Thermochimica Acta, 63 (1983) 255–260 255
Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

Note

FREE VOLUME DRIVEN CRYSTALLIZATION IN METALLIC GLASSES

J.M. BARANDIARÁN, I. TELLERIA, A. RIVACOBA

Departamento de Física, Facultad de Ciencias Químicas, Universidad del Pais Vasco, Alza, San Sebastián (Spain)

J. COLMENERO

Escuela Universitaria del Profesorado de E.G.B., Universidad del Pais Vasco, San Sebastián (Spain)

(Received 23 September 1982)

The crystallization of glasses when heating through the glass transition temperature is usually described by means of the Avrami equation

$$\xi = 1 - \exp[-(Kt)^n] \tag{1}$$

giving the transformed fraction ξ at time t and constant temperature (K is the rate constant and n is the Avrami index).

Expressions for the transformed fraction and its derivative can be obtained by heating at a constant rate R as [1,2]

$$\xi = 1 - \exp\left\{ -\left(1/R \int_{T_1}^{T_2} K(T)\,\mathrm{d}T \right)^n \right\} \tag{2}$$

$$\frac{\mathrm{d}\xi}{\mathrm{d}T} = n[K(T)/R](1-\xi)\left\{\ln(1-\xi)^{-1}\right\}^{(n-1)/n} \tag{3}$$

Rate constants K for these processes are usually taken as a combination of homogeneous nucleation and growth velocities I and U, respectively. The expressions commonly used for I and U are, with some approximations [3]

$$I = \frac{K_\mathrm{B} T N_\mathrm{v}}{3\pi a_0^3 \eta} \exp\left(-\frac{1.07}{\Delta T_\mathrm{r}^2 T_\mathrm{r}^3} \right) \tag{4}$$

and

$$U = \frac{K_\mathrm{B} T}{3\pi a_0^2 \eta} \left[1 - \exp\left(-\frac{\Delta T_\mathrm{r} \Delta H_\mathrm{m}}{K_\mathrm{B} T} \right) \right] \tag{5}$$

Thus the rate constant K depends on a great number of parameters (see ref. 3 for a complete description) and approximate expressions valid in a narrow temperature range are used to fit the experimental data mainly in the

0040-6031/83/$03.00

crystallization from the glass state, the Arrhenius expression being the most common.

In the temperature range at which crystallization occurs the viscosity is the most important factor affecting the nucleation and growth velocities, I and U. Therefore, expressions (4) and (5) can be approximated in this range by

$$I \simeq \frac{I_0}{\eta(T)} \text{ and } U \simeq \frac{U_0}{\eta(T)}$$

with I_0 and U_0 constants, and if $n = 4$ as mentioned above, rate constant K is of the form

$$K \simeq \frac{C}{\eta(T)} \tag{6}$$

with C a characteristic constant.

Two types of behaviour of η with temperature are usually found in glasses.

(a) *Arrhenius viscosities*

$$\eta \simeq \eta_0 \exp\left(\frac{E}{K_B T}\right) \tag{7}$$

where E is the activation energy and is typical of SiO_2 and other tetrahedrally coordinated glasses.

(b) *Vogel–Faulcher expressions*

$$\eta \simeq \eta_0 \exp\left(\frac{1}{\alpha_f (T - T_0)}\right) \tag{8}$$

where η_0 is a pre-exponential factor, α_f is the free volume expansion coefficient, and T_0 is the ideal liquid–glass transition temperature, and all are associated with polymeric and metallic glasses. In practice, however, only Arrhenius constants

$$K = K_{0A} \exp\left(-\frac{E}{K_B T}\right) \tag{9}$$

with $K_{0A} = C/\eta_0$ are used to fit the experimental data of crystallization processes in all kinds of glasses [4,5] because it is difficult to distinguish between the two expressions (7) and (8) in the narrow temperature range for the crystallization. This procedure leads to extremely high values for K_0 if the actual behaviour of K is given by a Vogel–Faulcher expression. In this note we propose a revision of the crystallization data in terms of Vogel–Faulcher expressions for the rate constant and give a method for obtaining the kinetic parameters K_{0v}, α_f and T_0' (see below) from experimental DSC data.

