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Complex behaviour of specific heat during structural relaxation of $Fe_{73}Co_{12}B_{15}$ metallic glass

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Abstract

The non-isothermal DSC thermograms of the metallic glass $Fe_{73}Co_{12}B_{15}$ were investigated. The complex analysis of the structural relaxation anomalies of the apparent specific heat of metallic glass samples was performed. The influence of ageing, pre-annealing and more complicated heat treatments, as well as of the heating rate, on the saturation of the structural relaxation enthalpy was demonstrated.

The relaxation exotherm is principally connected with the rapid cooling of the sample. The relaxation endotherm represents the retarded approach to a certain heat treatment (non-isothermal crossover effect). All results can be generalized and interpreted by the DNLR (distribution of non-linear relaxation) model.

INTRODUCTION

Metallic glasses, whatever the technology of their preparation, are never in a configurational equilibrium state. As a result of this, they are not stable to heat treatment and exhibit several characteristic phenomena such as structural relaxation and spontaneous crystallization. The heat effects of these two phenomena determined by differential scanning calorimetry (DSC) can be seen in Fig. 1. (In the case of a planary flow-casted FeCoB alloy, a continually heated glassy sample possesses spontaneously an exothermal multi-stage crystallization at temperatures $T_x > 350°C$. This crystallization is preceded by several exothermal and endothermal relax-

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

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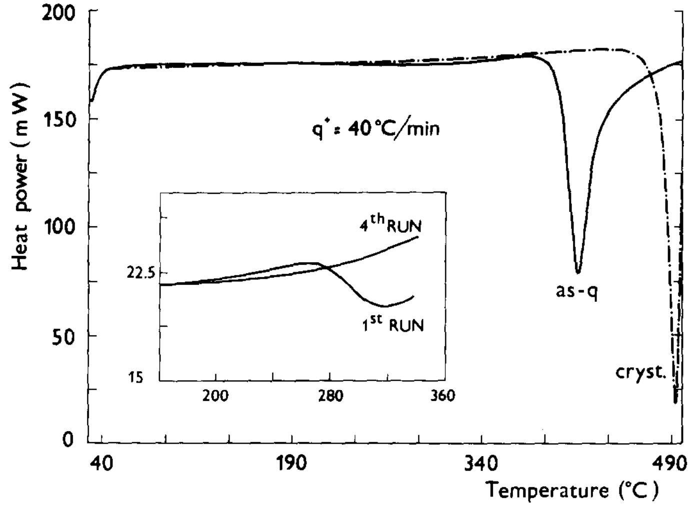

Fig. 1. Typical DSC thermogram of an $Fe_{73}Co_{12}B_{15}$ alloy: ———, the as-quenched sample; –·–·–, the heat-treated sample (previously heated to 500°C to complete the first-stage crystallization). In the detail, the enlarged structural relaxation anomalies in the 1st and the 4th heating runs of a pre-annealed ($T_a = 200°C$, $t_a = 180$ min) glassy sample.

ational events which are significantly less heat-effective than the crystallization ones.)

Various structural relaxation anomalies of metallic glasses can be observed and various methodological procedures for their visualization and evolution can be used. Exothermal and endothermal structural relaxation peaks are generally observed on the DSC thermograms of metallic glasses. Results somewhat comparable with those in the present paper, albeit for a different glass, have been published, e.g. in refs. 1–5. These results and others have been analysed in terms of various theoretical models, as for example the free-volume model [6] or the activation energy spectrum model [7].

This article presents some examples of the variation in the DSC thermograms of $Fe_{73}Co_{12}B_{15}$ glassy samples caused by their heat treatment.

