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Quantitative determination of free volume in $Pd_{40}Ni_{40}P_{20}$ bulk metallic glass

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For a long time, the determination of free volume has been a challenging problem in research on metallic glasses. An approach to determine quantitatively the free volume of metallic glasses from enthalpy measurements and calibration with the equilibrium free volume was developed and validated for as-cast and annealed $Pd_{40}Ni_{40}P_{20}$ bulk metallic glasses. The free volume change with annealing time is in good agreement with that calculated theoretically from the free volume annihilation kinetics and that deduced from the density measurement results.

Keywords: Bulk metallic glass; Differential scanning calorimetry (DSC); Suction casting; Annealing; Free volume

The free volume model, since proposed by Cohen and Turnbull [1] and developed by Cohen and Spaepen [2,3], has been widely employed to explain various properties of metallic glasses. Free volume is visualized as the physical space for atomic movement under the effect of temperature or mechanical stress. As a consequence, a large amount of free volume will enhance the plasticity of metallic glasses [4]. In the relaxed state, metallic glasses become more brittle due to the reduction of the free volume [5]. This also applies for other physical properties of metallic glasses, e.g., viscosity and atomic diffusivity [6,7], which may change by orders of magnitude with the variation of free volume. Therefore, the quantitative determination of free volume is crucial to understanding the structure and the properties of metallic glasses.

Up to now, numerous attempts have been made to use differential scanning calorimetry (DSC) to characterize free volume changes in metallic glasses, particularly after structural relaxation [8–11]. Van den Beukel and Sietsma presented a quantitative model to relate the relaxation of the free volume towards equilibrium to the glass transition phenomenon observed during constant heating rate DSC experiments [8]. The subsequent works applied this model to examine the influence of annealing time and temperature on the degree of relaxation [9,10]. However, most of these attempts are focused on the difference of free volume content between different glassy states [10,11]. The quantitative determination of the absolute free volume value based on DSC experiments for a monolithic glassy state has not been developed so far.

In the present work, an approach for the quantitative determination of the average free volume in metallic glasses is developed based on the measured enthalpy change during constant heating rate DSC measurements and the equilibrium free volume at the onset temperature of glass transition. By this method, the absolute value of the average free volume for a monolithic metallic glass at any state can be determined. As an example, the free volume values of the $Pd_{40}Ni_{40}P_{20}$ bulk metallic glass (BMG) in the as-cast state and in several relaxed states were determined. Furthermore, the free volume change with annealing time calculated theoretically from the free volume annihilation kinetics and from density measurements were compared to the free volume values determined by our method.

$Pd_{40}Ni_{40}P_{20}$ (at.%) BMG samples were prepared by suction casting method. The amorphous nature of the as-cast and annealed samples was identified using X-ray diffraction on an X'pert X-ray diffractometer with the Mo K_α radiation. The DSC measurements were preformed on a Perkin–Elmer Pyris 1 at heating rates of 10,

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20, 40, and 80 K min^{-1}. Isothermal annealing treatments were performed at 543 K for different times on the same instrument. Using a Sartorius MC201S electrical balance with a density measurement unit, the densities of the samples were measured at room temperature.

According to the model proposed by van den Beukel and Sietsma [8], the amount of the reduced free volume x can be expressed as $x = v_f/(\gamma v^*)$, where v_f is the average free volume per atom, v^* is the critical free volume for atomic diffusion, and γ is an overlap factor. (For simplicity, the reduced free volume x is called free volume hereafter in this work.) The value of x in metallic glasses changes with temperature during continuous heating. When a metallic glass is heated at a constant heating rate, e.g., during a DSC measurement, its structure relaxes towards equilibrium. The free volume x undergoes a decrease and a subsequent increase and then attains the equilibrium value with increasing temperature [8]. The free volume reduction leads to a release of energy and is observed as an exothermic event in the corresponding DSC trace. This exothermic event corresponds to the structural relaxation process for the system. Similarly, the increase of x is accompanied by an increase of the enthalpy, showing an endothermic event in the DSC trace. This endothermic event corresponds to the glass transition process for the system. The temperature at which x begins to increase corresponds to the onset temperature of glass transition T_g^{onset} and is observed as the onset of the endothermic DSC event. At T_g^{onset}, x crosses the equilibrium free volume line and thus equals the equilibrium free volume $x_{eq}(T_g^{onset})\{x_{eq}(T) = (T - T_0)/B$, where T_0 is the Vogel–Fulcher temperature and B the product of T_0 and the fragility parameter [11]} [8].

