Volume relaxation in ternary bulk Pd- and Pt-P based metallic glasses

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Abstract. The kinetics of volume relaxation for Pd₄₆Cu₃₅.₅P₁₈.₅ and Pt₆₀Ni₁₅P₂₅ BMGs were investigated by high-resolution density experiments at room temperature. The distinct two-steps relaxation behavior was observed for as-quenched BMGs. After pre-annealing as-quenched Pd₄₆Cu₳₅P₁₈.₅ BMG in the supercooled liquid region, the relaxation process changed into a single relaxation process well described by a stretched exponential relaxation function. Meanwhile, the pre-annealed Pt₆₀Ni₁₅P₂₅ BMG still remained a two-steps relaxation behavior. The volume relaxation data of as-quenched Pt₆₀Ni₁₅P₂₅ BMG was analyzed on the base of the structural inhomogeneity composed of volume compression and expansion regions in the like sites during structural relaxation.

1. Introduction
Since the systematic discovery of bulk metallic glass (BMG) [1], the study on the structural relaxation has advanced remarkably regarding to both the kinetic and dynamic behaviors. Isothermal relaxation of various physical properties such as viscosity [2], positron annihilation [3,4], enthalpy [5,6] and density [7,8], reveals that the structural relaxation of metallic glass is well described by a stretched exponential type (SE) relaxation function with a spectrum of relaxation times. Recent dynamical researches [9,10] using ultrasonic wave and inelastic neutron scattering verify that the structural inhomogeneity exists in the metallic glass. Reports [11,12] with regard to plastic deformation of monocilic BMGs suggest also the existence of the structural inhomogeneity because the propagation of the shear band is likely interrupted by such inhomogeneity instead of nano-crystallites or clusters. Cohen et al. [13] proposed the amorphous structure model that is composed of liquid-like cells and solid-like ones to explain the true glass transition mechanism for amorphous materials including metallic glasses. They pointed out [13] that the fraction \( p_L \) of liquid-like cell decreased with decreasing temperature and the true glass transition occurred in the vicinity of \( p_L = 0.2 \) for an Au₇₇Ge₃₃Si₉.₄ metallic glass. Cohen et al. also pointed out [14] that the structural relaxation occurs in only liquid-like cells with the framework of their free volume theory [15]. If the conventional free

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volume relaxation occurs in this region, the monotonous relaxation behavior usually observed in Zr-based BMGs can be understood by Cohen’s model. Meanwhile, we reported [16] that the densification of a Pd_{40}Ni_{40}P_{20} BMG occurred in two-steps process during the development of isothermal relaxation in sub-$T_g$ region. Ichitsubo et al. pointed out that a relatively fragile BMG, typically such as a Pd_{32.5}Cu_{30}Ni_{17.5}P_{20} BMG, is composed of weak-bonded region (WBR) and strong-bonded one (SBR) [9, 10]. Egami et al. pointed out [17, 18] that there exist the liquid-like sites as the sites with the local volume strain larger than 0.11 or smaller than -0.11. This suggests that if the structural relaxation occurs mainly in the liquid-like sites, the apparent volume reduction during relaxation is caused by the competition of the volume compressive and dilatational contributions.

In the present study, we will report the volume relaxation behaviors of a Pd_{40}Cu_{35.5}P_{18.5} and Pt_{60}Ni_{15}P_{25} BMGs by high-resolution density experiments. The fragility parameter $m$ is reported as 52.3 for Pd_{40}Cu_{35.5}P_{18.5} BMG [19] and 67.2 for Pt_{60}Ni_{15}P_{25} BMG [20]. Both values are well larger than $m=44.2$ for Zr_{46.5}Ti_{18.25}Cu_{7.5}Ni_{10}Be_{27.5} BMG [2]. Thus these glasses will be appropriate for the verification of the existence of the structural inhomogeneity.

2. Experimental

Metal chips of Pt (99.95%), Pd (99.95%), Ni (99.993%), and lump P (99.9999%) in the compositions of Pd_{40}Ni_{35.5}P_{18.5} and Pt_{60}Ni_{15}P_{25} were mixed and sealed in an evacuated quartz tube. The mixture was resolved completely at 1473 K for 8h and the alloy ingots were produced. The alloy ingots were homogenized by two times repetition of re-melting and subsequent casting to room temperature. After being flux-treated with a dehydrated B$_2$O$_3$ at 1300 K for 5 h, the melt was water-quenched into room temperature from 923 K, and BMGs with a size of 8 mm in diameter and 10 mm in length were prepared. The amorphous nature of the glass was confirmed by X-ray diffraction, DTA (differential thermal analysis) and optical microscopy. The density of bulk glass was measured at room temperature after each annealing step for a given time with a Mettler Toledo Ax26 electrical balance. The calorimetric measurements were performed with a RIGAKU-8270 DTA. CH$_3$(CH$_2$)$_3$CH$_3$ (n-Tridecane) was used as a working fluid because of low vapor pressure (3.4Pa) and small surface tension (2.77×10$^{-2}$ N/m) at room temperature. Disk-shaped bulk sample with a typical thickness of 4 mm was cut from rod-shape BMG ingot. The disk-shaped BMG was put into a preheated silicon oil bath during annealing. The calorimetric measurements were performed with a RIGAKU-8270 DTA.

