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Thermochimica Acta 404 (2003) 207–211

thermochimica acta

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Applying Kissinger analysis to the glass transition peak in amorphous metals

G. Ruitenberg*

Marnixstraat 135-H, 1015 VL Amsterdam, The Netherlands

Received 21 February 2003; accepted 24 February 2003

Abstract

Some amorphous metals show a glass transition peak in a linear heating differential scanning calorimetry (DSC) experiment before crystallisation occurs. The temperature at which this peak is observed is a function of the heating rate used in the DSC experiment. From this dependence, an effective activation energy can be obtained using Kissinger analysis. The literature suggests that the glass transition is a kinetic phenomenon, caused by the production and annihilation of structural defects. Starting from the differential equation that describes the rate of change of these defects, an analytic expression is derived for this effective activation energy. The energy is found to have two contributions: one corresponds to the migration of structural defects and the other is related to their equilibrium concentration. The analysis shows the relevance of experimentally determining the slope of a Kissinger plot of the glass transition peak in amorphous metals.

PACS: 64.70.Pf; 65.60.+a; 81.70.Pg

Keywords: Kissinger plot; Glass transition; Amorphous metals; Structural defects

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1. Introduction

When an amorphous metal is heated at a constant heating rate in a differential scanning calorimetry (DSC) experiment, the material undergoes structural changes and eventually crystallises. In addition to the large exothermal crystallisation peak, the DSC trace of some metallic glasses shows an endothermic peak before crystallisation occurs: the glass transition peak. This calorimetric glass transition is generally considered to be due to changes in the amorphous structure, which approaches a thermodynamic equilibrium state as the temperature of the system is increased [1–3].

Like the crystallisation peak, the position of the glass transition peak depends on the heating rate [4]. It is, therefore, tempting to make a Kissinger plot [5] of the glass transition peak and calculate an activation energy from the slope. However, whilst this procedure has been shown to yield a physically meaningful activation energy for the crystallisation peak [6,7], there is no a priori reason to believe that this is also the case for the glass transition peak.

In this paper, we make an attempt to resolve the relationship between the slope of a Kissinger plot of the glass transition peak and the parameters that determine the kinetics of the structural changes that underlie this glass transition. The glass transition will be treated in terms of the free volume model [8–11]. This model gives an adequate description of a range of effects related to structural relaxation [12–14].

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* Fax: +31-20-6382543.
E-mail address: gerard_ruitenberg@hotmail.com (G. Ruitenberg).

doi:10.1016/S0040-6031(03)00142-4

2. Theoretical background

In the free volume model, the concentration of structural defects c is related to the reduced free volume x [4] through [11]

$$c = \exp\left(-\frac{1}{x}\right). \tag{1}$$

In equilibrium, the defect concentration depends on temperature T through [11]

$$c_e = \exp\left(-\frac{B}{T - T_o}\right), \tag{2}$$

where $x_e \equiv (T - T_o)/B$ is the equilibrium free volume; T_o and B are constants of unit K. Note that when $T \gg T_o$, Eq. (2) has the mathematical form of a Boltzmann fraction, with $k_B B$ (where k_B is the Boltzmann constant) as the activation energy for the formation of the structural defects. When the defect concentration is not in equilibrium, it will approach the equilibrium value. The rate of change of the defect concentration is in that case equals to [11]

$$\frac{dc}{dt} = -kc(c - c_e). \tag{3}$$

The rate constant k has an Arrhenian temperature dependence [11]:

$$k = k_o \exp\left(-\frac{Q}{k_B T}\right), \tag{4}$$

where Q is the activation energy for the migration of the structural defects and k_o is a constant of unit per second. From Eqs. (1)–(3), it follows that the rate of change of the free volume is given by

$$\frac{dx}{dt}(x, T) = -kx^2(c - c_e). \tag{5}$$

Eq. (5) can be solved numerically to obtain $(dx/dt)(T)$ under linear heating conditions, i.e. $T = \varphi t$, where φ is the heating rate. This is done for $\varphi = 1\,\mathrm{K/s}$, using the values for k_o, Q, B and T_o from Table 1. The free volume at the beginning of the experiment was taken to be $x_o = 0.0315$, a typical value for an annealed amorphous sample [11]. The result is shown in Fig. 1.

