



Isothermal kinetics approach to investigate the structure relaxation of amorphous alloys



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ABSTRACT

The isothermal relaxation kinetics equations of free volume was derived based on the defect relaxation kinetics expressions. The equations were used to fit the isothermal thermal analysis curves of $\text{Al}_{85}\text{Ni}_8\text{Y}_5\text{Co}_2$ amorphous alloy at different temperature and giving out several crucial parameters associated with the structure relaxation kinetics and metastable structure for example the kinetic coefficient and the fragile strength coefficient. The fitted parameters indicate excellent consistence with the previously reported data, manifesting isothermal thermal analysis based on the kinetics equations presented in this paper is applicable to investigate the metastable structure and structure relaxation of amorphous alloys, providing a novel method more convenient than the traditional viscosity monitoring method.

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1. Introduction

Structure relaxation is a vital topic of amorphous alloy research in that it indicates the irreversible or/and reversible process from a metastable state to another metastable state with a lower energy as always described by the two level model and the energy landscape model in theory [1,2]. For amorphous alloys, a metastable state corresponds to an atomic configuration with certain defect concentration and distribution which would be changed as the amorphous alloy is exposed to energy loading (e.g. thermal annealing, mechanical stress), so inducing the so-called structure relaxation. It was well known that an extensive structure relaxation exists in the wide temperature range from room temperature to the undercooled liquid region of bulk metallic glasses, in a non-isothermal analysis for example the differential scanning calorimetry (DSC).

Experimentally, besides thermal analysis, structure relaxation of amorphous alloys also could be explored through several other methods depending on the monitored structure relevant physical property just like viscosity [3], volume [4], mean interatomic distance [5], stress-strain behavior [6] and enthalpy [7]. However, thermal analysis might be the most convenient and effective route since enthalpy can be easily monitored by thermal analysis

equipments including DSC, leading to that the non-isothermal DSC might have been a requisite method to study amorphous alloy. But unfortunately, the non-isothermal DSC analysis is utilized in most cases to just obtain the phase transition temperature including the glass transition point T_g and the phase transition activation energy E since these parameters could be easily got from the experimental data, up to now. Other important parameters for example the kinetic coefficient k , the ideal glass transition temperature T_0 , the fragility strength coefficient D are not flexibly obtained in the non-isothermal analysis. In this paper, these parameters were proposed can be obtained by simple fitting the isothermal structure relaxation data obtained through thermal analysis.

Theoretically, the parameters mentioned above including the activation energy E are introduced through the famous free volume model [8]. Free volume model indicates that the structure relaxation of amorphous materials is a process of free volume defects generation and annihilation, and the corresponding kinetics could be generally formulated as $\dot{C} = f(k, C)$, where C is defect concentration and bears relation with the reduced free volume $x = V_f/\gamma V^*$ through $C = e^{-1/x}$ (V_f is the free volume per atomic volume and V^* is the critical amount of free volume per atomic volume to form a defect. γ is a constant ranging from 0.5 to 1 [9]). k could be expressed as an Arrhenius type function of activation energy and temperature, $k = k_0 e^{-E/k_B T}$, k_0 is a kinetic constant. On the other hand, the monitored signal by thermal analysis, \dot{H} is proportional

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to the variation rate of reduced free volume when there is no chemical reaction [7], that is $dH/dt = \alpha dx/dt$ (α is a constant). This supplies the fundamental of structure relaxation kinetics researching through thermal analysis. Since the temperature dependence of k , isothermal analysis would be simpler than non-isothermal analysis.

Moreover, as stated by the energy landscape theory, amorphous alloy usually located at a metastable state close to a most stable local metastable state because of the liquid similar structure freezing due to high cooling rate. The amorphous alloy would gradually approach to the most stable local metastable state through structure relaxation [2]. This bears similarity to the chemical reaction [10]. The energy landscape of amorphous alloy is temperature-dependent, therefore the isothermal relaxation expresses more explicit physical picture than the non-isothermal relaxation and is more suitable for researching the metastable state and the relaxation kinetics. While isothermal analysis is not widely adopted in the investigations of amorphous alloys structure relaxation to date except a few literatures [5,11–13] trying to observe the evolution of viscosity, volume, density or recovered enthalpy in isothermal annealing. The front mentioned important parameters and their evolution in different conditions have never been explored.

Herein, the mathematic expression of dx/dt during isothermal process is obtained based on the structure relaxation kinetics equation, meanwhile, it can be directly utilized to fit the isothermal thermal analysis signal dH/dt , and then gives out the parameters k_0 , D , T_0 , E , and other derived important parameters. A series of experiments are suggested to explore the metastable state difference of varied amorphous alloy on the basis of that, which should shed more light on the understanding of the relation between the defect structure and the glass forming of amorphous alloys.