3. Results

Figure 1 shows DTA curves for Pd_{40}Cu_{35.5}P_{18.5} and Pt_{60}Ni_{15}P_{25} BMGs together with Pd_{40}Ni_{40}P_{20} BMG. Thermodynamic parameters such as $T_g$ (calorimetric glass transition temperature), $T_c$ (crystallization temperature), $T_m$ (melting temperature) and $T_l$ (liquidus temperature) are summarized in Table 1 along with $T_g$ (reduced glass transition temperature) and $\gamma$-parameter. We notice that $T_l$ for both Pd_{40}Cu_{35.5}P_{18.5} and Pt_{60}Ni_{15}P_{25} BMGs are almost similar, while $T_g$ is significantly different and it is about 70 K lower for Pt_{60}Ni_{15}P_{25} BMG.

Figure 1. DTA curves for Pt_{60}Ni_{15}P_{25} and Pd_{40}Cu_{35.5}P_{18.5} BMGs in comparison with Pd_{40}Ni_{40}P_{20} BMG.
Table I Thermodynamic parameters for Pd$_{46}$Cu$_{35.5}$P$_{18.5}$ and Pt$_{60}$Ni$_{15}$P$_{25}$ BMGs together with those of Pd$_{40}$Ni$_{40}$P$_{20}$ BMG.

| Glass       | $T_g$ [K] | $T_x$ [K] | $T_m$ [K] | $T_l$ [K] | $T_{fg}$ [K] | $\gamma$ |
|-------------|-----------|-----------|-----------|-----------|--------------|----------|
| Pd$_{46}$Cu$_{35.5}$P$_{18.5}$ | 559       | 615       | 845       | 884       | 0.632        | 0.426    |
| Pt$_{60}$Ni$_{15}$P$_{25}$     | 481       | 543       | 753       | 878       | 0.548        | 0.400    |
| Pd$_{40}$Ni$_{40}$P$_{20}$     | 575       | 645       | 872       | 980       | 0.587        | 0.415    |

Figure 2 shows the density relaxation curves for as-quenched and pre-annealed Pd$_{46}$Cu$_{35.5}$P$_{18.5}$ BMGs. The as-quenched BMG was annealed at 573 K for 540 s in supercooled liquid region to minimize the difference in the distribution of topological disorder introduced in as-quenched BMG. The change in the density of as-quenched BMG was negligible after the completion of pre-annealing, suggesting that the pre-annealing temperature $T_{pre}$ was almost the same as the fictive temperature $T_f$ of as-quenched BMG. The density relaxation curve for as-quenched BMG presents definitely multiple relaxation steps.

![Figure 2. Density relaxation curves for as-quenched and pre-annealed Pd$_{46}$Ni$_{35.5}$P$_{18.5}$ BMGs.](image)

Table II Fitting parameters for density relaxation curves of as-quenched and pre-annealed Pd$_{46}$Cu$_{35.5}$P$_{18.5}$ BMGs, and for specific relaxation curve of as-quenched Pt$_{60}$Ni$_{15}$P$_{25}$ BMG.

| Glass       | $\tau_1$ [s] | $\beta_1$ | $\tau_2$ [s] | $\beta_2$ | $\tau_r$ [s] |
|-------------|--------------|-----------|--------------|-----------|--------------|
| Pd$_{46}$   | 3939         | 0.66      | 29459        | 0.58      | 213165       |
| Pre-annealed| 18565        | 0.42      | -            | -         | -            |
| Pt$_{60}$   | 9324         | 0.65      | 7187         | 0.91      | -            |

