extremely doubtful that both the nucleation rate and the crystalline growth rate have the same Arrhenius temperature dependence in all the possible temperature range in which crystallization can occur. However, experimental observation indicates that this is in general the case at least in the small temperature range in which the crystallization process can be followed by measurements under isothermal or continuous heating conditions.

Experimental determination of a part of the *T–T–T* curves

In fact the study of the crystallization kinetics is just a part of the general determination of the *T–T–T* curve. Effectively, under isothermal conditions, the integrated form of the kinetic equation (1) is

$$g(x)=\int_0^x \frac{dx}{f(x)}=K(T)t \tag{11}$$

or

$$g(x)/K_o = t\cdot exp\,(-E/RT) \tag{12}$$

Therefore, differential scanning calorimetry (DSC) is very useful for determining at least a part of the *T–T–T* curve. That is, in general Eq. (12) may replace the *T–T–T* curve only in the temperature interval of validity of Eq. (1). Schematically, in Fig. 1 are plotted Eqs (6) and (12) for a fixed value of x. As seen in that figure, Eq. (12) reproduces rather well the lower part of the *T–T–T* curve. However, it deviates from it at temperatures near the nose of the *T–T–T* curve. Using Eqs (6) to (8) as a model, the highest temperature $T_{\max}$ to which Eq. (12) can reasonably well reproduce the *T–T–T* curve can be estimated to be $T_{\max}$ ~0.6 Tl, Tl being the liquidus temperature [26].

The low part of the *T–T–T* curves can be constructed, as indicated, once the crystallization parameters of the glassy material are known. The essential parameters are the apparent activation energy E and the function $K_of(x)$ (or $g(x)/K_o$). These parameters can be obtained from DSC measurements under isothermal or continuous heating regimes [27]. The general procedure has been applied to some Nd-Fe-B and Fe–Co–Nb–B based amorphous ribbons obtained by rapid solidification techniques [26, 28].

One of the important points in the construction, here proposed, of the lower temperature part of the *T–T–T* curve is the fact that it applies whatever is the form of the function $f(x)$ either if it can be fitted by a theoretical model already established or if it is not easy to reproduce by an analytical function but is known only from experiment. To illustrate this fact we will present the results obtained for crystallization processes which correspond to the second eventuality. Two different alloys have been studied

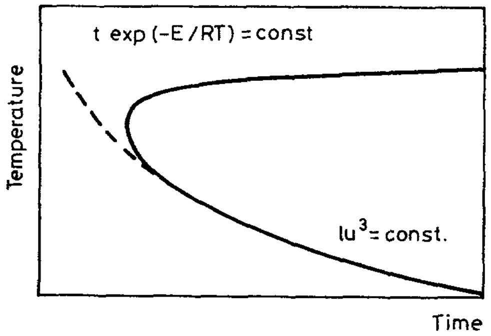

Fig. 1 Temperature–time diagram in which the solid line represents the Time–Temperature–Transformation curve as obtained by use of Equs (5) to (7) and the dashed line is its asymptotic behavior at low temperature given by equation (11)