2. Isothermal equation of dx/dt

A format of $f(k, C)$ widely accepted so far could be written as $\dot{C} = -kC(C - C_e)$ [3]. Integrating it leads to the expression of $C(t)$ like

$$C = \frac{C_e}{1 - \lambda_1 e^{-kC_e t}}, \quad \lambda_1 \equiv 1 - \frac{C_e}{C_{t=0}} \quad (1)$$

where C_e is the equilibrium defect concentration. Further based on $C = e^{-1/x}$, \dot{C} and $C(t)$, the dx/dt can be obtained as

$$\frac{dx}{dt} = \frac{-\lambda_1 k C_e e^{-kC_e t}}{(1 - \lambda_1 e^{-kC_e t}) \left(\ln \frac{1 - \lambda_1 e^{-kC_e t}}{C_e} \right)^2} \quad (2)$$

In addition, three other formats of $f(k, C)$ also have been always discussed previously. Here we also discussed them to explore their applicability in practice. They are $\dot{C} = -k(C - C_e)^2$, $\dot{C} = -kC^2$ and $\dot{C} = -k(C^2 - C_e^2)$ [3]. Similarly, we can get their corresponding $C(t)$ respectively as follow

$$C = (kt - \lambda_2)^{-1} + C_e, \quad \lambda_2 \equiv \frac{1}{C_e - C_{t=0}} \quad (3)$$

$$C = \frac{1}{kt + \lambda_3}, \quad \lambda_3 \equiv \frac{1}{C_{t=0}} \quad (4)$$

$$C = C_e \frac{1 + \lambda_4 e^{-2kC_e t}}{1 - \lambda_4 e^{-2kC_e t}}, \quad \lambda_4 \equiv \frac{C_{t=0} - C_e}{C_{t=0} + C_e} \quad (5)$$

and dx/dt respectively as

$$\frac{dx}{dt} = \frac{-k}{(kt - \lambda_2)(1 - \lambda_2 C_e + kC_e t) \left\{ \ln \left[(kt - \lambda_2)^{-1} + C_e \right] \right\}^2} \quad (6)$$

$$\frac{dx}{dt} = \frac{-k}{(kt + \lambda_3) \left[\ln(kt + \lambda_3) \right]^2} \quad (7)$$

$$\frac{dx}{dt} = \frac{-4\lambda_4 k C_e e^{-2kC_e t}}{(1 - \lambda_4 e^{-2kC_e t})^2 \left(\ln C_e \frac{1 + \lambda_4 e^{-2kC_e t}}{1 - \lambda_4 e^{-2kC_e t}} \right)^2} \quad (8)$$

And then using the relation $dH/dt = \alpha dx/dt$, the isothermal thermal analysis curve could be fitted in the region of structure relaxation with fitting parameters λ_i ($i = 1, 2, 3, 4$), k , C_e and α . Moreover, C_e is often supposed to obey the Vogel–Fulcher–Tammann (VFT) equation of temperature T , that is $C_e = e^{-DT_0/(T-T_0)}$. The parameters D and T_0 could be obtained by fitting C_e vs. T data, which can be obtained by using isothermal thermal analyses under different temperatures. And the parameters k_0 and E can be obtained through k vs. T fitting in accordance to the Arrhenius equation shown above, under the frequently adopted assumption that k_0 and E are temperature independent.

3. Simulation and application in the $Al_{85}Ni_8Y_5Co_2$ amorphous alloy

Fig. 1 shows the dx/dt curves simulated at $T = 500$ K with Eqs. (2) and (6)–(8). The parameters used for simulated respectively are $D = 18.59$, $T_0 = 355$ K, $k_0 = 3.4 \times 10^{25}$ Hz and $E = 154$ kJ/mol, got from the $Pd_{40}Ni_{40}P_{20}$ amorphous alloy [3]. It is obviously that there is no distinct variation in the curved simulated based on Eqs. (2), (6) and (7) when the initial defect concentration departs far from the equilibrium defect concentration, as seen in Fig. 1a. When $C_{t=0}$ is near C_e , slight difference would exist for curves simulated by the three equations, as shown in Fig. 1b. The curves got from Eq. (8) are obviously deviated from the curves simulated by Eqs. (2), (6) and (7) no matter the extent of $C_{t=0}$ departing from C_e (Fig. 1a and b). It seems implying that Eq. (8) so as well as $\dot{C} = -k(C^2 - C_e^2)$ is not applicable in modeling the structure relaxation of amorphous alloy and however all of Eqs. (2), (6) and (7) are applicable.

The equations were further used to fit the experimental isothermal structure relaxation data (DSC) of $Al_{85}Ni_8Y_5Co_2$ amorphous alloy at temperatures 473.2 K, 483.3 K and 493.3 K [14]. It was founded that Eq. (8) cannot thoroughly fit the data. The best fitted results of Eqs. (2), (6) and (7) are respectively demonstrated in Fig. 2(a–c). The data can be well fitted by them. The fitted C_e and k are illustrated in Fig. 3, and the data is got from three equations have sound consistence except Eq. (6) fitted k of the 473.2 K isothermal relaxation. These results agree with the founding in the former simulation. The fitted C_e and k are founded to well depend on temperature respectively according to the VFT equation and the Arrhenius equation, as shown in Fig. 3a and b, that gives the important parameters of $Al_{85}Ni_8Y_5Co_2$ amorphous alloy to be $D = 0.526$, $T_0 = 459.2$ K, $E = 139.7$ kJ/mol and $k_0 = 3.35 \times 10^7$ Hz.

The fragility strength coefficient D characterizes the resistance of glass forming liquid structure to temperature change, and it bears positive relevance to the resistance. In the frame of energy landscape theory, the magnitude of D implies the metastable state map of an amorphous system. A fragile liquid with small D would have a map with a large number of local deep energy valleys. The deep energy valleys will gradually decrease in number as the increase of D , so the system becomes stronger and stronger [15]. For a typical strong liquid, D is founded to be larger than 100, and D is much lower than 10 for liquid of high fragility [16]. It has been previously reported that D of $Al_{85}Ni_{8-x}(Ce, La)$ based amorphous alloy is in a range of 1.5–2, indicating [17] the aluminum based amorphous alloys are greatly fragile system. This is compatible to the present work fitted D of $Al_{85}Ni_8Y_5Co_2$ amorphous

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