It was found that a proportionality exists between the enthalpy change (ΔH) and the free volume change (Δx) during both the structural relaxation and glass transition processes [8,10]:

$$\Delta H = A\Delta x \qquad (1)$$

where A is a constant. Since the temperature range for the structural relaxation process is approximately from room temperature to T_g^{onset}, the enthalpy change during the whole structural relaxation process corresponds to the free volume difference Δx in the free volume between room temperature $x(RT)$ and the free volume at T_g^{onset}. $x(RT)$ can thus be obtained according to Eq. (1) from the enthalpy change during the whole structural relaxation process and $x(T_g^{onset})$. Similarly, at any temperature T during the structural relaxation process, Δx between $x(T)$ and $x(RT)$ corresponds to the enthalpy change from room temperature to T. Hence, $x(T)$ can be deduced from the enthalpy change from room temperature to T and $x(RT)$. Thus the free volume at any temperature can be determined from the enthalpy change with temperature and $x(T_g^{onset})$ heated at a constant heating rate.

Figure 1 displays the detailed process of the free volume quantification for the as-cast $Pd_{40}Ni_{40}P_{20}$ BMG. The specific heat data calculated from the corresponding DSC scans measured at 20 K min^{-1} are shown in Figure 1a. Figure 1a shows characteristic structural relaxation exothermic, glass transition endothermic, and subsequent crystallization exothermic events. The T_g^{onset} value determined from Figure 1a is about 572 K. The specific heat data are integrated for the structural relaxation temperature range and the temperature range from T_g^{onset} to the initial crystallization temperature [12]. Then the enthalpy changes for these two temperature ranges are obtained and shown in Figure 1b. As shown in Figure 1b, the enthalpy change is negative and decreases as temperature increases for the structural relaxation process. However, the enthalpy change is positive and increases with increasing temperature for the temperature range from T_g^{onset} to the initial crystallization temperature. Especially at the temperature range of around 610–640 K, the enthalpy change exhibits almost a linear increase with increasing temperature.

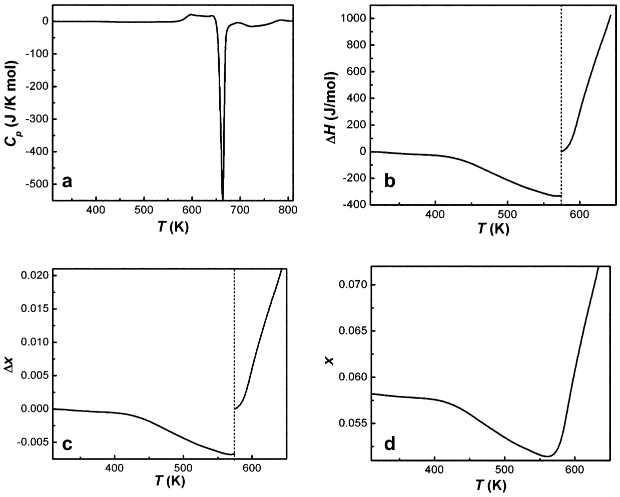

Figure 1. The specific heat C_P calculated from the DSC scans measured at 20 K min^{-1} (a), the enthalpy change ΔH based on the integration of the specific heat data (b), the free volume difference Δx deduced from the enthalpy change (c), and the quantified free volume x (d) for the $Pd_{40}Ni_{40}P_{20}$ BMG sample in the as-cast state.

Combining Eq. (1) with Eq. (2) in Ref. [11], B and T_0 were determined to be 3100 and 415 K, respectively, for the $Pd_{40}Ni_{40}P_{20}$ BMG. In addition, the glassy system achieves the equilibrium state in the supercooled liquid temperature region; and Eq. (1) can be presented as $(C_P)_{eq} = A\frac{dx_{eq}}{dT} = \frac{A}{B}$ (C_P represents the specific heat for a glassy system) [8]. Then A can be calculated with $(C_P)_{eq}$ and B. According to $(C_P)_{eq}$ deduced from the DSC results, $A \approx 49$ kJ mol^{-1} is obtained for the $Pd_{40}Ni_{40}P_{20}$ BMG. Dividing the enthalpy change shown in Figure 1b by $A = 49$ kJ mol^{-1}, the change of the free volume difference (Δx) with temperature is deduced and shown in Figure 1c. In Figure 1c, the change of the free volume difference (Δx) at temperature T indicates the free volume difference $\Delta x(T) = x(T)$–$x(RT)$ in the temperature range from room temperature (RT) to T_g^{onset}. Obviously, $\Delta x(T_g^{onset}) = x(T_g^{onset}) - x(RT)$. Hence the free volume at RT can be calculated as $x(RT) = x(T_g^{onset}) - \Delta x(T_g^{onset})$. Since $T_g^{onset} \approx 572$ K, the free volume $x(T_g^{onset})$ at T_g^{onset} equals $x_{eq}(572)$, i.e., 0.051. Then $x(RT)$ is obtained from $x(T_g^{onset})$ and $\Delta x(T_g^{onset})$. Subsequently, $x(T)$ at T is deduced by adding $x(RT)$ and $\Delta x(T)$ in the temperature range from RT to T_g^{onset}. In a similar way, the free volume $x(T)$ is obtained by adding $x(T_g^{onset})$ and the corresponding $\Delta x(T)$ in

