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Study of the kinetics of free volume in $Zr_{45.0}Cu_{39.3}Al_{7.0}Ag_{8.7}$ bulk metallic glasses during isothermal relaxation by enthalpy relaxation experiments

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ABSTRACT

Enthalpy relaxation experiments were conducted to study the kinetics of free volume in $Zr_{45.0}Cu_{39.3}Al_{7.0}Ag_{8.7}$ bulk metallic glasses (BMGs) during isothermal relaxation using differential scanning calorimetry (DSC) at the temperature within the range from 648 to 684 K. Stretched exponential relaxation functions and the Šesták–Berggren SB (m, n) model were employed to analyze the kinetics of free volume. It is found that the relaxation time decreases from 2643.5 to 242.8 s while the Kohlrausch exponents increase from 0.717 to 0.892 in the investigated temperature range. The activation energy fluctuates slightly in the course of the relaxation process and its mean value is determined to be 239.7 kJ/mol. By fitting the first derivative of the conversion degree as a function of annealing time using the Šesták–Berggren SB (m, n) model, it is found that the values of m at all annealing temperatures are very small and can be approximated as zero. The values of the pre-exponential factors Z and the kinetic parameter n are found to be slightly varying with the annealing temperature, indicating the complexity of the kinetics of the isothermal relaxation. Finally, an approximate rate equation describing the kinetics of free volume during isothermal relaxation is proposed.

1. Introduction

Bulk metallic glasses (BMGs) are generally thought to be in thermodynamically metastable states compared to their crystalline counterparts [1]. Structural relaxation takes place upon isothermal annealing at elevated temperatures in the vicinity of glass transition [2], which is accompanied with the substantial change of many properties of BMGs, such as diffusivity [3], plasticity [4] and electrical resistivity [5], etc. Structural relaxation in BMG is usually interpreted by the free volume model (FVM) that was first formulated by Turnbull and Cohen [6] and thereafter developed by Cohen and Grest [7] and Spaepen et al. [8]. According to the FVM, structural relaxation during isothermal annealing results from a reduction of the excess free volume that was trapped in the BMG during preparation [9]. A direct evidence for the reduction of free volume during structural relaxation is the densification experiment performed by Haruyama [10–12]. It was shown that the densities of $Pd_{40}Ni_{40}P_{20}$ and $Pd_{42.5}Cu_{30}Ni_{7.5}P_{20}$ BMGs increase with the annealing time and approach saturation values.

Two kinetic models have been employed to describe the change in free volume during isothermal structural relaxation of metallic glasses, i.e. the flow defect model and the stretched exponential relaxation model. Earlier results of isothermal viscosity relaxation measurements were explained by the flow defect model [13–16]. Thereafter, Beukel et al. [9,17] and Wen et al. [18,2] have succeeded in simulating the differential scanning calorimetry (DSC) curves of $Pd_{48}Ni_{32}P_{20}$, $Pd_{77.5}Cu_6Si_{16.5}$ and $Zr_{46.25}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ BMGs qualitatively using the flow defect model. However, it was shown recently that the results of viscosity and

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enthalpy relaxations of some Zr- [19–21], Pd- [10–12] and La- [22] based BMGs cannot be fitted by the flow defect model but were well fitted by a stretched exponential relaxation model with the Kohlrausch exponents less than unity. Nevertheless, the mechanism of relaxation of free volume is still under debate.

In the present study, enthalpy relaxation experiments of a $Zr_{45.0}Cu_{39.3}Al_{7.0}Ag_{8.7}$ BMG are conducted at temperatures within the range from 648 to 684 K to study the kinetics of free volume during isothermal relaxation. Besides the stretched exponential functions, attempts are made to study the kinetics of free volume using an empirical two parametric Šesták–Berggren SB (m, n) equation [23]. In detail, the isothermal relaxation is treated as a process during which the excess free volume in the investigated sample reduces to the equilibrium value of the corresponding temperature, which is consistent with the FVM. The activation energy of the isothermal relaxation is determined by the isothermal–isoconversional method without assuming the kinetic model function.

2. Theoretical background

An important relationship that provides the possibility to study the relaxation of free volume through calorimetric measurements is:

$$\Delta H = \beta \cdot \Delta \upsilon_f, \tag{1}$$

where β is a constant with a dimension of energy, ΔH and $\Delta \upsilon_f$ are the changes in the enthalpy and the average free volume during structural relaxation, respectively. Eq. (1) has been demonstrated experimentally by density and enthalpy relaxation measurements in a $Zr_{55}Cu_{30}Ni_5Al_{10}$ BMG [24].

2.1. The flow defect model

Within the framework of the flow defect model, the kinetics of free volume in BMGs during isothermal relaxation can be described by the following rate equation:

$$dC_f/dt = -K_f C_f (C_f - C_{f,eq}), \tag{2}$$

where K_f is a reaction coefficient following the Arrhenius relationship, C_f is the concentration of flow defects, $C_{f,eq}$ is the equilibrium value of C_f as $t \to \infty$. The physical meaning of C_f is the possibility that an atom in the glass has a free volume larger than a certain critical value v^*.

