Determination of the fictive temperature for a hyperquenched glass

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Abstract

Based on heat capacity measurements, we propose a simple approach to determine the fictive temperature (T_f) of a hyperquenched glass. The recovered enthalpy of heating is estimated, which equals the released amount of the excess inherent structure energy stored in the glass. The hyperquenching is reached by means of the fiber spinning. We analyze relationships between the released enthalpy, changes in the internal energy, and changes in the configurational entropy. © 2002 Published by Elsevier Science B.V.

1. Introduction

The fictive temperature (T_f) of a glass is the temperature, at which the structure of an equilibrium liquid is frozen-in. T_f is important for the glass science and technology because mechanical and optical properties of a glass strongly depend on thermal pre-history and fictive temperature [1]. The microstructure, relaxation behavior and physical properties of hyperquenched (rapidly cooled) glasses substantially differ from those of a normally cooled glass [2–6], even if the substances have the same chemical composition. The term 'normally cooled glass' refers here to 'glass cooled with a rate of 0.167 K/s (10 K/min)'. The cooling rate is a deciding factor in determining T_f.

An approach for determining T_f of glass was first proposed by Moynihan [7]. This approach is

used for the determination of T_f of slowly cooled glass at low heating rates during the DSC measurement. This approach is, however, not suitable for the determination of T_f of a glass subjected to hyperquenching (e.g. 10^6 K/s). This is because the dependence of the heat capacity (C_p) of a fiber on temperature is rather different from that of a bulk glass at normal cooling (e.g., 0.167 K/s). To obtain the same C_p curve of a fiber as that of a bulk glass, a heating rate for calorimetric measurement is required to coincide with the rate of cooling of a fiber at the stage of its forming. Then T_f can be determined by using Moynihan's approach [7]. Such a calorimetric measurement is not easy, because the heating time required is so short that it is far beyond the experimental time window of a conventional calorimeter. Furthermore, a combined TN [8,9] – KWW [10,11] – AG [12] model was successfully used to fit C_p data of fibers cooled at a normal rate, but failed to fit those of rapidly cooled fibers [13]. In terms of that model, T_f of rapidly cooled fibers could not be determined

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accurately. Later on, a thermorheologically complex (TC) model was proposed [14], which successfully accounts for the structural relaxation and determines T_f of a rapidly cooled fiber. However, it is still not an easy task to use the TC model to determine T_f due to the fact that three adjustable and two dependent parameters are required for applying that model. In this Letter, we report a simple area-matching method for determining the fictive temperature of a hyperquenched glass. We also demonstrate thermodynamic grounds for the derivation of this method.

2. Experimental

Hyperquenching (about 10^6 K/s) was achieved by means of fiber spinning. Fibers were drawn and hyperquenched from a basalt-like glass melt with the composition: 49.3 SiO_2, 15.6 Al_2O_3, 1.8 TiO_2, 11.7 FeO, 10.4 CaO, 6.6 MgO, 3.9 Na_2O, and 0.7 K_2O (wt%) in the temperature range from 1473 to 1573 K by using a cascade technique. The average diameter of the fibers is 3.5 μm.

The heat capacity of the fibers was measured by using a differential scanning calorimeter (DSC) Netzsch STA 449C. The fibers were placed into a platinum crucible situated on a sample holder of the DSC at room temperature. The fibers were heated to $T = 1013$ K and, afterwards cooled to room temperature. Both the heating and cooling rate, were 0.167 K/s. To determine the heat capacity (C_p) of the fibers, both the baseline (blank) and the reference sample (Sapphire) were measured. The fibers were subjected to two runs of upscans.

