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Determination of T–T–T and T–HR–T curves from non-isothermal crystallization kinetic experiments

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Abstract

Non-isothermal crystallization kinetic experiments on glassy materials are easily performed using a scanning differential calorimeter. The method has been used very often to determine the activation energy of a process and sometimes even a reaction mechanism. Of more fundamental interest is the establishment of the evolution of the transformation temperature with the heating rate of the glass. A new set of temperature–heating rate–transformation curves is proposed to characterize such behaviour. The classical time–temperature–transformation curves are also of interest. We demonstrate that the low temperature part of both kinds of curves can be obtained from the study of the crystallization kinetics. The study of a metallic glass is given to show some of the advantages and limitations of the procedure.

INTRODUCTION

The use of diagrams in which curves representing different theories or models are compared with experimental results, is widely used to check the validity of the theory or models. Theoretical models often provide insight into the behaviour of a physical system in regions far from those that are experimentally accessible. In particular, there is a theoretical basis for the crystallization of an undercooled melt [1,2], which is derived from the assumptions of homogeneous nucleation and three-dimensional phase-boundary-controlled crystal growth for congruently melting alloys.

In this paper such transformation theories will be used to propose a new set of temperature versus heating (cooling) rate diagrams for the character-

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Dedicated to Professor Joseph H. Flynn in honour of his 70th birthday.

ization of crystallization behaviour in amorphous materials. In such diagrams one can construct the temperature–heating rate–transformation (T–HR–T) and the temperature–cooling rate–transformation (T–CR–T) curves which give the loci of points where a certain degree of crystallization has been achieved at each temperature as a function of the heating or cooling rate used in the experiment respectively. In principle, the high temperature part of the T–CR–T curves may be obtained from continuous cooling experiments, but in general the crystallization of the melt occurs from inhomogeneous nucleation and it is very difficult to obtain reproducible results. In contrast, the crystallization of a glass is very often a reproducible process. We will demonstrate that the low temperature part of the T–HR–T curves can be obtained from the study of the crystallization kinetics by means of non-isothermal experiments. This study can be easily achieved using a short-time-response calorimeter such as a differential scanning apparatus. The method can also be used to predict the low temperature part of the isothermal time–temperature–transformation (T–T–T) curves.

CLASSICAL THEORY OF NUCLEATION AND CRYSTAL GROWTH

To illustrate how the different transformation curves can be constructed we will assume that we have an element or a congruently melting compound in an amorphous state that crystallizes on heating from the amorphous phase, following a homogeneous nucleation rate and three-dimensional phase-boundary-controlled growth kinetics. This is a well-known model that gives at least qualitatively good predictions for a large number of materials. According to this theory, the fraction crystallized x as a function of time under isothermal conditions follows a general Johnson–Mehl–Avrami–Erofe'ev equation of the form

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

where I is the homogeneous nucleation rate, u the growth rate, both being dependent only on temperature and not on time, and given by, respectively

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

$$u = \frac{fkT}{3\pi a^2 \eta}\left[1 - \exp\left(-\frac{\Delta H_m\,\Delta T}{RTT_m}\right)\right] \tag{3}$$

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

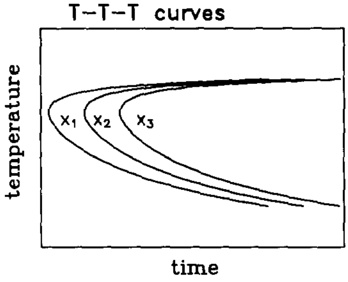

Fig. 1. Schematic T–T–T curves obtained for three values of the crystalline fraction (x_1, x_2, x_3) by use of eqns. (1)–(3).

the undercooling and f is the fraction of sites at the crystal–liquid interface where atoms may be preferentially added or removed.

T–T–T CURVES DEDUCED FROM CLASSICAL THEORY

The general form of the T–T–T curves, with the aforementioned assumptions, is depicted in Fig. 1. From a knowledge of the viscosity as a function of temperature, the melting behaviour and a reasonable assumption for the value of the molar free interface enthalpy, eqns. (1)–(3) have been used by several authors to evaluate theoretically the T–T–T curves for various alloy compositions [3–8]. Another approach consists of 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 made to relate the T–T–T curves to the so-called continuous heating (CHT) and continuous cooling (CT) curves [12–14].