2.2. The stretched exponential relaxation model

The enthalpy of the as-cast or preheated sample at a certain temperature T below the glass transition temperature T_g is usually much higher than its corresponding equilibrium value $H_{eq}(T)$. The excess enthalpy can be released by long-time sub-T_g isothermal annealing. As a consequence, the glass relaxes gradually into the metastable supercooled liquid state. The released enthalpy $\Delta H(T_a, t)$ as a function of the annealing time t at temperature T_a is found to follow the stretched exponential relaxation function which can be formulated as:

$$\Delta H(T_a, t) = \Delta H_{eq}(T_a)\{1 - exp[-(t/\tau)^\beta]\}, \tag{3}$$

where $\Delta H_{eq}(T_a)$ is the equilibrium value of $\Delta H(T_a, t)$ as $t \to \infty$, τ is the relaxation time and β $(0 < \beta < 1)$ is the Kohlrausch exponent. The released enthalpy during the isothermal annealing can be recovered by a subsequent heating of the relaxed sample through the glass transition. Moreover, the released enthalpy is equal to the recovered enthalpy. In the present study, the recovered enthalpy as a function of annealing time is fitted by Eq. (3).

2.3. The Šesták–Berggren SB (m, n) kinetic model

From the viewpoint of thermal analysis, the kinetics of an isothermal process can be described by:

$$d\alpha/dt = Z \cdot exp[-E/(RT)] \cdot f(\alpha), \tag{4}$$

where α, Z, E and $f(\alpha)$ are the conversion degree, pre-exponential factor, activation energy and model function of the process, respectively. It was proposed by Šesták and Berggren that in most cases $f(\alpha)$ can be well described by the following empirical expression [25,26]:

$$f(\alpha) = \alpha^m (1 - \alpha)^n, \tag{5}$$

Eq. (5) is usually named as the SB (m, n) model, where m and n are kinetic parameters and they reflect the relative contributions of the acceleratory and decay regions of the kinetic process, respectively. The physical meaningful values of m should be in the range of $0 < m < 1$. Substituting Eq. (5) into Eq. (4) gives:

$$d\alpha/dt = Z \cdot exp[-E/(RT)] \cdot \alpha^m (1 - \alpha)^n, \tag{6}$$

The conversion degree of the isothermal relaxation process can be defined as:

$$\begin{aligned} \alpha &= \Delta H(T_a, t)/\Delta H_{eq}(T_a) \\ &= [v_{f,0}(T_a) - v_f(T_a, t)]/[v_{f,0}(T_a) - v_{f,eq}(T_a)], \end{aligned} \tag{7}$$

where $\Delta H_{eq}(T_a)$ and $\Delta H(T_a, t)$ have the same meaning as those in Eq. (3), $\upsilon_{f,0}(T_a)$, $\upsilon_f(T_a, t)$ and $\upsilon_{f,eq}(T_a)$ are the initial, the instantaneous and the equilibrium values of average free volume of the isothermal relaxation process, respectively. The change in enthalpy is converted into the change in average free volume with the help of Eq. (1). Therefore, the change in the content of average free volume with respect to the annealing time can be formulated by differentiating Eq. (7) and substituting the resultant expression into Eq. (6) as:

$$dv_f(t)/dt = -bZ \cdot exp[-E/(RT_a)][v_f(T_a,t) - v_{f,eq}(T_a)]^n [v_{f,0}(T_a) - v_f(T_a,t)]^m, \tag{8}$$

where $b = [\upsilon_{f,0}(T_a) - \upsilon_{f,eq}(T_a)]^{1-(m+n)}$, which is a constant at given initial content of free volume and isothermal annealing temperature.

2.4. The isothermal–isoconversional method

In principle, the $d\alpha/dt$ as a function of the conversion degree α determined by enthalpy relaxation measurements can be directly fitted using Eq. (6). However, there are altogether four parameters to be determined (Z, E, m and n). Moreover, it can be seen that Z and E are correlative parameters, i.e. the change in E can be adapted by the change in Z with the same set of m and n values. In the present study, the isothermal–isoconversional method was firstly employed to determine the values of E, then the experimental data were fitted using Eq. (6) with a constraint of $0 < m < 1$. The isothermal–isoconversional method can be expressed as:

$$ln\, t = -ln Z + ln[g(\alpha)] + E/(RT), \quad g(\alpha) = \int [f(\alpha)]^{-1} d\alpha. \tag{9}$$

It can be seen that the first and the second terms at the right hand of Eq. (9) are constants under the same α, so E can be derived from the slope of the curves by plotting the reciprocal of T_a against the logarithm of annealing time t.

3. Experimental

$Zr_{45.0}Cu_{39.3}Al_{7.0}Ag_{8.7}$ master alloys were prepared by arc melting of the component elements with purities ranging from 99.9% to 99.999%. The master alloys were remelted five times under high