Comparison of crystallization kinetics studied by DSC and TGA [a]

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Abstract

Crystallization kinetics of amorphous materials can be studied isothermally below the crystallization temperature T_x. The data is then analyzed with the Johnson–Mehl–Avrami equation. In a DSC, the fraction crystallized at time t is directly obtained from the change in enthalpy at t. For amorphous magnetic materials, a modified TGA method can be used if $T_{c1} < T_x < T_{c2}$ when T_{c1} and T_{c2} are the Curie temperatures of the amorphous and crystalline phases. The crystallized fraction is then proportional to the magnetization at t. For a critical comparison of these methods we have selected the amorphous alloy $Fe_{75}V_1B_{24}$ which crystallizes polymorphously into tetragonal $(Fe,V)_3B$. The results of the kinetic analysis are presented together with a discussion of the merits of the two methods.

INTRODUCTION

Amorphous metals (or metallic glasses) are in metastable equilibrium and upon heating crystallize through a nucleation and growth process into a more stable phase. A study of the kinetics of crystallization gives information about the stability of the amorphous phase which is of the utmost importance when these are used in technological applications.

The crystallization process, being an exothermal process, is commonly studied by differential scanning calorimetry (DSC) in isothermal mode below the crystallization temperature, T_x. The time evolution of the integral under the crystallization exotherm, normalized to the total enthalpy of transformation, gives the crystallized fraction $x(t)$. It is customary to describe $x(t)$ by the well known Johnson–Mehl–Avrami (JMA) equation [1,2]

$$x(t) = 1 - \exp\left[-(t/\tau)^n\right] \qquad (1)$$

where the constant n is the Avrami exponent whose value depends on the nucleation rate and the type of growth process. Thus, an Avrami plot,

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$\ln \ln (1/(1 - x))$ against $\ln(t)$, should yield a straight line of slope n. τ is a temperature dependent characteristic time and can be used to determine the activation energy, E_a, of the crystallization process assuming an Arrhenius relation

$$\tau(T) = \tau_0 \exp[E_a/kT] \tag{2}$$

where τ_0 is a constant and k is Boltzmann's constant.

Recently, we have suggested that thermogravimetry (TGA) can also be used in an effective way to study the crystallization process [3]. The TGA is converted into a thermomagnetic analyzer by the introduction of a magnetic field. The force applied (apparent change in weight) is then directly proportional to the fraction of magnetic material present. For this fraction to equal $x(t)$, the crystallized fraction, the following two conditions must be met. (1) The first crystallization product must be a magnetically ordered phase with its Curie temperature $T_{c2} > T_x$. (2) The amorphous phase should have its Curie temperature $T_{c1} < T_x$.

In this study, we have selected the metallic glass $Fe_{75}V_1B_{24}$ which satisfied the aforementioned conditions and crystallizes polymorphously into tetragonal $(Fe,V)_3B$. The kinetics of crystallization are studied by both DSC and TGA allowing critical comparisons to be made between the two methods.

EXPERIMENTAL METHODS

Glassy ribbons (20 μm thick, 1 mm wide) of composition $Fe_{75}V_1B_{24}$ were obtained by the melt-spinning process. The amorphous nature of the ribbons was checked by X-ray diffraction. For the DSC studies we used a calibrated Perkin-Elmer DSC-2C under a flow of oxygen-free argon. The sample mass for the DSC studies was kept below 5 mg to ensure good thermal contact between samples and sample pan. The TGA studies were done with a calibrated Perkin-Elmer TGA-7 under a flow of oxygen-free argon. The TGA was operated with a magnetic field gradient acting at the sample space. For reproducible results the ribbon (about 0.5 mg) was positioned along the field direction. The ribbon was also centered so that the lateral forces are negligible. Isochronal scans at 40 K min^{-1} for the TGA and DSC are shown in Fig. 1. The composition of the amorphous alloy was chosen so that the crystallization proceeds polymorphously, i.e. with no change in composition, with a single exothermal peak at $T_x = 767$ K, as shown in Fig. 1 for the DSC scan. In this way the results of the kinetic analysis can be interpreted in a simple and straightforward manner. It is clear from the TGA scan in Fig. 1, that T_{c1} (691 K) $< T_x$ (767 K) $< T_{c2}$ (787 K). The addition of 1 at.% V to $Fe_{75}B_{25}$ has decreased T_{c1} by 46 K while T_x has increased by 8 K resulting in an overall increase in the range of temperatures for isothermal crystallization studies.

RESULTS AND DISCUSSION

Selected DSC and TGA isothermal runs, in the temperature range 697–717 K are shown in Figs. 2 and 3, respectively. The activation energy E_a of the crystallization process was obtained from the slope of ln τ_{50} versus $1/T$ (see eqn. 2), where τ_{50} is the time to 50% crystallization. The DSC results give 2.64 ± 0.01 eV while the TGA gives a value of 2.48 ± 0.02 eV for E_a. The small difference in these values is due to errors in baseline determination which affect the precise determination of the onset of crystallization or incubation time.