NEW T–HR–T AND T–CR–T CURVES DEDUCED FROM CLASSICAL THEORY

Equations (1)–(3) give respectively the fraction x crystallized at time t under isothermal conditions, the nucleation rate I (assumed homogeneous) and the growth rate u (phase boundary controlled). More generally, differentiating eqn. (1) under isothermal conditions and expressing the result as a function of temperature and crystalline fraction, one obtains

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

This expression gives the general kinetic equation which is also valid, with the aforementioned assumptions, for non-isothermal crystallization regimes.

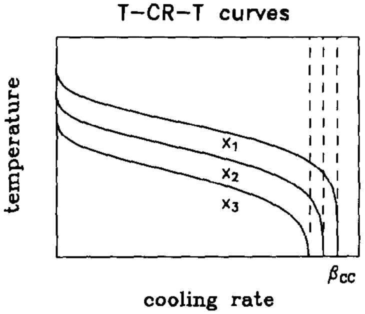

Fig. 2. Schematic T–CR–T curves obtained from eqns. (2), (3) and (5) for three values of the crystalline fraction ($x_1 = 10^{-6}$, x_2, x_3). Also shown is the critical cooling rate, β_{CC}, above which the melt does not crystallize on cooling.

When cooling the melt from the melting point T_m at a constant cooling rate $\beta_{CR} = |dT/dt|$, the integration of eqn. (4) gives

$$\int_0^x \frac{dx}{4(1-x)[-\ln(1-x)]^{3/4}} = \frac{-1}{\beta_{CR}} \int_{T_m}^{T} \left(\frac{\pi I u^3}{3} \right)^{1/4} dT \tag{5}$$

whereas on heating the glass at a constant heating rate $\beta_{HR} = dT/dt$, the integration of eqn. (4) gives

$$\int_0^x \frac{dx}{4(1-x)[-\ln(1-x)]^{3/4}} = \frac{1}{\beta_{HR}} \int_0^{T} \left(\frac{\pi I u^3}{3} \right)^{1/4} dT \tag{6}$$

Equation (5) and (6) allow the study of the progress of crystallization as a function of the temperature for a fixed cooling and heating rate respectively. There are, however, some particular types of representations that can be constructed from eqns. (5) or (6). For instance, those corresponding to a temperature–cooling-rate or temperature–heating-rate diagram in which the curves traced are the loci of the points where a fixed amount of crystalline fraction is achieved under constant cooling or heating rate conditions. The first set of curves will be called temperature–cooling rate–transformation (T–CR–T) curves and are shown in Fig. 2. As expected, at very low cooling rates, crystallization begins at temperatures very close to the melting point, the degree of undercooling needed to promote crystallization increasing with cooling rate. At intermediate cooling rates, the temperature of the beginning of appreciable crystallization is somewhat independent of cooling rate, and finally, on further increasing the cooling rate, a limiting cooling rate is reached above which no more progress in crystallization will take place, yielding, therefore a partially crystalline sample. It is normal procedure to define the critical cooling rate, β_{CC}, as the limiting cooling rate for a crystalline fraction of $x_1 = 10^{-6}$ which is

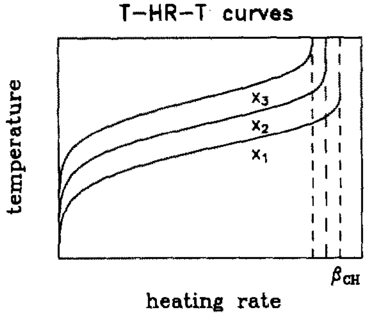

Fig. 3. Schematic T–HR–T curves obtained from eqns. (2), (3) and (6) for three values of the crystalline fraction ($x_1 = 10^{-6}$, x_2, x_3). Also shown is the critical heating rate, β_{CH}, above which the glass does not crystallize on heating.

taken as the barrier between partially crystalline sample and amorphous material.