The measured signal in a DSC instrument is proportional to the apparent specific heat of the sample $c_{pM}(T, t)$ [8,9]

$$c_{pM}(T, t) \approx \frac{\Delta J_{(M-R)}(T, t) - \Delta J_{(S-R)}(T, t)}{w m_M} + \frac{m_S}{m_M} c_{pS}(T, t) \qquad (1)$$

where M, S and R denote the measured unknown sample, the measured standard sample having the well-known $c_{pS}(T, t)$ dependence and the reference sample being in the second measuring position in the DSC instrument; ΔJ represents the measured differential DSC signal, w is the heating rate and m is the mass of the sample.

The $c_{pM}(T, t)$ dependence provides information on the following:

(1) The thermodynamical quantities such as excess enthalpy change ΔH_{excess}

$$\Delta H_{\text{excess}} = \int_{T_{\text{init}}}^{T_{\text{final}}} m \Delta c_{pM}(T, t)\, \mathrm{d}T \tag{2}$$

where $\Delta c_{pM}(T, t)$ is the difference between the actual and "relaxed" specific heats $(c_{pM}(T, t) - c_{pM(\text{relaxed})}(T))$ of the sample, and T_{init} and T_{final} are the initial and final temperatures of the structural relaxation anomaly of specific heat.

(2) The kinetics of the associated relaxation processes which determine the thermodynamical state of the sample

$$c_{pM}(T, t) = [1 - \alpha(T, t)]c_{p1}(T) + \alpha(T, t)c_{p2}(T) + \frac{\mathrm{d}\alpha(T, t)}{\mathrm{d}T}\frac{\Delta H_{\text{excess}}}{m_{\text{M}}} \tag{3}$$

where $\alpha(T, t)$ is the degree of transformation fulfilling a reasonable kinetic equation, ΔH_{excess} is the enthalpy change of the transformation (structural relaxation), and $c_{p1}(T)$ and $c_{p2}(T)$ are the specific heats of initial (as-quenched) and final (relaxed) glassy phases.

A complex analysis of the variability of the structural relaxation anomalies of the DSC first-run thermograms of $Fe_{73}Co_{12}B_{15}$ metallic glass was performed. The influence of the various parameters of the heat treatment was investigated. All the results can be generalized. They were interpreted by the distribution of non-linear relaxation (DNLR) model [10,11].

EXPERIMENTAL

Glassy ribbons of $Fe_{73}Co_{12}B_{15}$, 30 μm thick and 10 mm wide, were prepared by the planar flow-casting technique and stored in air at room temperature. Glassy samples of about 50 mg were analysed under a flow of nitrogen gas in the Perkin–Elmer DSC-7 instrument. The as-quenched samples or samples annealed in situ inside the DSC cell were scanned thermally at the heating rate $q^+ = 40°\text{C min}^{-1}$ from 30°C to $T_x - 50°\text{C}$ to avoid the crystallization processes which start at the crystallization temperature, $T_x \approx 350°\text{C}$. The samples were then immediately cooled down to room temperature at a cooling rate $q^- = -200°\text{C min}^{-1}$ and reheated to obtain the "reference" run. This procedure was repeated until no further relaxation evolution of the thermograms could be observed, i.e. until the thermograms had "saturated" for the time scale of the experiment.

The structural relaxation processes in the investigated glassy samples were monitored by the sequence of heat-power DSC continual heating thermograms $\Delta J_{(\text{M}-\text{R})}(T, t)$ or by the sequence of the differences between the two heat-power thermograms which were proportional to the apparent specific heat $\Delta c_{pM}(T, t)$ (in eqn. (1)). The initial temperatures T_{init} and the extremes of the structural relaxation anomalies, $\Delta c_{p\text{min}}$ (in the case of exotherms) or $\Delta c_{p\text{max}}$ (in the case of endotherms), were used to quantify the amount of structural relaxation because it was not possible to measure and calculate the total structural relaxation enthalpy ΔH_{relax} (eqn. (2)) in one measuring run, avoiding the destruction of the glassy sample by its crystallization.