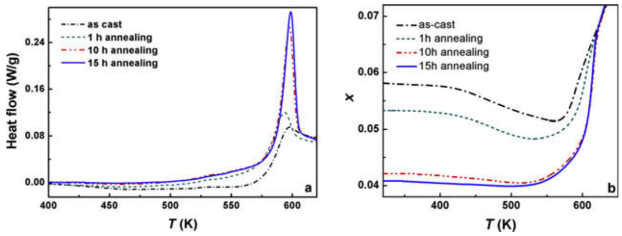

Figure 2. The DSC curves measured at a heating rate of 20 K min^{-1} (a) and the free volume x in variation with temperature determined from the enthalpy change (b) for the $Pd_{40}Ni_{40}P_{20}$ BMG samples in the as-cast state and after annealing at 543 K for 1, 10, and 15 h.

the temperature range from T_g^{onset} to the initial crystallization temperature. The absolute free volume values for these two temperature ranges are obtained and shown in Figure 1d. The free volume at 310 K is about 0.058 (the initial free volume of the as-cast $Pd_{40}Ni_{40}P_{20}$ BMG system); and it keeps almost constant below 400 K. The free volume decreases subsequently as temperature increases in the temperature range of 400–572 K. As temperature increases further thereafter, the free volume begins to increase. Especially in the temperature range of 610–640 K, the free volume exhibits a linear increase with increasing temperature, indicating that the equilibrium state is achieved for the system in this temperature range [8].

Figure 2a shows the DSC curves measured at a heating rate of 20 K min^{-1} for the as-cast $Pd_{40}Ni_{40}P_{20}$ BMG sample and the $Pd_{40}Ni_{40}P_{20}$ BMG samples annealed at 543 K for 1, 10, and 15 h. One can clearly see that with increasing annealing time, the area of the exothermic relaxation event decreases while the endothermic glass transition peak area increases as a consequence of the free volume reduction with increasing annealing time. Using the same method used to quantify the free volume for the as-cast $Pd_{40}Ni_{40}P_{20}$ BMG mentioned above, the free volumes in variation with temperature are quantitatively determined for these annealed samples. The results, as well as that for the as-cast state, are shown in Figure 2b. The temperature dependence of the free volume for the $Pd_{40}Ni_{40}P_{20}$ BMG samples annealed at 543 K for 1, 10, and 15 h exhibit a similar variation to that for the as-cast sample. The initial free volume decreases as the annealing time increases. The free volume at 310 K becomes 0.041 when annealed at 543 K for 15 h, about 29% lower than that in the as-cast sample.

The kinetics of free volume annihilation has been quite well established theoretically from the isothermal changes of viscosity, elastic constants, and resistivity [13,14]. Based on these results, the theoretical temperature dependence of free volume for glassy materials heated at a constant heating rate β can be deduced and expressed by

$$\frac{dx}{dT}=\left(-\frac{v_0}{\beta}\right)\exp\left(-\frac{E_r}{RT}\right)x^2\left[\exp\left(-\frac{1}{x}\right)-\exp\left(-\frac{B}{T-T_0}\right)\right], \qquad (2)$$

where v_0 is an attempt frequency, E_r the relaxation activation energy, and R the gas constant [15–18]. As described above, the free volume $x(T_g^{onset})$ equals the equilibrium free volume x_{eq} at T_g^{onset}. Using $x_{eq}(T_g^{onset})$ as an initial value, the theoretical free volume and its temperature dependence at a constant heating rate can then be calculated by solving Eq. (2). This was used in Ref. [8] to evaluate the free volume of PdNiP and PdCuSi amorphous alloys. To verify the rationality of our calculation results, this approach is also used here to evaluate the free volume of our $Pd_{40}Ni_{40}P_{20}$ BMG sample. For the $Pd_{40}Ni_{40}P_{20}$ BMG, $E_r \approx 180$ kJ mol^{-1} was calculated using the method reported [15,17]. With $v_0 = 2.1 \times 10^{23}\ \text{s}^{-1}$ (cited from Ref. [8]) and other related parameters, the theoretical free volume values for the as-cast and annealed $Pd_{40}Ni_{40}P_{20}$ BMG samples heated at 20 K min^{-1} were calculated and plotted in Figure 3. The free volume at 310 K decreases with annealing time. Compared with the as-cast sample, the free volume at 310 K decreases about 31% for the 15 h annealed sample. Both the annealing time and temperature dependences of the theoretical free volume when heated at 20 K min^{-1} calculated with Eq. (2) are in agreement with those deduced from the enthalpy change in Figure 2b.