The second set of curves are called [15] temperature–heating rate–transformation (T–HR–T) curves, plotted schematically in Fig. 3. The general behaviour follows, as for the T–CR–T curves, three steps. At low heating rates, crystallization begins at temperatures that increase with heating rate. At intermediate heating rates, there is a plateau and on further increasing the heating rate a limiting heating rate is reached above which the crystallization rate becomes negligible. By analogy we will define the critical heating rate, β_{CH}, as the limiting heating rate for a crystalline fraction of $x_1 = 10^{-6}$. Intermediate heating rates, located in the plateau region of Fig. 3, are normally the most useful in practical applications because they combine the attainment of the desired proportion of crystallized sample with a moderate energy cost. Another point of interest of the T–HR–T curves is that they can be used to predict how high in temperature one can go when heating an amorphous sample without inducing crystallization. They establish, therefore, a new tool for the study of crystallization.

In a very similar way, T–CR–T and T–HR–T curves can be obtained from theoretical considerations by taking into account other assumptions such as zero nucleation rate (pre-existing nuclei), two- or one-dimensional growth, and diffusion-controlled growth [16].

DETERMINATION OF THE CRYSTALLIZATION KINETICS

The different transformation curves considered can be constructed, as indicated, from a kinetic treatment based on classical nucleation and crystallization theories. However, real alloy glasses often have compositions that do not correspond to congruently melting ones. Furthermore, homogeneous nucleation is a very unlikely process because pre-nuclei are often present in the glassy phase. 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 [16–21]. The interpretation of the results obtained is made following the general scheme below. The equation giving the relationship between the reaction rate dx/dt, temperature T and crystalline fraction already present x has the general form

$$dx/dt = K(T)f(x) \tag{7}$$

where $K(T)$ is the rate constant and $f(x)$ is a function which reflects the mechanism of crystallization. It is expected that $K(T)$ could exhibit 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

$$K(T) = K_0 \exp(-E/RT) \tag{8}$$

where E is the apparent activation energy and K_0 the pre-exponential factor.

There are many kinds of glasses (oxide, chalcogenide, halide, metallic, polymer etc.) whose crystallization behaviour can be described by the general kinetic equations (7) and (8) in a certain temperature range. This is the main reason for the common use of the peak method [22,23] for the determination of the apparent activation energy of the crystallization process.

EMPIRICAL DETERMINATION OF THE T–T–T AND T–HR–T CURVES

More empirically, the construction of the transformation curves will be possible once the crystallization parameters of the amorphous material are known. As is well known, isothermal crystallization kinetic experiments can only be performed in a small temperature interval. At low temperatures, the rate of reaction is very low and this inhibits its measurement. At high temperatures there is no such problem, but the previous heating needed to reach these temperatures induces the uncontrolled beginning of crystallization. Furthermore, when several crystallization processes are involved it is by no means obvious which is proceeding under isothermal conditions. In contrast, continuous heating experiments can be performed in a wide temperature interval, mostly enlarged in the high temperature range. This enables a much more precise determination of the activation energy involved in the crystallization process, except when several crystallization processes with different activation energies appear overlapping in temperature.

As indicated by eqns. (2)–(4), 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 ranges in which crystallization can occur. However, experimental observation indicates that this is generally the case, at least in the temperature range in which the crystallization process can be followed by measurements under isothermal or continuous heating conditions.

The values for the crystallization process that are obtainable from differential scanning calorimetry experiments [21] and which are essential in the empirical determination of the low temperature part of both the T–T–T and T–HR–T curves are the apparent activation energy, which appears in the Arrhenius equation, eqn. (8), and the function $K_0 f(x)$ of eqns. (7) and (8).

It should be noted that integration of eqn. (7) at constant T gives

$$g(x) = \int \frac{\mathrm{d}x}{f(x)} = K(T)t \tag{9}$$

which when shown as a plot of temperature against the time needed to crystallize a certain fraction of material at a temperature T, is the T–T–T curve. Unfortunately only the low temperature part of the T–T–T curve is experimentally accessible by this procedure [24].