RESULTS

The heat-power DSC thermograms, $\Delta J_{(M-R)}(T, t)$ proportional to the apparent specific heat $c_{pM}(T)$ (eqn. (1)), of $Fe_{73}Co_{12}B_{15}$ glassy ribbon samples were measured during several successive heating runs in the temperature region below crystallization, e.g. from 80 to 340°C. Step by step, the influence of various elementary heat treatments such as the primary rapid quenching of the melt during the technological production of the glassy ribbon, the continual linear heating of a sample, the annealing of a "relaxed" sample or the pre-annealing of an as-quenched sample at an annealing temperature $T_a = 150$, 200 or 250°C for the annealing time $t_a = 180$ min, was determined and eliminated.

The results of this analysis of the elementary heat-treatment influences, as well as of the influence of the more complicated sequential partial linear

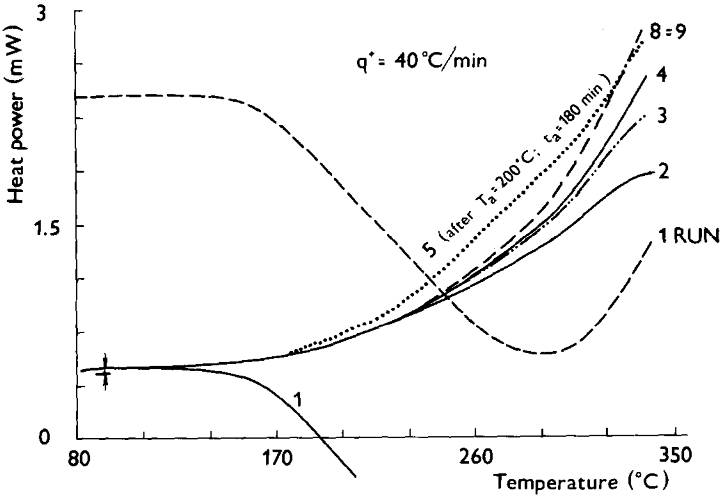

Fig. 2. A succession of DSC heating runs from 30 to 340°C of an as-quenched $Fe_{73}Co_{12}B_{15}$ glassy sample.

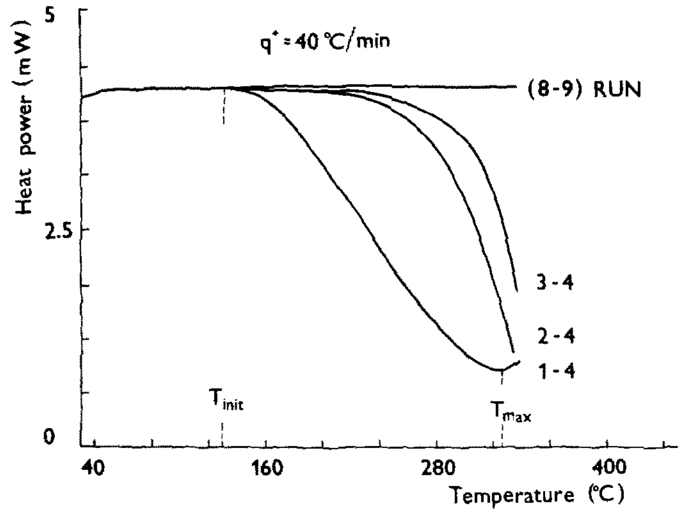

Fig. 3. A succession of subtracted DSC heating runs from Fig. 2 of an as-quenched $Fe_{73}Co_{12}B_{15}$ glassy sample.

heating to 150, 200, 250 and 300°C on the measured thermograms can be summarized as follows:

(1) The thermogram of an as-quenched glassy $Fe_{73}Co_{12}B_{15}$ sample exhibits one big exothermal anomaly $\Delta H_{excess} = \Delta H_{exo} \leqslant 0$, see, for example, the detailed curve 1 in Fig. 2 or subtracted curve 1-4 in Fig. 3.