In order to check the statements mentioned above we have determined as an example the behaviour of

$$K = (\pi/3)^{1/4} I^{1/4} U^{3/4}$$

in the crystallization temperature range for a standard metallic glass with parameters $N_{0v} = 8 \times 10^{22}$ cm^{-3}; $a_0 = 2.5$ Å; $\Delta H_m/R = 1152$ K; $T_m = 1200$ K, and viscosity (in poise) given by

$$\eta(T) = 4.86 \times 10^{-4} \exp\frac{3312.6}{(T-575)}$$

In the range of interest (700–735 K) the value of C can be approximated by a mean value of 1.7×10^{-5}, giving for K_{0v} a value of 3.5×10^{8} in the expression

$$K(T) = K_{0v} \exp\left(\frac{1}{\alpha_f (T - T_0)}\right) \tag{10}$$

The fitting between this approximate expression and the starting one is shown in Fig. 1. If an Arrhenius behaviour is supposed the fit is only good in

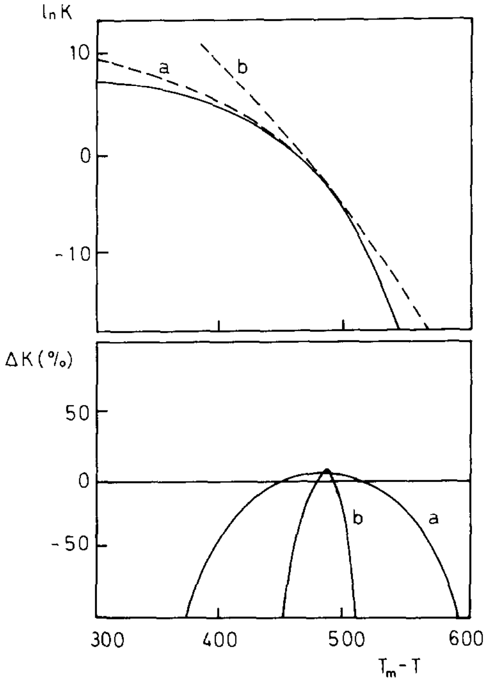

Fig. 1. Comparison between a theoretical rate constant K_t (full line) and Vogel–Faulcher (a) and Arrhenius (b) approximations K_a. The lower part shows the relative difference $(K_t - K_a)/K_t$ for the two cases.

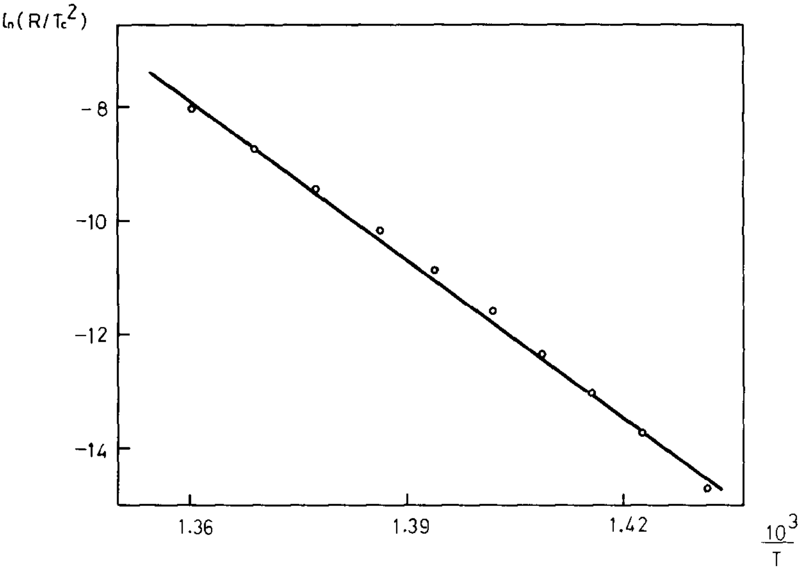

Fig. 2. Kissinger plot for the standard glass of Fig. 1 showing the curvature of the line.

a narrow temperature range, giving an activation energy of 7.5 eV as well as a value for K_{0A} of 2×10^{51}.

DSC crystallization peaks can be simulated in a computer by means of eqns. (2) and (3) with heating rates between 0.5 and 160 K min^{-1} so that the temperature of the maximum, T_c, lies between 700 and 735 K.

A Kissinger plot, $\ln(R/T_c^2)$ vs. $1/T$, of these DSC simulated peaks can be fitted to an Arrhenius expression with values of 7.9 eV for the activation energy, 3×10^{50} for K_{0A} and a regression coefficient of 0.996. However, a slight curvature is apparent in the plot (see Fig. 2), indicating some systematic deviation. This, together with the unrealistic value for K_{0A}, can be taken as evidence for Vogel–Faulcher behaviour.

OBTENTION OF VOGEL–FAULCHER PARAMETERS FROM EXPERIMENTAL DATA

In order to obtain the Vogel–Faulcher parameters, K_{0v}, α_f and T_0, we have developed a computer program which fits the temperature of the maximum of the DSC peaks for different heating rates to an expression of the form

$$\ln\frac{(T_c - T_0)^2}{R} = \frac{1}{\alpha_f(T_c - T_0)} + \ln\{1 - 2\alpha_f(T_c - T_0)\} + \text{cte} \qquad (11)$$

which can be viewed as a generalization of the Kissinger formula. The program is based on the Newton–Kantorovich method and found the set of values of T_0, α_f and K_{0v} that minimizes the standard deviation of the experimental points to expression (11) by means of linear approximation. When applied to the example above it gives the values: $T_0 = 587$ K, $\alpha_f = 4 \times 10^{-4}$ and $K_{0v} = 4 \times 10^7$.