3. Results and discussion

Fig. 1 shows the heat capacity curves obtained from the first and second upscans, which are denominated C_{p1} and C_{p2}, respectively. The C_{p1} curve reflects thermal and mechanical history of the fibers determined by the forming process. The C_{p2} curve reflects the thermal history of the fibers determined by the cooling rate of 0.167 K/s. The difference between C_{p2} and C_{p1} equals the enthalpy
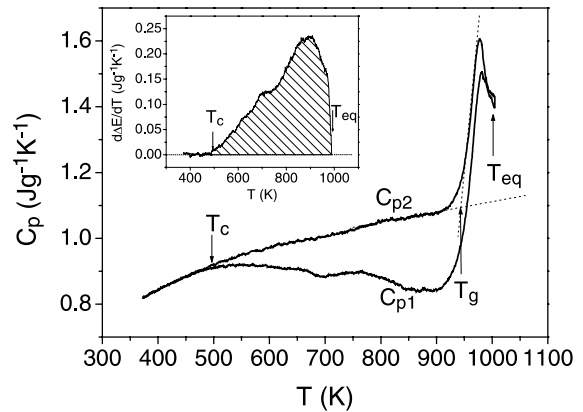

Fig. 1. The heat capacity curves of rapidly cooled glass fibers (the composition is given in Section 2). C_{p1} is the heat capacity curve measured during the first upscan of DSC measurements and C_{p2} is that measured during the second upscan. The inset shows the rate of energy release from the fibers as a function of temperature. T_c stands for the temperature, at which the release of enthalpy starts, and T_{eq} is the temperature, at which $C_{p2} = C_{p1}$.

released (per Kelvin per one gram): $(\partial\Delta H/\partial T)_p = C_{p2} - C_{p1}$, where ΔH stands for the enthalpy released from the fibers up to a temperature T, and the subscript p means ambient pressure. ΔH is the difference between the enthalpy H_2 measured in the second upscan, and the enthalpy H_1 in the first upscan: $\Delta H = H_2 - H_1$. In what follows, $(\partial\Delta H/\partial T)_p$ is written as $d\Delta H/dT$. The inset of Fig. 1 shows $d\Delta H/dT$ as a function of temperature. The total enthalpy released during the entire heating process, ΔH_{tot}, is calculated by the following equation

$$\Delta H_{tot} = \int_{T_c}^{T_{eq}} \frac{d\Delta H}{dT} dT = \int_{T_c}^{T_{eq}} (C_{p2} - C_{p1}) dT, \quad (1)$$

where T_c is the onset temperature, at which the release of enthalpy starts, and T_{eq} is the temperature, at which $C_{p2} = C_{p1}$, as shown in Fig. 1. This equation means that ΔH_{tot} is the area between the $d\Delta H/dT$ curve and the zero-line as shown in the inset of Fig. 1 or the area between the C_{p2} and C_{p1} curves. After the first upscan, the enthalpy recovers to the level typical of fibers cooled at 0.167 K/s, ΔH_{tot}. The recovered enthalpy can be treated as the total excess internal energy (ΔE_{tot}) stored during hyperquenching over that of the fibers cooled at

0.167 K/s. A reason for this is that the melt is incompressible under ambient pressure, so that the pressure–volume work can be neglected, which means that the relation $\Delta H_{tot} \approx \Delta E_{tot}$. The hatched area in the inset of Fig. 1 represents ΔE_{tot} as well. $\Delta E/\mathrm{d}T$ is considered as the rate of release of the excess energy from the fibers, because it indicates the amount of energy released from 1-g fibers by raising one Kelvin.

The heat capacities of the fibers measured at the second upscan and that of the first one merge at the temperature T_{eq}, at which the melt returns to internal equilibrium, i.e. $C_{p2} = C_{p1}$ (see Fig. 1). Therefore, the change of the Helmholtz energy ($\mathrm{d}A$) due to a temperature increment ($\mathrm{d}T$) should be minimized. At $T > T_{eq}$, we have the relation

$$\mathrm{d}A = \mathrm{d}E - T\mathrm{d}S = 0, \qquad (2)$$

where $\mathrm{d}E$ and $\mathrm{d}S$ are the increments of internal energy and entropy induced by a temperature increment $\mathrm{d}T$. According to [15,16], $\mathrm{d}E = \mathrm{d}E_{is} + \mathrm{d}E_{har} + \mathrm{d}E_{anh}$, where $\mathrm{d}E_{is}$ is the increment of the average inherent structure energy, and $\mathrm{d}E_{har}$ and $\mathrm{d}E_{anh}$ are the average harmonic and the anharmonic contributions to $\mathrm{d}E$, respectively, due to thermal excitations about the inherent structure. $\mathrm{d}S$ in Eq. (2) originates from vibrational and configurational contributions, $\mathrm{d}S_v$ and $\mathrm{d}S_c$. The increment of the average inherent structure energy $\mathrm{d}E_{is}$ is balanced by the increment of configurational entropy, $T\mathrm{d}S_c$, i.e.