According to ref. [15], the DSC signal is described by:

$$\frac{dH}{dt} = \alpha\frac{dx}{dt} + \beta\frac{d\psi}{dt}, \tag{6}$$

where H is the internal free energy of the amorphous structure and ψ is an order parameter that characterises the amount of chemical order in the material; α and β are constants (cf. the Borchard assumption [16,17]). The authors conclude that the basic features of the glass transition are preserved when the changes in chemical order are neglected. Adopting this approximation, we will assume that the DSC signal is proportional to the trace shown in Fig. 1. Thus, the glass transition as observed in a linear heating DSC experiment is treated as a calorimetric effect caused by the annihilation and production of structural defects. The glass transition peak corresponding to Fig. 1 occurs at $T_g = 600\,\mathrm{K}$.

Table 1
List of the parameters that describe the glass transition peak of $Pd_{40}Ni_{40}P_{20}$, as determined by Duine et al. [12]

Parameter (unit)	Value
Q (eV/atom)	1.7
B (K)	6600
T_o (K)	355
k_o (Hz)	3.4×10^{25}

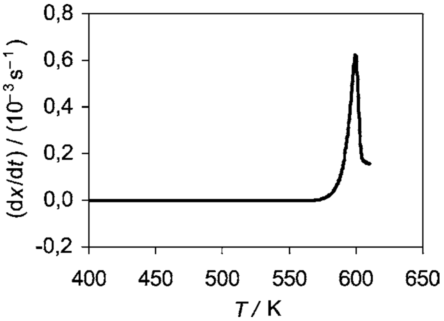

Fig. 1. Plot of dx/dt vs. T, obtained by solving Eq. (5) numerically under linear heating conditions, with a heating rate of $\varphi = 1\,\mathrm{K/s}$ and the free volume in the material prior to the scan equal to $x_o = 0.0315$. The values for k_o, Q, B and T_o are taken from Duine et al. [12] and correspond to $Pd_{40}Ni_{40}P_{20}$.

3. Calculating the slope of the Kissinger plot

3.1. Numerical calculation

We now solve Eq. (5) numerically for different heating rates to obtain T_g as a function of φ. Fig. 2 shows

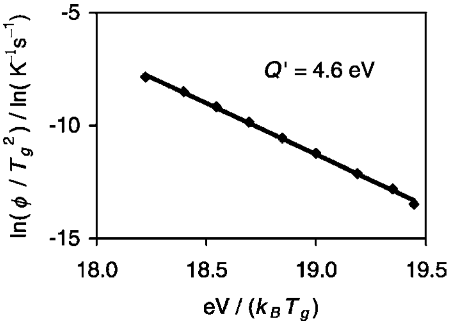

Fig. 2. Kissinger plot of the glass transition peak, obtained from a series of plots as shown in Fig. 1, for heating rates equal to $\varphi = 0.5$, 1, 2, 5, 10, 20, 40, 80 and 160 K/s. A least square fit of a straight line to the data yields a slope of −4.6 eV.

a plot of $\ln(\varphi/T_g^2)$ versus $1/K_B T_g$, a Kissinger plot [5], for the glass transition peak, for heating rates in the range of $\varphi = 0.5$–160 K/s. The plot can be seen to yield a fairly straight line. Fitting a straight line to the data yields a slope of −4.6 eV.

3.2. Approximate analytic expression

In the remainder of this section, we shall attempt to derive an analytic expression for this slope, in terms of the kinetic parameters, k_o, Q, B and T_o. As it stands, Eq. (5) is too complex to handle analytically. Therefore, we start by making two simplifying assumptions. Expanding Eq. (1) around the equilibrium free volume, gives

$$\exp\left(-\frac{1}{x}\right) = \exp\left(-\frac{1}{x_e}\right) + \frac{1}{x_e^2}\exp\left(-\frac{1}{x_e}\right)(x - x_e) + \cdots . \tag{7}$$

3.3. First approximation

Retaining only the first two terms of this expansion and substituting into Eq. (5) yields

$$\frac{dx}{dt} \approx -k\frac{x^2}{x_e^2}(x - x_e)\exp\left(-\frac{1}{x_e}\right) \tag{8}$$

to second order.