We tentatively describe the density relaxation curve by a linear combination of two densification processes, \( d(t) = d_{as} + \Delta d_1 \left[ 1 - \exp\left( - \left( \frac{t}{\tau_1} \right)^{\beta_1} \right) \right] + \Delta d_2 \left[ 1 - \exp\left( - \left( \frac{t - \tau_r}{\tau_2} \right)^{\beta_2} \right) \right] \), where we assume that second process occurs with a delay time $\tau_r$. Relaxation times $\tau$, Kohlrausch index $\beta$, and $\tau_r$ are summarized in Table II. Meanwhile, the density relaxation curve for pre-annealed BMG appears to be a single relaxation process and can be well fitted by a SE relaxation function. The relaxation time and Kohlrausch index are also presented in Table II. Next, we examined the volume relaxation behaviors for as-quenched and pre-annealed Pt$_{60}$Ni$_{15}$P$_{25}$ BMGs. The pre-annealing treatment for as-quenched BMG was conducted at $T_{pre}$=506 K ($T_x$=37) in supercooled liquid region. Figure 3 shows the density relaxation curve measured during pre-annealing. The density decreases with time and reaches an equilibrium value after annealing for about 480 s. This decrement of density during relaxation at $T_{pre}$ means that the $T_f$ of as-quenched Pt$_{60}$Ni$_{15}$P$_{25}$ BMG was located at a lower position than $T_{pre}$ so that the
pre-annealing treatment caused the increment of volume, i.e. the decrement of density. The pre-annealed BMG along with as-quenched BMG was successively annealed at 461 K (T_g-20) to investigate the relaxation behavior. The specific volume relaxation curves are calculated from density relaxation data and the results are shown in Fig. 4. Due to the shortage of experimental time for pre-annealed BMG, the saturation of curve is not realized yet. However, we can observe definite two-steps relaxation process for both as-quenched and pre-annealed BMGs.

Figure 3. Density relaxation curve measured at T_pre=506 K in the supercooled liquid region for as-quenched Pt_{60}Ni_{15}P_{25} BMG. The broken line is drawn as a guide of eyes.

Figure 4. Specific volume relaxation curves for as-quenched and pre-annealed Pt_{60}Ni_{15}P_{25} BMGs. The calculation curve (solid line) for as-quenched BMG is obtained by fitting equation (2) to data. Also, the broken line is for a guide of eyes.

4. Discussion

We assume here that the liquid-like sites contain the volume compression part and dilatation one. The specific volume v(t) of BMG is expressed as next.

\[ v(t) = \frac{V_l(t) + V_s(t)}{M} = \frac{m_l}{M} \cdot V_l(t) + \frac{m_s}{M} \cdot V_s(t) = p_L \cdot v_l(t) + (1 - p_L) \cdot v_s(t), \]  

(1)

where M is the total mass of BMG, V_l(t) and V_s(t) are the volume of the liquid-like and the solid-like sites, respectively, also p_L is the weight fraction of liquid-like sites. Also, we neglect the structural relaxation in solid-like sites. Both specific volumes in the liquid-like sites are expected to be described by a SE relaxation function. By applying the same consideration as eq. (1) to the liquid-like sites, we get finally next equation against v(t).

\[ v(t) = v_{as} - p_L \cdot p \Delta v_d \left\{ 1 - \exp\left[ -\left( t / \tau_i \right)^\delta \right] \right\} - p_L \cdot (1 - p) \Delta v_c \left\{ 1 - \exp\left[ -\left( t / \tau_2 \right)^\delta \right] \right\}, \]  

(2)

where \( \Delta v_d = v_i^d(0) - v_i^d(\infty) \) and \( \Delta v_c = v_i^c(0) - v_i^c(\infty) \) are the volume reduction and expansion after the completion of relaxation, p is the fraction of local volume expanded. In the case of present estimation, we cannot determine p and p_L. Considering Egami’s result that liquid-like sites fraction p_L is 0.243 [18] at the glass transition temperature of metallic glass, we assumed p \approx 0.5. Eq. (2) was fitted to relatively noise-less relaxation curve of as-quenched Pt_{60}Ni_{15}P_{25} BMG in Fig. 4, and the result is illustrated in Fig. 4 as well. Relaxation times and Kohlrausch indices are presented in Table II. The volume reduction \( \Delta v_d \approx 1.1 \times 10^{-3} \) cm^3/g is obtained and this value is much larger than apparent densification of volume \( \Delta v = v_{as} - v_{eq} \approx 3.7 \times 10^{-5} \) cm^3/g because \( \Delta v \) is caused by the competition of volume reduction and expansion sites, estimated as \( \Delta v_c \approx 7.4 \times 10^{-4} \) cm^3/g that is smaller than volume compression counterpart. The reason why two-steps relaxation disappears in the pre-annealed Pd_{46}Cu_{35.5}P_{18.5} BMG may be explained by inferring that relative high-supercooled liquid temperature annihilates the difference in the structure of liquid-like sites and solid-like sites.
5. Conclusion
The volume relaxation behavior of two fragile Pd_{46}Cu_{35.5}P_{18.5} and Pt_{60}Ni_{15}P_{25} BMGs were investigated by high-resolution density experiments conducted at room temperature. In as-quenched state, both glasses showed distinct two-steps relaxation behavior. Against Pt_{60}Ni_{15}P_{25} BMG that exhibited more remarkable two-steps relaxation, the volume relaxation data was fitted to a linear combination of two stretched exponential relaxation functions in which the structural inhomogeneity effect was taken into account. Then, it was crucial to allow for the local volume expansion as well as usual volume reduction counterpart during structural relaxation.

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