Journal of Alloys and Compounds 434–435 (2007) 131–134

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Analyses of glass transition phenomena by solving differential equation with delay effect

A. Takeuchi *, A. Inoue

Institute for Materials Research, Tohoku University, Katahira 2-1-1, Aoba-Ku, Sendai 980-8577, Japan

Available online 29 September 2006

Abstract

A linear differential equation for the analyses of glass transition phenomena has been proposed by taking into account the delay effect due to the change in transportation of atoms near the glass transition temperature (T_g). Under the condition maintaining the order of the differential equation as the second, the non-linear differential equation proposed by Van Den Beukel and Sietsma is modified to obtain the analytic solution for a linear equation by introducing the following points: the delay effect which is described with a term of Mackey–Glass model, a concept of effective free volume (x_{fe}^{eff}) and its concentration expression (C_{fe}^{eff}) which correspond to the equilibrium, and an additional term associated with C_{fe}^{eff}. In analyzing the linear equation, Doyle's *p*-function was used for the integral of reaction rate with respect to temperature (T). It is found that the linear equation proposed in the present study can describe the changes in free volume (x) with increasing temperature in the $dx/dT - T$ chart, the sharp increase in free volume at T_g, and over shooting phenomena of free volume slightly above the T_g, as experimentally in thermal analyses for metallic glasses. The linear solution obtained in the present study is of great importance for the analyses of the glass transition because the change in free volume with increasing temperature on heating is described with fundamental functions.

Keywords: Metallic glasses; Amorphous materials; Heat capacity; Computer simulations; Thermal analysis

1. Introduction

Recently, metallic glasses have been studied intensively because of both their scientific and engineering importance as well as the successful fabrication of bulk metallic glasses most of which have been found over the last decade [1]. Metallic glasses are metallic materials exhibiting glass transition. Experimentally, one can rather easily observe glass transition phenomenon as a glass transition temperature by carrying out thermal analyses at constant heating rate. One can also reproduce glass transition computationally by analyzing the change in free volume on heating on the basis of a differential equation proposed by Van Den Beukel and Sietma [2]. This analysis is powerful for understanding the glass transition phenomena of metallic glasses; however, it is difficult to evaluate the effect of the parameters needed for calculations on the glass transition because of the non-linearity of the equation. Accordingly, we have investigated how to obtain the linear solution to the non-linear equation.

In our previous study [4], we succeeded in obtaining an approximate solution to the non-linear equation; however, the solution was not optimal especially regarding physical implication and the overshooting behavior, which is frequently observed in heat capacity measurements for metallic glasses. Therefore, a more accurate solution to the non-linear equation was desirable.

The purpose of this paper is to modify the non-linear equation proposed by Ven Den Beukel and Sietma and to obtain its linear solution as expressed by analytic functions.

2. Calculation methods

Calculations were carried out for (1) the non-linear differential equation proposed by Ven Den Beukel and Sietsma, (2) approximate solution to the non-linear equation derived by Takeuchi and Inoue, and (3) a new linear solution which is proposed in the present study. The details of each calculation methods are described below.

2.1. Van Den Beukel and Sietsma model [2]

Since the detailed calculation method is given in Ref. [2], we only describe the main points here. Eq. (1) is the non-differential

* Corresponding author. Tel.: +81 22 215 2114; fax: +81 22 215 2111.
E-mail address: takeuchi@imr.tohoku.ac.jp (A. Takeuchi).

0925-8388/$ – see front matter
doi:10.1016/j.jallcom.2006.08.154

equation which Beukel and Sietma [3] proposed for describing the behavior of the free volume (x) on heating with respect to time (t)

$$\frac{dC_f}{dt} = -kC_f(C_f - C_{fe}) \tag{1}$$

In Eq. (1), C_f and C_{fe} are the concentration expressions of x and equilibrium free volume (x_{fe}) which are defined as Eqs. (2) and (3), respectively, k the reaction rate with a formula of Arrhenius type expressed as Eq. (4)

$$C_f = \exp\left(-\frac{1}{x}\right) \tag{2}$$

$$C_{fe} = \exp\left(-\frac{1}{x_{eq}}\right) \tag{3}$$

$$k = C_0 \exp\left(-\frac{E}{RT}\right) \tag{4}$$

On the right-hand of Eq. (4) we have the pre-exponential constant (C_0), activation energy (E), gas constant (R) and absolute temperature (T).