In a very similar way, putting eqn. (8) in eqn. (7) and integrating at a constant heating rate β, gives

$$g(x) = \int \frac{\mathrm{d}x}{f(x)} = \frac{K_0}{\beta} \int \exp(-E/RT)\,\mathrm{d}T \tag{10}$$

Once the integration is done the result can be shown in a plot of the temperature versus the heating rate used to crystallize a certain fraction of the sample. These are the T–HR–T curves.

APPLICATION OF THE METHOD TO A METALLIC GLASS OF COMPOSITION $Nd_{16}Fe_{76}B_8$

To illustrate both the advantages and the limitations of the method, we present here its application to the determination of the low temperature part of the T–HR–T and T–T–T curves from non-isothermal crystallization experimental results of a metallic glassy alloy of composition $Nd_{16}Fe_{76}B_8$. Metallic glasses were prepared by rapid solidification (melt-spinning) of the molten alloy. Figure 4 shows the DSC curve obtained on heating the metallic glass at 80 K min^{-1}. The crystallization exotherm shows two overlapping peaks, as is often the case on heating most metallic glasses. The analysis was done by assuming that the overall process follows the kinetic equations, eqns. (7) and (8). The apparent activation energy E was evaluated from a plot of $\ln(\mathrm{d}x/\mathrm{d}t)$ against $1/T$ for a fixed crystallized fraction at various heating rates [21]. The value $E = 299 \pm 3$ kJ mol^{-1} was obtained.

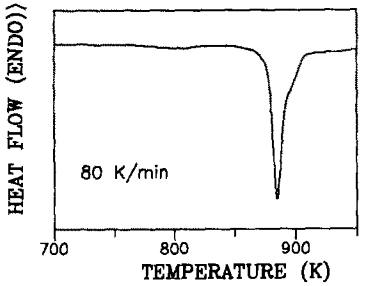

Fig. 4. DSC curve (heating rate, 80 K min^{-1}) obtained for the crystallization of $Nd_{16}Fe_{76}B_8$ melt-spun metallic glass.

To check the validity of eqns. (7) and (8), and to determine the function $K_0 f(x)$ for each constant heating rate DSC curve, the value of

$$\ln(dx/dt) + E/RT = \ln(K_0 f(x)) \tag{11}$$

was obtained. Figure 5 shows the plot of $\ln(K_0 f(x))$ against $-\ln(1-x)$ for four non-isothermal experiments at different heating rates. As shown in Fig. 5, there is a scatter between the several experimental values which is probably related to the inherent reproducibility limits of both the crystallization process and the preparation of the glassy samples. The many crystallization kinetic studies we have performed in the past lead us to the conclusion that it is quite general to obtain an uncertainty of ±0.2 in the $\ln[K_0 f(x)]$ values. However for this metallic glass the inaccuracy is multiplied by a factor of two probably because it is quite difficult to fully amorphize this material by melt spinning. Of course, instead of taking a fixed value of E and attaching reproducibility limits to $\ln[K_0 f(x)]$ one can take $K_0 f(x)$ as fixed and the uncertainty coming from the reproducibility limits will be associated with the accuracy of the value of E (in this case about $\pm 0.4RT$).

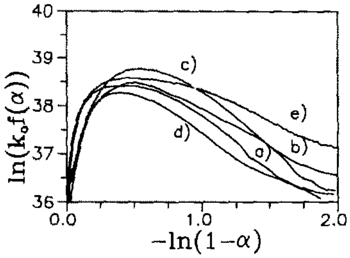

Fig. 5. Plots of $\ln(K_0 f(x))$ vs. $-\ln(1-x)$ for the crystallization of $Nd_{16}Fe_{76}B_8$ alloys ($E = 299$ kJ mol^{-1}) studied under non-isothermal conditions at different heating rates: curve a, 5 K min^{-1}; curve b, 10 K min^{-1}; curve c, 40 K min^{-1}; curve d, 80 K min^{-1}; curve e, isothermal results at 825 K.