(2) Upon repeating the heating runs, the relaxation processes in the sample saturate continually. It can be seen that the initial temperature of the structural relaxation exotherm T_{init} rises, and the absolute value of its enthalpy ΔH_{exo} gradually diminishes until it finally disappears after the 7th run (see Figs. 2 and 3). The sample reaches the "relaxed" state when any subsequent continual heating does not change its thermodynamical isoconfigurational state. None of the subsequent thermograms show any structural relaxation anomaly; they are always identical to the 8th run thermogram.

(3) After annealing such a relatively "relaxed" sample at an annealing temperature, $T_a < T_x - 100°C$ for time t_a, an anneal-induced endothermal relaxation anomaly, $\Delta H_{excess} = \Delta H_{endo} \geqslant 0$ (interpreted in ref. 10 as an anisothermal crossover effect), can be observed on the next linear heating-run thermograms (the dotted line on Fig. 2, equivalent to the corresponding subtracted line on Fig. 4). The position of the temperature T_{init} as well as the magnitude of the enthalpy ΔH_{endo} of this relaxation anomaly are strongly dependent on the annealing temperature T_a and time t_a (see Fig. 4 and refs. 2, 10–12). Repeating the heating runs two or three times, the anneal-induced endotherm quickly disappears and the "relaxed" sample state (curve 8 on Fig. 2) is reached again.

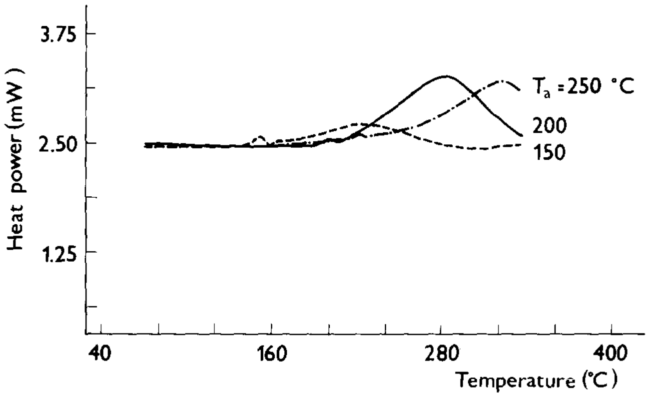

Fig. 4. The temperature of annealing T_a influence on a subtracted relaxation endotherm for a "pre-relaxed" (after the 8th run) $Fe_{73}Co_{12}B_{15}$ glassy sample (T_a as parameter, $t_a = 180$ min).

(4) The "1st run" thermogram of the as-quenched glass can exhibit a complicated behaviour, possessing both the structural relaxation exotherm and one or more than one anneal-induced endotherms, when the sample was first pre-annealed at some temperature T_a (Fig. 5) or when it was sequentially, partially, thermally pre-scanned to various lower final temperatures (Fig. 6). The pre-annealing as well as the sequential partial heating significantly increased T_{init}, diminished the absolute value of ΔH_{exo} and,

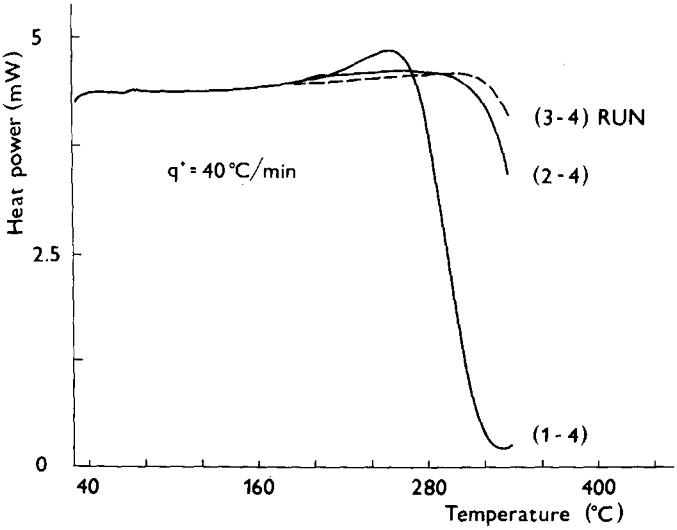

Fig. 5. A succession of subtracted heating runs of a pre-annealed $Fe_{73}Co_{12}B_{15}$ glassy sample ($T_a = 200$°C, $t_a = 180$ min).