The x_{eq} has a relationship with viscosity (η) of metallic glasses, which is frequently expressed by Vogel–Fulcher–Tammann (VFT) equation as in the following equation:

$$\eta = \eta_0 \exp\left(\frac{B}{T - T}\right) \tag{5}$$

where η_0 is the pre-exponential constant, B the constant and T_0 the ideal glass transition temperature. The relationship of η to x_{eq} is more precisely described as in the following equation:

$$x_{eq} = \frac{T - T_0}{B} \tag{6}$$

The numerical analyses of Eq. (1) were first obtained using Eqs. (3) and (6), then C_f calculated on the basis of Eq. (1) as a function of T was converted to x using the inverse relationship expressed by Eq. (2). Finally, plotting dx/dT as a function of T yields a curve similar to that for the heat capacity of the metallic glass [2].

2.2. Approximate solution by Takeuchi and Inoue [3]

As for Section 2.1, the detailed calculation methods are given elsewhere [3] leading to an approximate solution to the non-linear equation as expressed by the following equation:

$$C_f = \frac{C_{f0}}{[1 + (C_0'/E\alpha)C_{f0}\exp(-E/RT)]} + \exp\left(-\frac{B}{T - T_0}\right) \tag{7}$$

where C_{f0} represents the initial concentration expression of free volume using Eq. (2), α the heating rate, C_0' the constant in $C_0' = C_0/T^2$ which was originally used for an integral of k. Eq. (7) was obtained by combining two different linear solutions of free volume on heating: the decrease due to relaxation and increase caused by the approaching of x to x_{eq}.

2.3. Derivation of a linear equation and its solution

In the present study, Doyle's p-function and a function used in the Mackey–Glass model are introduced in order to derive linear differential equation to the non-linear one expressed by Eq. (1). In the following, we describe the details of the functions and the mathematical procedures to derive the solution to the linear equation.

2.3.1. Doyle's p-function [4,5]

In obtaining an analytic solution to Eq. (1), one needs to integrate k with respect to t or T. for the range $t_1 \le t \le t_2$ or $T_1 \le T \le T_2$. Since k with the form of Eq. (4), Arrhenius type, is not an integrable function, we used the Doyle's p-function [5,6] with variable p defined by Eq. (8). In practice, we selected to use Eq. (9) from various p-function because of its simplicity and handling ease in formula

$$\theta = \int_{t_1}^{t_2} \exp\left(-\frac{E}{RT}\right) dt = \frac{E}{\alpha R}\left[p\left(\frac{E}{RT_2}\right) - p\left(\frac{E}{RT_1}\right)\right] \approx \frac{E}{\alpha R} p\left(\frac{E}{RT_2}\right) \tag{8}$$

$$p(y) = \frac{\exp(-y)}{y^2} \tag{9}$$

Eq. (9) is valid for y in the range of $20 < y < 50$. In the case of E with 160 kJ/mol [2], the range of y mentioned above corresponds to $385\,K < T < 962\,K$, which includes the T_g range for metallic glasses.

2.3.2. Mackey–Glass model [6]

Recently, there has been some interest in the differential equations previously factored in the time scale, e.g., the delay effect. For instance, such phenomena can be seen in the delayed logistic equation, which is based on the logistic equation accompanied by a certain time lag. A similar phenomenon takes place in glassy materials near T_g as a result of a sharp increase in viscosity with temperature.