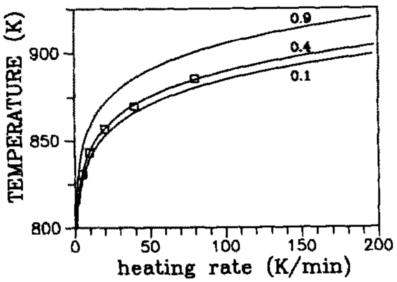

Fig. 6. Low temperature part of the T–HR–T curves for $Nd_{16}Fe_{76}B_8$ metallic glasses corresponding to crystalline fractions of $x = 0.1$, 0.4 and 0.9 as indicated on the graph. Experimental points correspond to the evolution of the peak temperature ($x = 0.4$) as a function of heating rate.

It is useful in general to perform, in addition, at least one isothermal experiment to check that the same process (or processes) is (are) in progress under continuous heating and under isothermal conditions. The procedure to obtain $\ln(K_0 f(x))$ is the same for isothermal and for continuous heating curves. Therefore, in Fig. 5 there is also a curve resulting from the isothermal measurements. It differs from the non-isothermal ones for high values of x (or $-\ln(1-x)$) because under isothermal conditions only the main exothermic peak is activated. This must be taken into account and means that when there is overlapping between several peaks in the non-isothermal measurements, only the low values of x of the T–T–T curves can be reasonably well reproduced from the non-isothermal results.

Once the kinetic results needed were known, the low temperature part of the T–HR–T and T–T–T curves corresponding to the $Nd_{16}Fe_{76}B_8$ alloy were calculated. Figure 6 shows the T–HR–T curves calculated for several values of the crystalline fraction ($x = 0.1$, 0.4, 0.9). Allowing for the uncertainty in the absolute value of $K_0 f(x)$ or E, the estimated error in temperature of such calculated curves is ± 5 K. The major application of the T–HR–T curves is the prediction of the amount of material crystallized

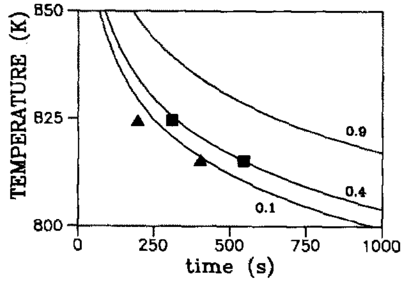

Fig. 7. Low temperature part of the T–T–T curves for $Nd_{16}Fe_{76}B_8$ metallic glasses corresponding to crystalline fractions of $x = 0.1$, 0.4 and 0.9. Experimental points correspond to the results obtained under isothermal conditions for $x = 0.1$ (▲) and 0.4 (■).

under a certain constant heating rate treatment of the samples. As an example we verify that the experimentally obtained temperatures at which the crystalline fraction reaches the value of 0.4 under different heating rate treatments of the samples (represented by the points in Fig. 6) agree with the respective T–HR–T curves.

Figure 7 shows the T–T–T curves constructed for the same alloy with $x = 0.1$, 0.4 and 0.9. The points correspond to the experimental results obtained under isothermal conditions for the alloy studied with crystalline fractions of 0.1 and 0.4. As can be seen in this figure, the agreement between the T–T–T curve calculated from the non-isothermal results and the experimental results is quite good provided, as mentioned above, that only small values of x are considered.

CONCLUSIONS

It is possible to represent the crystallization behaviour of a glassy material in terms of the T–HR–T curves as well as the T–T–T curves usually used. The qualitative results are not very different, but the use of the T–HR–T curves allows the amount of transformation achieved when heat-treating the glassy material to be visualized and the way in which the crystallization temperatures respond on increasing the heating rate to be illustrated quantitatively.

The determination of the low temperature part of the T–HR–T curves is possible by the study of the crystallization kinetic behaviour using differential scanning calorimetry because it can be assumed that crystallization is a thermally activated process over a wide temperature range.

The general procedure is exemplified in its application to the $Nd_{16}Fe_{76}B_8$ metallic glass. The possibility of extending the method to the determination of the low temperature part of the T–T–T curves is also shown, with particular emphasis on the limitations of the calculations.

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