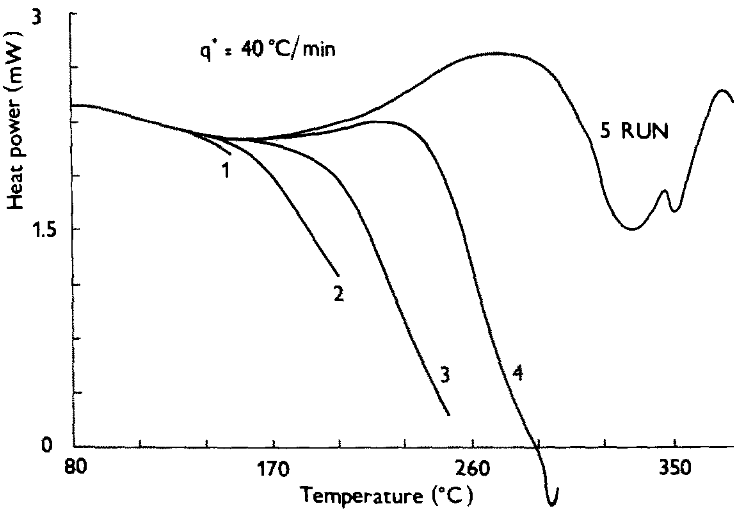

Fig. 6. A succession of partial heating runs of an as-quenched $Fe_{73}Co_{12}B_{15}$ glassy sample.

equivalent to the annealing (analysed below), induced and governed a superimposed relaxation endotherm ΔH_{endo}. During the subsequent runs, the relaxation exotherm and endotherm both disappear.

(5) Structural relaxation processes in the investigated glassy ribbons, being kinetic processes, are related to the measuring regime. Therefore, the behaviour of the structural relaxation anomalies of $c_{pM}(T)$ is strongly affected by the heating rate q^+: the higher the q^+ the higher the absolute value of Δc_{pmin}, and T_{init} also changes measurably (Fig. 7).

BASES OF THE DNLR MODEL

Using a thermodynamic point-of-view developed elsewhere [10,11], we can try to explain these experiments.

Following the approach, called the DNLR (distribution of non-linear relaxation) model, we can consider the glass as a frozen-in system. The freezing is induced by a quick change of the externally applied temperature. Thus, to describe such a perturbation it is possible to assume the existence of successive infinitesimal steps. Each step corresponds to two types of contributions (Fig. 8): a reversible one related to the frozen-in state of the initial configuration (without dissipation or having a zero entropy production $\Delta_i S = 0$) (—); and an irreversible one related to the recovery of the new equilibrium properties (dissipation processes or a non-zero entropy production (|).

If we follow any property $P(T, t)$, its departure from equilibrium at each time t is