Mackey–Glass model can be used for the analysis of the delay effect. It uses a differential equation expressed by the following equation:

$$\frac{dz}{dt} = -\gamma z(t) + \frac{\beta z(t - \tau)}{1 + [z(t - \tau)^{10}]} \tag{10}$$

where z is the variable, χ and β constants and τ the time lag. In the present study, we focus on the second term on the right-hand of Eq. (10), which is defined as a function of $f(T)$

$$f(T, T_0, \tau, \delta) = \frac{T}{1 + ((T - T_0)/\tau)^{\delta}} \tag{11}$$

where the constant τ has dimension of temperature, and δ the fitting parameter. In the present study, we adapt $f(t)$ for expressing the delay effect as an additional term to Eq. (1), as described below.

2.3.3. Linear equation for describing the behavior of free volume and its solution

We assume here that Eq. (12), which corresponds to Eq. (1), can describe the behavior of free volume on heating

$$\frac{\mathrm{d}C_\mathrm{f}}{\mathrm{d}t} = -k(C_\mathrm{f} - C_\mathrm{fe})^2 + \frac{\mathrm{d}C_\mathrm{fe}^\mathrm{eff}}{\mathrm{d}t} \quad (12)$$

Equation (12) differs from Eq. (1) in the following: in the first term on the right-side $(C_\mathrm{f} - C_\mathrm{fe})^2$ in Eq. (12) is different from $C_\mathrm{f}(C_\mathrm{f} - C_\mathrm{fe})$ in Eq. (1), the order of the exponent with respect to C_f is the second. Also, the right-hand of Eq. (12) has an additional term.

The most important features of Eq. (12) is that it has a form to be solved with analytic functions and $C_\mathrm{f} = C_\mathrm{fe}^\mathrm{eff}$ is a singular solution to Eq. (12). Accordingly, on the basis of a fundamental mathematical technique to solve a differential equation with a singular solution, Eq. (12) can be expresses as Eq. (13) by introducing another variable of u, which has a relationship to C_f as $C_\mathrm{f} = C_\mathrm{fe}^\mathrm{eff} + u$. Here, $C_\mathrm{fe}^\mathrm{eff}$ is assumed to have a form expressed as the following equation:

$$C_\mathrm{fe}^\mathrm{eff} = C_\mathrm{fe}(1 - f(T)) \quad (13)$$

Under the assumptions mentioned above, Eq. (12) can be simplified to Eq. (14)

$$\frac{\mathrm{d}u}{\mathrm{d}t} = -ku^2 \quad (14)$$

and then, Eq. (14) is integrated

$$\int \frac{1}{u^2}\,\mathrm{d}u = -\int k\,\mathrm{d}t \quad (15)$$

For the integral of k with respect to t, we used the p-function described in Section 2.3.1, and the relationship $\mathrm{d}T = \alpha\,\mathrm{d}t$ which is valid for the constant heating rate of α.

Then, the solution of Eq. (15) can be expressed as

$$u = \left[\frac{C_0 RT^2}{\alpha E}\exp\left(-\frac{E}{RT}\right) + \frac{1}{C_\mathrm{init}}\right]^{-1} \quad (16)$$

where C_init is the concentration expression of initial free volume.

From the relationship $C_\mathrm{f} = C_\mathrm{fe}^\mathrm{eff} + u$ mentioned above, one can obtain C_f as

$$C_\mathrm{f} = \left[\frac{C_0 RT^2}{\alpha E}\exp\left(-\frac{E}{RT}\right) + \frac{1}{C_\mathrm{init}}\right]^{-1} + C_\mathrm{fe}^\mathrm{eff} \quad (17)$$

Finally, x is obtainable substituting Eq. (17) into the inverse expression of Eq. (2).

2.4. Calculation conditions

Calculations were conducted for $Pd_{40}Ni_{40}P_{20}$ metallic glass. Table 1 summarizes the calculation conditions.