$$\mathrm{d}E_{is} = T\mathrm{d}S_c = (C_{pl} - C_{pg})\mathrm{d}T, \qquad (3)$$

where C_{pl} and C_{pg} are the liquid and glass heat capacities. In contrast, the increments of the harmonic and anharmonic energies are balanced by that of the vibrational entropy.

ΔE_{is} is the integral of the average inherent structure energy of fibers from T_g to T_f. When the fibers are subjected to hyperquenching, ΔE_{is} is frozen-in at T_f. It is expected that ΔE_{is} should be equal to the total enthalpy (ΔH_{tot}) released from the fibers during the first upscan up to T_{eq}, hence to the total excess (ΔE_{tot}), since the excess vibrational enthalpy is not frozen at T_f during quenching.

Based on Eqs. (1) and (3) and the relations $\Delta H_{tot} \approx \Delta E_{tot} = \Delta E_{is}$, we have the following relation:

$$\int_{T_c}^{T_{eq}} (C_{p2} - C_{p1})\mathrm{d}T = \int_{T_g}^{T_f} (C_{pl} - C_{pg})\mathrm{d}T. \qquad (4)$$

The left-hand side of Eq. (4) can be obtained by calculating the area covered by C_{p2} and C_{p1} curves as shown in Fig. 2. This equation, together with the relations $\Delta H_{tot} \approx \Delta E_{tot} = \Delta E_{is}$, provides a physical basis, on which the area A can match the area B (see Fig. 2). The latter is represented by the right-hand side of Eq. (4), while T_f is determined by the right borderline of the area B.

The accuracy of determining T_f depends on the C_{pl} and C_{pg} values. C_{pl} can be obtained directly from the DSC measurements in the temperature range between T_{eq} and T_f. To obtain C_{pg} values above T_g, the following equation is used which describes the temperature dependence of C_{pg} [17]:

$$C_{pg} = a + bT + c/T^2 + d/T^{0.5}, \qquad (5)$$

where a, b, c and d are constants. In this study, $a = 0.56$, $b = 0.00037$, $c = -33\,342$ and $d = 6.95$, which are obtained from a best fit of Eq. (5) to the measured C_{pg} values. Thus, T_f can be estimated by substituting Eq. (5) into Eq. (4) and using the measured C_{pl} values. However, to resolve Eq. (4) and, hence, to determine T_f, the simplest ways is to find the right borderline by matching the areas A and B as shown in Fig. 2. The lower borderline of the area B is obtained by extrapolating the
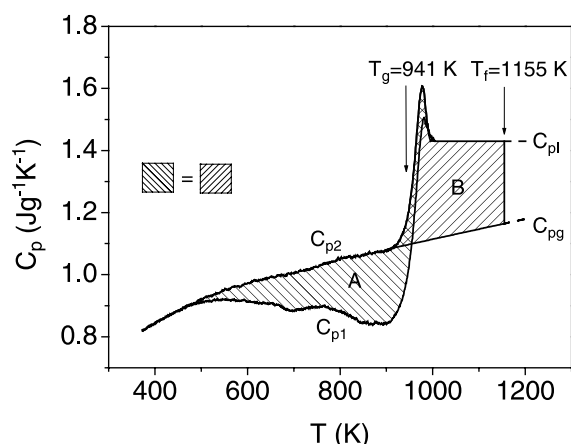

Fig. 2. Determination of fictive temperature (T_f) by using the energy-matching method. The heating and cooling rates in DSC measurements are 0.167 K/s.

experimental C_{pg} with the help of Eq. (5). In this manner, T_f of the fibers studied in this paper is found to be 1155 K, i.e. $T_f = 1.23T_g$.