The JMA plots at selected temperatures are shown in Fig. 4. The Avrami exponent, using a linear regression method, averaged for the six isothermal runs for $x(t) \geqslant 0.01$ is 2.9 ± 0.1 and 3.0 ± 0.1 for the DSC and TGA measurements, respectively. A crystallization process with $n = 3$ corresponds to interface controlled growth of a fixed number of nuclei [1]. The excellent agreement between the two methods again confirms the validity of the modified TGA method. For $x(t) < 0.01$, there are some differences between the two methods as shown in Fig. 5 for $T = 697$ K. The higher sensitivity of the TGA allows us to obtain an Avrami number of $n = 1.6 \pm 0.1$ for $x(t) < 0.01$. An exponent of $n = 1.5$ corresponds to a diffusion controlled growth of a fixed number of nuclei. This mechanism describes a surface selective oxidation [4] at the early stages of crystallization which results in the formation of crystalline α-Fe near the surfaces of the ribbons. In fact, some slight coloration was observed on all ribbon surfaces after annealing at these temperatures. The oxidation process does not involve the formation of $(Fe,V)_3B$ crystals: just before the merging of the two plots in Fig. 5, the $x(t)$ for TGA is slightly greater than that of the DSC indicating the larger magnetic moment of Fe in α-Fe ($2.2\ \mu_\beta$) than in Fe_3B ($1.8\ \mu_\beta$). This, we believe, is the first experimental observation of the kinetic process of surface oxidation.

The sensitivity of the TGA allows measurements of $x(t)$ down to 10^{-5}, which is an order of magnitude smaller than that of the DSC. If one also
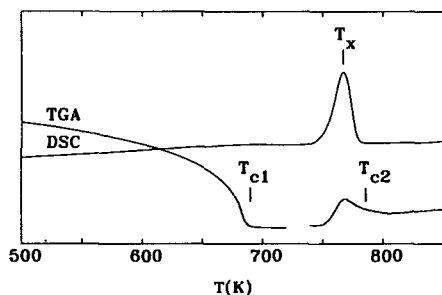

Fig. 1. Isochronal TGA and DSC scans at 40 K min^{-1}. For the TGA, the scan above 730 K is magnified $\times 50$ for clarity.
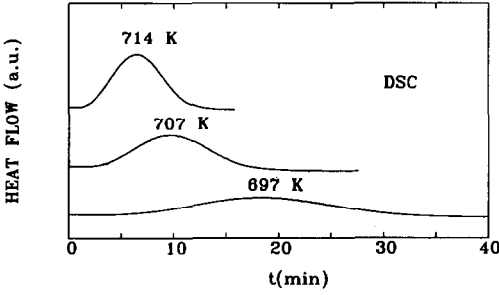
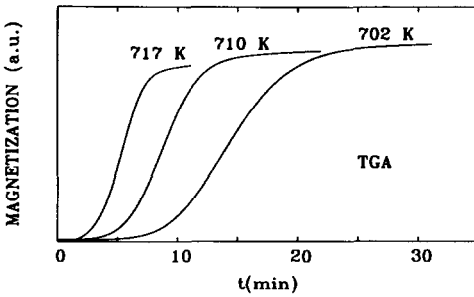Fig. 2. Selected DSC isothermal scans.

Fig. 3. Selected TGA isothermal scans.

considers the amounts of sample required for the TGA and DSC then the overall sensitivity of the TGA is 100 times higher than that of the DSC. It must be recalled, however, that the TGA method described here can only work for very specific materials.
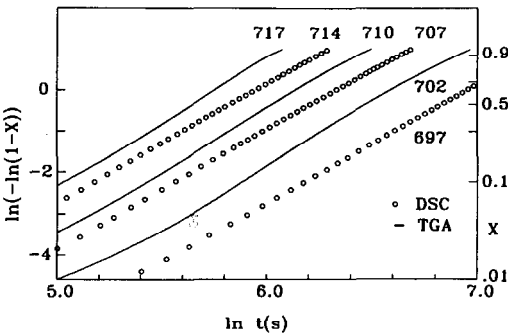

Fig. 4. JMA plots for the crystallized fraction x between 0.01 and 0.90. The isothermal temperatures (in K) are indicated for the selected TGA and DSC scans.
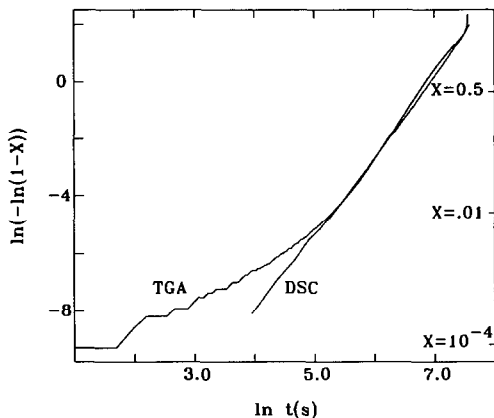
Fig. 5. JMA plots for DSC and TGA extended to very low values for x.

ACKNOWLEDGEMENTS

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