3. Results and discussion

Fig. 1 shows the calculation results for (a) changes in x with T on heating, (b) the enlarged chart of (a) near the T_g, and (c) change in the value of $\mathrm{d}x/\mathrm{d}T$ with T. In Fig. 1, three kinds of plots for (1) the solution to non-linear equation with computers, (2) the approximate solution and (3) the analytic solution presented in the present study, and two kinds of free volume x_fe, and $x_\mathrm{fe}^\mathrm{eff}$ are plotted. The curves are remain close over a wide range of temperature. However, as shown in Fig. 1(b), these values of x differ at the temperatures near 650 K. In addition, $\mathrm{d}x/\mathrm{d}T$ calculated from Fig. 1(a) differs in curves 1 and 3 versus curve 2 regarding the overshooting phenomenon. From the close similarity of the curves 1 and 3 in Figs. 1(a)–(c), we conclude that analytic solution obtained in the present study is sufficient to reproduce the characteristics of glass transition phenomena. Thus, the difference between the values of $\mathrm{d}x/\mathrm{d}T$ obtained in terms of Eqs. (1) and (17) is sufficiently small for the present purpose.

Table 1
Calculation conditions for the calculation in the present study

Alloy	$Pd_{40}Ni_{40}P_{20}$
Heating rate, α	0.67 K/s
Initial free volume, x_init	0.514
Pre-exponential constant for k, C_0	$2.1 \times 10^{23}\ \mathrm{s}^{-1}$
Delay effect constant, τ	130 K
Fitting parameter, δ	45

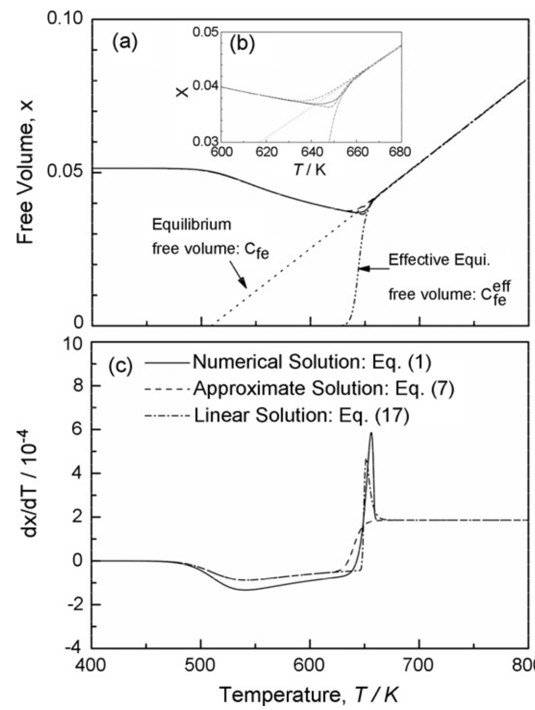

Fig. 1. Calculation results for numerical solution by Eq. (1), approximate solution by Eq. (7) and linear solution by Eq. (17). (a) changes in x with T on heating, (b) the enlarged chart of (a) near T_g, and (c) change in $\mathrm{d}x/\mathrm{d}T$ with T.

4. Conclusions

The linear solution corresponding to the non-linear equation proposed by Beukel and Sietsma has been obtained by giving approximations. With Doyle's p-function and a term due to Mackey–Glass model, changes in free volume (x) with temperature (T) are analyzed. The main results obtained from the present study are as follows.

1. The linear solution plotted in the $dx/dT - T$ chart reproduces the characteristics of the glass transition phenomenon with respect to the following points: sharp increase in free volume at T_g, and over shooting of free volume slightly above the T_g, which both are measurable experimentally on specific heat curves for metallic glasses.
2. The concept of effective-equilibrium free volume introduced in the present study as a delay effect of atomic transportation takes out the non-linearity of the glass transition phenomenon.

References

[1] A. Inoue, Acta Mater. 48 (2000) 279–306.
[2] A. van den Beukel, J. Sietsma, Acta Metall. Mater. 38 (1990) 383–389.
[3] A. Takeuchi, A. Inoue, Mater. Trans. 43 (2002) 1205–1213.
[4] C.D. Doyle, J. Appl. Polym. Sci. 5 (1961) 285–292.
[5] C.D. Doyle, Nature 207 (1965) 290–291.
[6] M.C. Mackey, L. Glass, Science 197 (1977) 287–288.