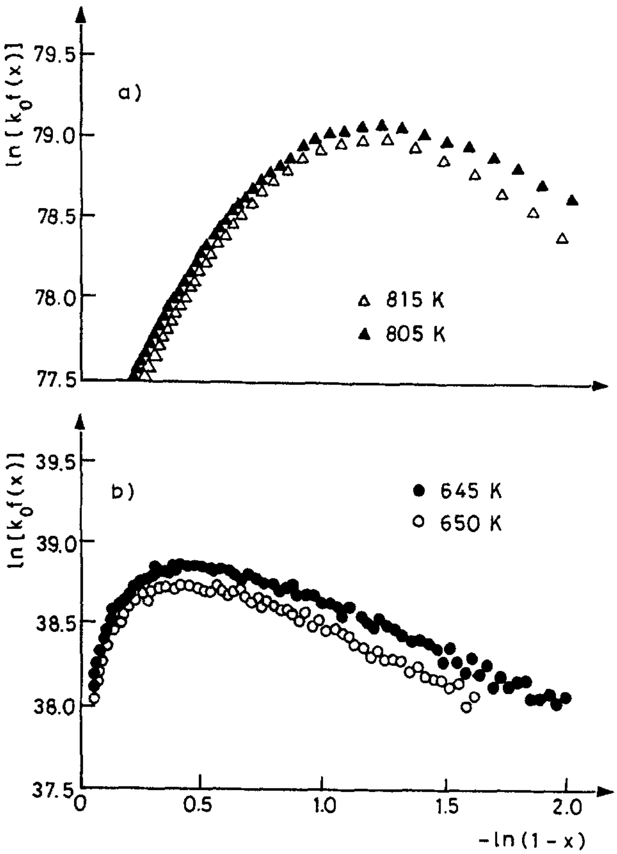

Fig. 2 $\ln[K_0 f(x)]$ *vs.* $-\ln(1-x)$ for the first crystallization peak of alloys studied under isothermal conditions at different temperatures. (a) $Nd_3Fe_{77}B_{20}$; (b) $Fe_{67.5}Co_{15}Nb_{1.5}B_{16}$

and its calorimetric behaviour is the following. The amorphous $Nd_3Fe_{77}B_{20}$ ribbons obtained by melt spinning show three crystallization peaks partially overlapped in temperature when observed under continuous heating conditions [26]. These peaks can be separated by isothermal treatment. The important kinetic parameters for the first crystallization peak have been obtained and are given in Table 1. The function $K_0 f(x)$ as obtained for the first crystallization peak is plotted *vs.* ln (1–*x*) in Fig 2 (a). This function can not be reproduced by the JMAE model. The amorphous $Fe_{67.5}Co_{15}Nb_{1.5}B_{16}$ ribbons obtained by planar flow casting exhibit calorimetrically two peaks of crystallization on heating [28]. The kinetic results needed to construct the *T–T–T* curves corresponding to the first crystallization peak are presented in Table 1 and Fig. 2 (b). The form of $f(x)$ is quite different from that obtained for the Nd–Fe–B amorphous ribbon but it cannot be reproduced by the JMAE expression either. In Fig. 3 are presented the *T–T–T* curves corresponding to the beginning ($x=0.1$), peak (under isothermal conditions) and end ($x=0.9$) of the first crystallization process for the $Nd_3Fe_{77}B_{20}$

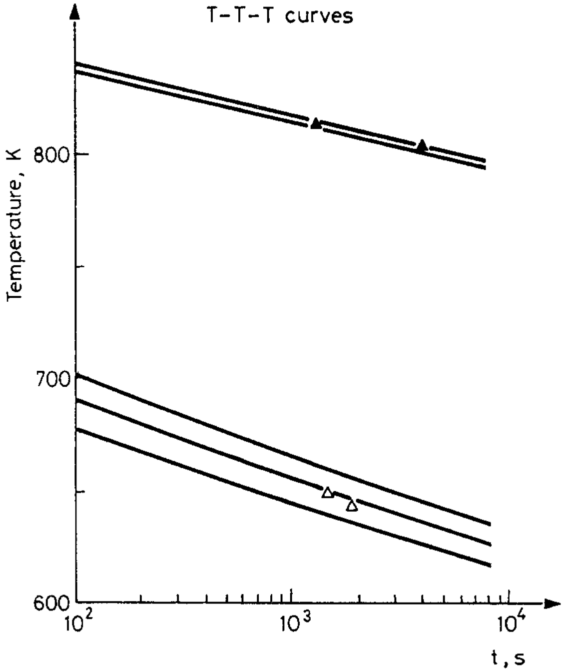

Fig. 3 *T–T–T* curves obtained for the first stage of crystallization of $Nd_3Fe_{77}B_{20}$ (upper set of curves) and $Fe_{67.5}Co_{15}Nb_{1.5}B_{16}$ (lower set of curves) amorphous ribbons. Extreme curves correspond to a crystalline fraction of $x=0.1$ (bottom curve) or $x=0.9$ (top curve) and intermediate curves correspond to the fraction crystallized at the maximum of the peak seen in DSC, that is for $x=0.7$ in the $Nd_3Fe_{77}B_{20}$ alloy and $x=0.4$ for the $Fe_{67.5}Co_{15}Nb_{1.5}B_{16}$ alloy. Triangles and diamonds correspond to the experimental points (at the crystallization peak)