A rough estimate of T_f is based on the Adam–Gibbs assumption that $C_{pl} - C_{pg}$ is constant [12]. Thus, Eq. (4) is turned into the expression $\Delta E_{tot} = (T_f - T_g)(C_{pl} - C_{pg})$, from which T_f can be calculated

$$T_f = \Delta E_{tot}/(C_{pl} - C_{pg}) + T_g. \tag{6}$$

From Fig. 1 and Eq. (6), T_f is found to be 1135 K, which is 20 K lower than the one calculated from Eqs. (4) and (5). This means that Eq. (6) can be used as an approximate alternative to determine T_f of hyquenched glasses.

It should be mentioned that ΔE_{tot} of the fibers is calculated as the excess energy compared to that of the glass cooled at 0.167 K/s. However, the maximum excess energy (ΔE_{max}) should be estimated over that of a 'ideal' glass

$$\Delta E_{max} = \int_{T_K}^{T_f} (C_{pl} - C_{pg}) \mathrm{d}T, \tag{7}$$

where T_K is the Kauzmann temperature [18]. Below T_k, the excess configurational entropy vanishes for the 'ideal glass' [18,19]. In reality, it is impossible to measure ΔE_{max}, because the corresponding C_p curves should be measured at an extremely low heating rate, which is not available within the experimental time window. But if ΔE_{max} were available, from it we would get the same T_f as that obtained in the present work. T_f of the fibers depends on the cooling rate used in fiber forming only, not on the cooling rate of the fibers used for the DSC downscan.

Fig. 3 is the high temperature region of Fig. 2. It shows that besides T_f, T_g of the fibers relaxed with the heating rate 0.167 K/s is found to be 941 K by using the area-matching method proposed in this letter. The so-obtained T_g value coincides with that determined by the intersection point between the extrapolated line of the C_{pg} curve (measured in the second run) and the maximum tangent of the rapid rising part of the C_p curve, as shown in Fig. 1. For the latter method, the C_p curve obtained in the second run should be used, since it reflects the near-equilibrium conditions. As demonstrated in Fig. 3, the way to find T_g of the glass cooled with a
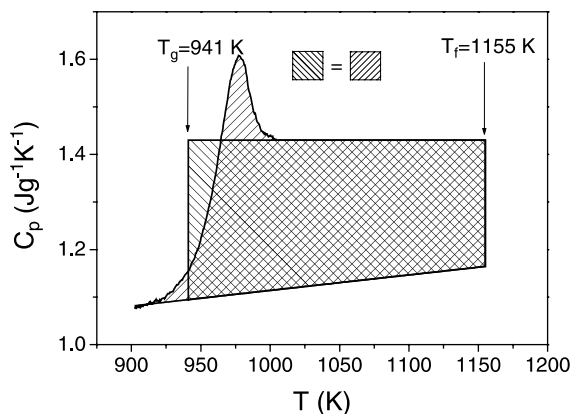

Fig. 3. The high temperature region of Fig. 2 which includes the left borderline (the line for determining T_g) and the right borderline (the line for determining T_f). The way of placing the left borderline was described in [3].

cooling rate lying in the experimental time window is identical to that proposed in [7].

T_f determined here is the average fictive temperature of the fibers for the following reasons. First, diameters of the fibers are not constant and they are distributed in a certain range. Under comparable drawing conditions, the higher is the drawing speed, the thinner the fiber is, and the higher the cooling rate is. Hence, the fibers with different diameters have different fictive temperatures. Second, there could be a small fictive temperature gradient in the cross-section of the fibers. This gradient increases with increasing diameter of the fiber, because the time of heat transfer from the fiber core to its surface increases with diameter of the fiber.

4. Conclusions

A method is proposed to determine the fictive temperature of a hyperquenched glass. The excess energy stored in the glass due to hyperquenching is determined from two rounds of DSC upscan. This energy equals the increase in the average inherent structure energy at heating from T_g to T_f, which is accompanied by a change in the configurational entropy. This correlation makes it possible to match area A enclosed by C_{pl} and C_{p2} curves into

the area B enclosed by C_{pl} and C_{pg} curves. In this manner, the right borderline is found, which coincides with T_f.

Acknowledgements

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