3.4. Second approximation

We now use the same idea again to disregard the quadratic terms in Eq. (8) to give

$$\frac{dx}{dt} \approx -k(x - x_e)\exp\left(-\frac{1}{x_e}\right). \tag{9}$$

At the glass transition peak, dx/dt goes through a maximum, so that $d^2x/dt^2 = 0$ at T_g. Taking the derivative of Eq. (9) with respect to time, gives

$$\begin{aligned}\frac{d^2x}{dt^2} = -k_o\Bigg[\frac{dx}{dt} - \frac{dx_e}{dt} + \varphi(x - x_e) \\ \times \left(\frac{Q}{k_B T^2} + \frac{B}{(T - T_o)^2}\right)\Bigg] \\ \times \exp\left(-\frac{Q}{k_B T} - \frac{B}{T - T_o}\right),\end{aligned} \tag{10}$$

where we have used Eq. (4) and the fact that $dx/dt = \varphi dT/dt$ under linear heating conditions. Setting Eq. (10) to zero gives

$$\frac{dx_g}{dt} = \frac{\varphi}{B} - \varphi(x_g - x_e)\left(\frac{Q}{k_B T_g^2} + \frac{B}{(T_g - T_o)^2}\right), \tag{11}$$

where we have used the expression for the equilibrium free volume and defined $x_g \equiv x(T_g)$. Alternatively, the value of dx/dt at T_g follows directly from Eq. (9):

$$\frac{dx_g}{dt} = -k_o(x_g - x_e)\exp\left(-\frac{Q}{k_B T_g} - \frac{B}{T_g - T_o}\right). \tag{12}$$

Equating Eqs. (11) and (12) would give an implicit equation for the glass transition peak.

3.5. Third approximation

The implicit expression for T_g obtained by equating Eqs. (11) and (12) is rather cumbersome, but simplifies greatly when the first term on the r.h.s. of Eq. (11) is ignored. For the parameters corresponding to Fig. 1, this term is indeed much smaller (but not quite negligible) compared to the second term. With this approximation, T_g follows from

$$k_o k_B\left(\frac{T_g^2}{\varphi}\right)\exp\left(-\frac{Q}{k_B T_g} - \frac{B}{T_g - T_o}\right) = Q', \tag{13}$$

where we have defined

$$Q'(T_g) = Q + k_B B \frac{T_g^2}{(T_g - T_o)^2} \tag{14}$$

for convenience. From Eq. (13), it then follows that

$$\ln\left(\frac{\varphi}{T_g^2}\right) = \ln(k_o k_B) - \ln(Q') - \frac{Q}{k_B T_g} - \frac{B}{T_g - T_o} \tag{15}$$

3.6. *Fourth approximation*

Note that the first term on the r.h.s. of Eq. (15) has no temperature dependence and the dependence of the second term on T_g is weak due to the logarithm, since $Q' \gg 1$. Ignoring this dependence on T_g, it is easy to show that taking the derivative with respect to reciprocal temperature finally gives

$$\frac{\partial \ln[\varphi/T_g^2]}{\partial(1/k_B T_g)} = -Q' \tag{16}$$

for the slope of the Kissinger plot. This completes our derivation of the slope of the line in a Kissinger plot of the glass transition peak. Note that, according to Eqs. (14) and (16), the slope of the Kissinger plot shows no implicit dependence on k_o. However, there is an *implicit* dependence because T_g itself depends on k_o, as is shown by Eq. (13).

The accuracy of Eq. (16) is tested by comparing a plot of $Q'(T_g)$ from Eq. (14) with the value for Q' found in Fig. 2. The result is shown in Fig. 3 and shows that Eq. (16) differs from the accurate numerical calculation by as little as 5% on average.

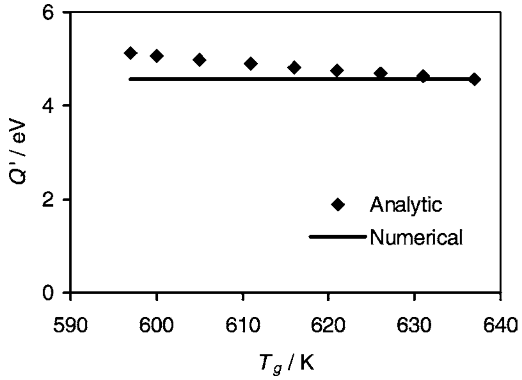

Fig. 3. Comparison of Eq. (14), the analytic expression derived in this paper (shown as full diamonds) and the numerical result, corresponding to Fig. 2, shown as a full line.