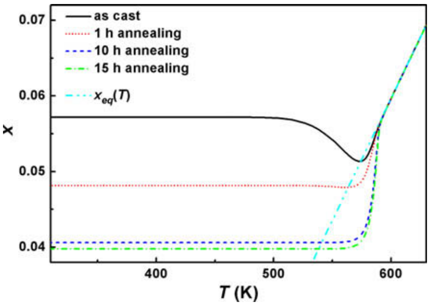

Figure 3. The temperature dependence of the theoretical free volume x calculated using Eq. (2) for the $Pd_{40}Ni_{40}P_{20}$ bulk metallic glass samples in the as-cast state and after annealing at 543 K for 1, 10, and 15 h.

As an additional validation of the method presented in this letter, the values of the free volume were calculated from the measured densities of the as-cast and annealed $Pd_{40}Ni_{40}P_{20}$ BMG samples. The free volume can be deduced from the density using $x \approx \frac{M}{N_0}\left(\frac{1}{d}-\frac{1}{d_x}\right)\frac{1}{\gamma v^*}$, where d and d_x are densities of real glass and ideal glass, respectively, N_0 is the Avogadro constant, M the molar weight, and $\gamma v^* \approx 0.5(1/d_x)M/N_0$ [19]. The density of the corresponding crystalline phase was often used instead of the ideal glass as the difference in the density between the ideal glass and the corresponding fully crystallized

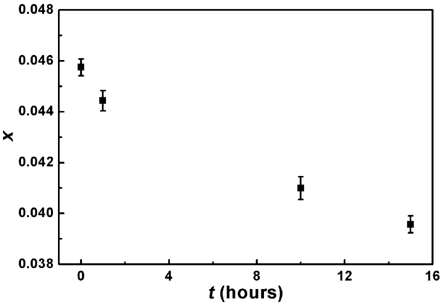

Figure 4. The free volume x deduced from the density measurements for the $Pd_{40}Ni_{40}P_{20}$ bulk metallic glass samples in variation with the annealing time t at 543 K (the as-cast state given at $t = 0$).

state for metallic glasses is small [19,20]. Using $d_x = 9.4565\ \mathrm{g\,cm^{-3}}$ of the crystallized sample instead of the ideal glassy sample and the measured densities of the as-cast and annealed $Pd_{40}Ni_{40}P_{20}$ BMG samples, the free volume values were calculated and are shown in Figure 4. As expected, the free volume decreases with increasing annealing time. Compared with Figure 2b, the values of the free volume deduced from the density measurements are smaller than those determined from the enthalpy measurements. The reason may be because v^* is approximated as the average atomic volume $(1/d_x)M/N_0$ of the corresponding crystalline state in the calculation of the free volume according to $x \approx \frac{M}{N_0}\left(\frac{1}{d} - \frac{1}{d_x}\right)\frac{1}{\gamma v^*}$ [19]. However, as pointed in Ref. [20], v^* is roughly equal to the volume of metal ion core which should be smaller than the corresponding average atomic volume of the crystalline state. Nevertheless, the change of the values calculated from the density measurement reflects the free volume change with annealing time in metallic glasses. This is comparable with the free volume variation trend with annealing time obtained from the enthalpy measurements. The agreement between the free volume variation trends with annealing time deduced from the enthalpy measurements and from the density measurements implies that the quantitative determination of free volume from the enthalpy measurements and the calibration with the equilibrium free volume at T_g^{onset} is a feasible and simple approach to quantitatively study the free volume of metallic glasses.

In summary, based on the enthalpy change measured by DSC and the equilibrium free volume at T_g^{onset}, the quantitative determination of the free volume in metallic glasses was realized. The free volume and its temperature dependence for the as-cast and annealed $Pd_{40}Ni_{40}P_{20}$ BMG samples were determined quantitatively. The free volume deduced from the enthalpy measurements for these BMG samples are in reasonable agreement with the values determined using a theoretical model and those deduced from density measurements. The quantitative determination of the free volume values for metallic glasses from the enthalpy measurements may provide a rational, simple approach for studying the structure and related properties of metallic glasses.

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