(upper set of curves) and $Fe_{67.5}Co_{15}Nb_{1.5}B_{16}$ (lower set of curves) amorphous alloys studied, respectively. As a consequence of the different form of $g(x)$ the spread in temperature of the *T–T–T* curves corresponding to $x = 0.1$ and $x = 0.9$ is very different in the two alloys studied.

Table 1 Crystallization kinetic quantities corresponding to the first crystallization peak which are needed to construct the *T–T–T* curves: Apparent activation energy, E, and logarithm of the function $g(x)/K_0$, $\ln [g(x)/K_0]$ at several values of x

Alloy	E,	$\ln [g(x)/K_0]$ with K_0 in s^{-1}			+
	eV	$x = 0.1$	$x = 0.4$	$x = 0.7$	$x = 0.9$
Nd–Fe–B	5.91	–77.2		–77.0	–76.9
Fe–Co–Nb–B	2.58	–39.7	–38.9		–38.2

The major utility of the *T–T–T* curves is the prediction of the amount of material crystallized under isothermal conditions as a function of time. As an example we verify that the experimentally observed crystalization fractions achieved at the maximum reaction rate (peak in the DSC curve) when annealing at different temperatures occur at the times predicted with the *T–T–T* curves corresponding to that amount of crystallized material. These points are also presented in Fig. 3 for the first crystallization peak of the alloys studied. As can be seen in this figure the agreement is quite good between the calculated *T–T–T* curves and the experiment.

Conclusions

The utility of the crystallization kinetic theories to construct the *T–T–T* curves assuming isothermal transformation conditions, spatially random nucleation rate and growth rate dependent only on temperature is reviewed.

The limitations of the applicability of the theoretical calculations are discussed and it is shown that in general the low temperature part of the *T–T–T* curve can be obtained from experiment.

Emphasis is made in the possibility of experimental determination of the low temperature part of the *T–T–T* curves from crystallization kinetics data. These data can be easily obtained, for instance, with a differential scanning calorimeter.

The theoretical calculations are exemplified with two particular cases in metallic glasses, $Nd_3Fe_{77}B_{20}$ and $Fe_{67.5}Co_{15}Nb_{1.5}B_{16}$ obtained by rapid solidification techniques. The *T–T–T* curves obtained for both alloys agree with some experimentally determined points.

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This work was supported by the Comision Interdepartamental de Cienca y Tecnologia, CICYT (project No. MAT88–0439) which are acknowledged.

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Zusammenfassung — Es wird gezeigt, daß die Untersuchung der Kristallisationskinetik von amorphen Legierungen genutzt werden kann, die korrekte Form des Niedertemperaturbereiches der Zeit-Temperatur-Transformation (T-T-T) Kurven zu erhalten. Es wird ein einheitlicher Überblick über die jüngsten Untersuchungen von Kristallisationskinetiken gegeben und an der allgemeinen Gleichung der Reaktionsgeschwindigkeit als eine Funktion von Temperatur und Kristallanteil wird gezeigt, daß sie Informationen bezüglich der T-T-T-Kurven beinhaltet. Letztlich wird eine Anwendung an zwei, durch schnelles Erstarren gewonnenen metallischen Gläsern $Nd_3Fe_{77}B_{20}$ und $Fe_{67.5}Co_{15}Nb_{1.5}B_{16}$ dargelegt. Zwischen Theorie und Praxis konnte eine ausreichende Übereinstimmung festgestellt werden.