$$\delta(T, t) = P(T, t) - P_{(eq)}(T, \infty) \qquad (4)$$

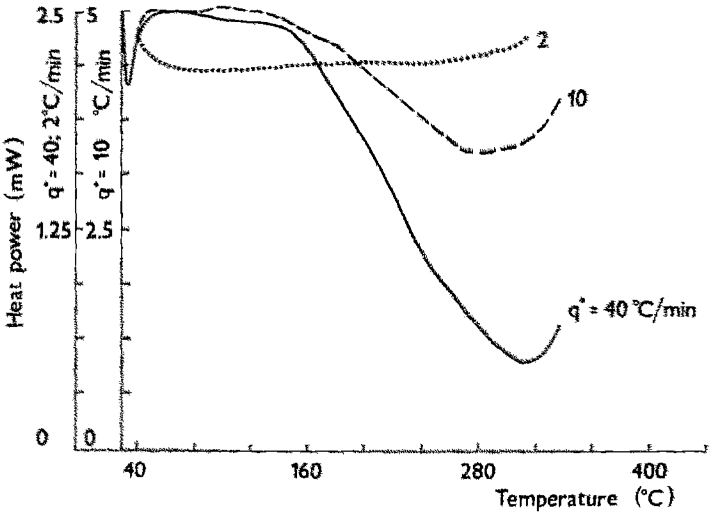

Fig. 7. The influence of the heating rate q^+ on the relaxation exotherm of an as-quenched $Fe_{73}Co_{12}B_{15}$ glassy sample (q^+ as a parameter).

Thus, taking into account the preceding considerations

$$\frac{d[\delta(T,t)]}{dt} = \frac{\partial[\delta(T,t)]}{\partial T}\frac{dT}{dt} - \frac{\delta(T,t)}{\tau_{\text{eff}}} \tag{5}$$

The first term on the right side induces the reversible contributions related to the temperature change, with

$$\delta(T) = P_{(g)}(T) - P_{(eq)}(T) \tag{6}$$

where $P_{(g)}$ represents the property P of the sample with the frozen-in configuration. The second term accounts for the dissipation effects (entropy production) and τ_{eff} is the effective relaxation time of the recovery.

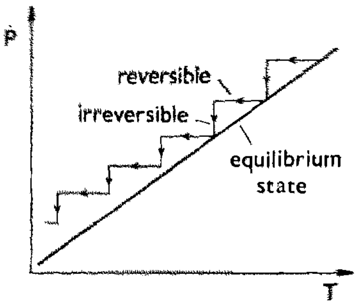

Fig. 8. A qualitative scheme explaining the two types of idealized evolution of the property P during cooling.

If we assume a distribution of some processes acting in the recoverable part of the structural relaxation, we can write

$$1/\tau_{\text{eff}}(t) = \sum_j g_j(t)/\tau_j(t) \tag{7}$$

where g_j represents the weight of the jth process of the total recovery.

Near the equilibrium, in the irreversible linear range, it is possible to show that we can always assume uncoupled processes [13] for each isotherm and even for anisotherms for a large variety of materials and for many properties [11]. If we assume the origin of the multiplicity of processes in thermal fluctuations, it is possible to propose a universal shape for the spectrum $g_{j(\text{eq})}(\tau_{j(\text{eq})})$

$$g_{j(\text{eq})} = B\tau_{j(\text{eq})}^{1/2} \tag{8}$$

$$\sum_j g_{j(\text{eq})} = 1 \tag{9}$$

where B is a constant.

Using the assumption of activated processes with an activation enthalpy ΔH^+ and activation entropies ΔS_j^+, we obtain

$$\tau_{j(\text{eq})}(T) = (h/(kT)) \exp(\Delta H^+/(RT)) \exp(-\Delta S_j^+/R) \tag{10}$$

Thus the physical origin of the spectrum is only configurational; such an assumption is verified by the existence of a "universal isothermal master curve" to describe recoveries [11].

In fact the irreversible linear range corresponds only to small departures from the equilibrium but such conditions can be used as a starting point in the solution of the differential equation, eqn. (5).

For large departures from the equilibrium, the DNLR model introduces some correlation effects between the processes and allows us to write

$$\tau_j(T, t) = \tau_{j(\text{eq})}(T) \exp(K\delta(T, t)/(RT)) \tag{11}$$

where K is the non-linear factor corresponding to the first-order term of the expansion of the free energy with respect to the actual state of the material [10].