4. Discussion

The first two approximations made in deriving Eq. (16) are a good approximation, as by its nature the kinetic glass transition occurs just before the free volume reaches its equilibrium value. Note, however, that the approximation is slightly paradoxical, because when the free volume is exactly in equilibrium, i.e. $x = x_e$, then $dx/dt = 0$ and there is no glass transition at all. Nonetheless, Eq. (9) is a good approximation of Eq. (5). The fact that x_g does not appear in Eq. (13) means that in ignoring the first term in Eq. (11), we have ignored the dependence of T_g on x_o. From the work by Tuinstra et al. [4] it is clear that although the *height* of the glass transition peak strongly depends on x_o, its *position* varies only weakly with x_o. This justifies our rather crude approximation that finally lead to Eq. (13). The fourth and final approximation can be shown to be valid as long as $Q/k_B \gg T_g$ and $B \gg T_g - T_o$, which is satisfied as $Q/k_B = 19,200\,K$, $B = 6600\,K$ and the glass transition temperature is of the order of $T_g = 600\,K$. The fact that these four approximations are accurate is reflected in the fact that Eq. (16) overestimates Q' by as little as 5% on average.

More important than the numerical accuracy of Eq. (16) is the fact that our analytic expression for Q', Eq. (14), reveals the physical significance of this effective activation energy. Eq. (14) shows that there are two contributions to Q'. The first contribution is equal to the activation energy for the migration of a structural defect. This is the energy we would find from the slope of an Arrhenius plot of the rate constant. From Eq. (4), it is easy to show that

$$\frac{\partial \ln k}{\partial(1/k_B T)} = -Q. \tag{17}$$

The second contribution is related to the equilibrium defect concentration. From Eq. (2), it follows that an Arrhenius plot of c_e yields a slope equal to

$$\frac{\partial \ln c_e}{\partial(1/k_B T)} = -k_B B \frac{T^2}{(T - T_o)^2}. \tag{18}$$

The relationship between Eqs. (14) and (16) on the one hand and Eqs. (17) and (18) on the other hand is rather a remarkable result, given the mathematical complexity of the derivation. Note that only when $T \gg T_o$, Eq. (18) yields the same effective activation energy for the formation of a structural defect as the one that appears in Eq. (2), viz. $k_B B$.

Including chemical ordering and using the same parameters as in Table 1, Tuinstra et al. [4] calculated the slope of the Kissinger plot of the glass transition peak and found $Q' = 5.4\,\text{eV}$, which differs significantly from $Q' = 4.6\,\text{eV}$ (see Fig. 2). This suggests that neglecting changes in the chemical order does not give a very accurate expression for Q'. Including the chemical order would presumably add a third term to Eq. (14), characterising the effective contribution of the spectrum of activation energies used to describe the rate of change of the chemical order parameter [15]. Incorporating the second term in Eq. (6), however, would make this problem very difficult to treat analytically. As Eq. (14) gives a good first order approximation for Q', we did not attempt to include chemical ordering.

Tuinstra et al. [4] found that a Kissinger plot of the glass transition peak determined *experimentally* for $Pd_{40}Ni_{40}P_{20}$ does not give a straight line. Due to the thermal lag of the DSC apparatus, the line is curved. Obviously, this thermal lag goes to zero when the heating rate goes to zero. As T_g decreases with decreasing φ, the slope of an experimentally determined Kissinger plot at *high reciprocal temperature* should give the best estimate of Q'. From Fig. 12 in reference [4], it can be shown that $Q' = 5.1\,\text{eV}$ in this limit. This compares well with the numerical value $Q' = 5.4\,\text{eV}$ quoted in the previous paragraph. For this reason, we chose not to model the thermal lag of a DSC apparatus, but rather to compare calculations with experiments in the limit of small heating rate.

5. Summary and conclusions

It is shown that, within the free volume model, the slope of a Kissinger plot of the glass transition peak is approximately equal to

$$Q' = Q + k_B B \frac{T_g^2}{(T_g - T_o)^2}$$

This effective energy is simply the sum of two contributions: the first term on the r.h.s. corresponds to the migration of structural defects and the second is related to their equilibrium concentration. This expression compares very well with an accurate numerical calculation. For small heating rates, φ (i.e. for small T_g or large $1/k_B T_g$), the expression also compares very well with experiment.

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