Experimental data for the crystallization of Metglas 2826 from Allied Chemicals have been fitted with this program. Measurements were made on a Perkin-Elmer DSC-2 using samples of about 1 mg, and uncorrected data give $T_0 = 586$ K, $\alpha_f = 1.23 \times 10^{-3}$ and $K_{0v} = 56.7$, while when fitting to an Arrhenius expression $E = 3.9$ eV and $K_{0A} = 10^{28}$ are obtained. If the temperature of the maximum in the DSC peaks is corrected for the temperature lag at different rates using the melt temperature of a Zn standard, the curvature of the Kissinger plot (see Fig. 3) is much lowered but an Arrhenius fit still gives an unrealistic value of $K_{0A} = 3 \times 10^{30}$, E being 4.4 eV, which is evidence for Vogel–Faulcher behaviour. For the corrected data we have obtained $T_0 = 500$ K, $\alpha_f = 2.8 \times 10^{-4}$ and $K_{0v} = 3 \times 10^6$.

Values found in the literature are always obtained from the Arrhenius expression [6,7], giving activation energies of about 4 eV, and no values of K_{0A} are reported. From the published data, however, $K_{0A} = 10^{28}$ can be obtained. On the other hand, values of viscosity reported by Anderson and Lord [8] are consistent with Vogel–Faulcher behaviour, with $T_0 = 575$ K and $\alpha_f = 3 \times 10^{-4}$.

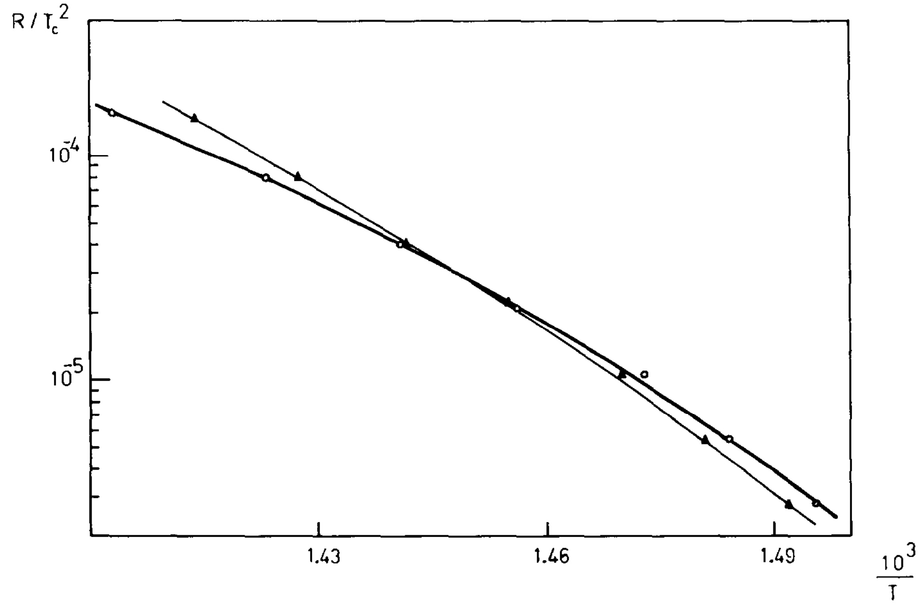

Fig. 3. Kissinger plot for DSC peaks of Metglas 2826. ○, Uncorrected data; ▲, corrected data for the temperature lag.

In conclusion, a more adequate description of the crystallization of this glass, and probably of a great number of metallic glasses would be a Vogel–Faulcher one, so that the mechanism responsible for crystallization is related to a free volume process.

ACKNOWLEDGEMENTS

The authors wish to thank Dr. Largo at the Colegio Universitario de Alava for performing DSC measurements.

REFERENCES

1 H.S. Chen, J. Non-Cryst. Solids, 27 (1978) 257.
2 J. Colmenero and J.M. Barandiarán, J. Non-Cryst. Solids, 30 (1979) 263.
3 H.A. Davies, Phys. Chem. Glasses, 17 (1976) 159.
4 E. Coleman, Mater. Sci. Eng., 23 (1976) 161.
5 J. Colmenero and J.M. Barandiarán, Phys. Status Solidi A, 62 (1980) 323.
6 F.E. Luborsky, Mater. Sci. Eng., 28 (1977) 139.
7 M.G. Scott, J. Mater. Sci., 13 (1978) 291.
8 P.M. Anderson III and A.E. Lord, Jr., J. Non-Cryst. Solids, 37 (1980) 219.