Thus if we know the physical parameters characterizing the material properties, ΔH^+, ΔS_j^+, K and $\partial[P_{(q)}(T) - P_{(\text{eq})}(T)]/\partial T$, we can simulate every history for a given initial spectrum $g_j(\tau_j)$. We have verified [11] that for a large width of a spectrum (about 6 decads) and for several processes ($n > 10$), the recovery curve $P(T, t)$ can be "masterized" on a single curve after an adapted reduction of the scales. So it is sufficient to know just a single value of ΔS_j^+, for example ΔS_{min}^+, rather than all the ΔS_j^+ values.

INTERPRETATION AND CONCLUSION

We have shown the variability of the "1st run" exothermal relaxation effect ΔH_{exo} of an as-quenched metallic glassy sample. The connection between the complex thermal history of the sample and the shape of the measured structural relaxation anomalies was demonstrated.

All these phenomena may be generalized for glassy materials and they can be exploited theoretically by the DNLR model.

For example we can compare the shape of the successive runs of an as-quenched sample (Fig. 3) with the qualitatively predicted exothermal effects obtained by simulations (Fig. 9).

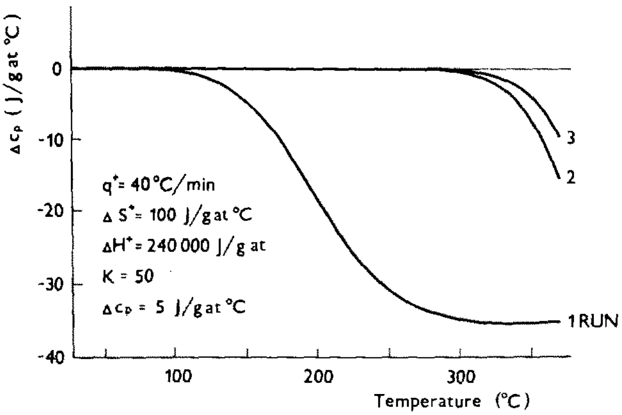

Fig. 9. The simulation of successive heating runs ($q^+ = 40°C\ min^{-1}$) of an as-quenched sample ($q^- = -10^{6\circ}C\ s^{-1}$) using the DNLR model.

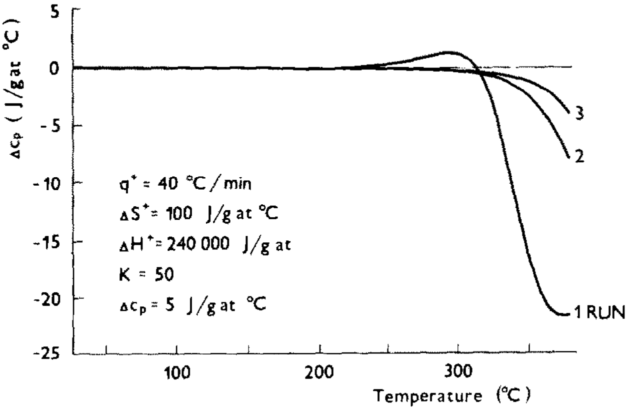

Fig. 10. The simulation of successive heating runs ($q^+ = 40°C\ min^{-1}$) of an as-quenched ($q^- = -10^{6\circ}C\ s^{-1}$) and pre-annealed ($T_a = 180°C$, $t_a = 160$ min) sample using the DNLR model.

In another way it is possible to predict the correct anisothermal crossover effects of pre-annealed samples (Fig. 10) and to compare these with measurements (Fig. 5).

Note that the qualitative simulations presented above (Figs. 9 and 10) use the same values for the model parameters, only the thermal histories are changed.

REMARKS

The adequacy, constancy and reality of the terms in this article, such as "initial temperature" T_{init} or the "relaxed sample", are relative to the real time scale. The glassy material relaxes at every temperature. The rate of the relaxation processes and the measured relaxation effects are related to the activation free enthalpy of the structural relaxation ΔG^{+}, to the non-linear effects characterized by K, to the measuring temperature T and to the corresponding coupling functions.

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