Comparison of Structural Relaxation Behavior in As-Cast and Pre-Annealed Zr-Based Bulk Metallic Glasses Just below Glass Transition

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The α-relaxation of pre-annealed Zr53Cu30Ni5Al10 bulk metallic glasses (BMGs) was compared with that of as-cast Zr-based BMGs including Zr37Cu20Ni5Al10. The α-relaxation was investigated by volume relaxation. The relaxation behavior was well described by a stretched exponential relaxation function, \( \Phi(t) \sim \exp[-(t/\tau_\alpha)^\beta] \), with the isothermal relaxation time, \( \tau_\alpha \), and the Kohlrausch exponent, \( \beta_\alpha \). The \( \beta_\alpha \) exhibited the strong temperature dependence for the pre-annealed BMG, while the weak temperature dependence was visualized for the as-cast BMG similar to the dynamic relaxation. The \( \tau_\alpha \)'s were modified by Moynihan and Narayanaswamy-Tool-Moynihan methods that reduce the difference in the thermal history of sample. As a result, the relaxation kinetics in the glass resembled that of a liquid deduced from the behavior of viscosity in the supercooled liquid. [doi:10.2320/matertrans.M2015023]

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1. Introduction

When the bulk metallic glasses (BMGs) are subjected to dynamic mechanical analysis (DMA) of the relaxation behavior in the supercooled liquid region near the glass transition temperature, \( T_g \), they exhibit the α-relaxation or the main relaxation due to corporative rearrangement of atoms. Despite short relaxation times in supercooled liquid, the DMA can keep up with the response of liquid in a thermal equilibrium. However, it is very difficult to successfully perform the static relaxation analysis (SRA) because of reduced relaxation times in the supercooled liquid state. On the other hand, for the glassy solid state, the SRA enables us to investigate the relaxation process with sufficient reliability because of the prolonged relaxation times. Particularly, the isothermal relaxation experiments at sufficiently lower temperatures than \( T_g \) are best carried out by SRA, which can measure long relaxation times of the order of 10^8 s. According to SRA of BMGs in the glassy solid region, the relaxation is identified as the α-relaxation and its isothermal behavior is well described by a stretched exponential function, \( \Phi(t) \sim \exp[-(t/\tau_\alpha)^\beta] \), with the relaxation time, \( \tau_\alpha \) and the Kohlrausch exponent or the Kohlrausch-Williams-Watts parameter, \( \beta_\alpha \). It has been observed that the behavior of the Kohlrausch exponent, \( \beta_\alpha \), is different for the static and dynamical relaxations near \( T_g \). The temperature dependence of \( \beta_\alpha \) is more pronounced for static experiments, and is characterized by a trend that \( \beta_\alpha \) approaches unity near \( T_g \) with increasing annealing temperature. On the other hand, in the case of the dynamical relaxation, the value of \( \beta_\alpha \) was found to be always around 0.5 for various BMGs including Zr-based quaternary and quinary BMGs, such as Vit1, Vit106a and Vit4, Pd-based BMGs and La-based BMGs.5 Although the result suggests that the dynamic relaxation time appears to be more widely distributed than that of the static relaxation, the plausible explanation is not presented so far. The SRA assumes that the thermodynamic states experienced by the glass during relaxation are equivalent to supercooled liquid states. Thus the relaxation process depends on both the initial thermodynamic state as well as the final one. However, after sufficient pre-annealing or pre-stabilizing the as-cast BMG the relaxation time becomes independent of the initial condition. In order to achieve this process, a sophisticated procedure is required in which isothermal relaxation experiments at \( T \pm \Delta T \) are carried out with different temperature steps of \( \Delta T \) and, after that, the limit of \( \Delta T \to 0 \) is taken as previously pointed out.4,3 In reality, however, it is very difficult to accomplish such isothermal relaxation experiments at different relaxation temperatures. Instead, the Moynihan method and Narayanaswamy-Tool-Moynihan method have been used to estimate the relaxation time by compensating the thermal history of organic and non-organic glasses. The former method was already applied to some metallic glasses,5 but the later is not within our knowledge.

In the present study, we investigated the pre-annealing effect on the α-relaxation of Zr53Cu30Ni5Al10 BMGs in a region under \( T_g \) by SRA. The isothermal relaxation experiment was also performed for a variety of Zr-based BMGs to compensate for a serious shortage for relaxation data of as-cast BMGs.

2. Experimental Procedure

Master alloys, Zr_{x}Cu_{90-x}Al_{10} (x = 45–65), Zr_{57}Cu_{30}M_{1}Al_{10} (M = Ti, Pd), Zr_{60}Cu_{27}M_{1}Al_{10} (M = Ag, Au), Zr_{70}Cu_{6}Ni_{10}A_{8} and Zr_{50}Cu_{15}Ni_{10}Al_{10} were prepared by arc-
melting the mixture of constituent metal tips with a purity of 99.99 at%, where, regarding Zr tips, the crystal-Zr with less oxygen content (≈ 100 ppm) was used. Rod-shaped BMGs were produced by tilted copper-mold casting or suction copper-mold casting techniques with a variety of sizes from 3 to 8 mm in diameter. The amorphous nature of the sample was verified by X-ray diffraction with Cu-Kα radiation and differential thermal analysis (DTA) conducted at a heating rate of 0.33 K/s. The thermodynamic parameters of glasses such as the glass transition temperature (Tg), crystallization temperature (Tc) are summarized in Table 1. The relaxation behavior was investigated by volume relaxation, where the volume of glass was determined from the physical density measured at room temperature after relaxing the sample under a given condition. The bulk sample, which had a weight of about 2 g, was put into the evacuated quartz tube under a given condition. The bulk sample, which had a weight of about 2 g, was put into the evacuated quartz tube with pure Ar gas. The tube was placed into a pre-heated salt-bath for annealing the sample, and it was quickly quenched into water held at room temperature just after accomplishing a given relaxation. We believe that the structure of the relaxed glass was quenched during such an operation except for the thermal expansion effect. The surface of sample was mechanically polished with fine abrasive papers to remove the oxide layer formed during annealing prior to the density measurement. The detail of the density experiment is shown in Refs. 6, 7).

3. Results

3.1 Kinetics of the static α-relaxation

The volume relaxation for as-cast and pre-annealed Zr55Cu30Ni5Al10 BMGs was investigated at temperatures below Tg. Hence, the pre-annealed state was prepared by annealing the as-cast BMG at Tp = 715 K for tps = 300 s in the supercooled liquid region to reduce the variation of the fictive temperature and to equilibrate the as-cast state. We confirmed that the volume of the as-cast BMG almost reached the saturation in 300 s. Also we measured the incubation time, tinc of crystallization at 720 K (5 K higher than Tp) by isothermally holding the as-cast sample at 720 K in a DSC apparatus. A tinc of 460 s was estimated and it is much longer than tps at Tp. Therefore, we conclude that no crystallization was occurred during pre-annealing at 715 K (highest annealing temperature in the present study). Figure 1 shows the volume change, ∆V(t)/V0 = [V(t) − V0]/V0, at room temperature for (a) the as-cast and (b) the pre-annealed BMGs that were relaxed for time t at various temperatures, where V0 denotes the initial volume, V(t), the volume of the as-cast BMG, and, Vp, the volume of the pre-annealed BMG. The volume decreases with increasing time and the total changes in volume during the relaxation are larger at lower temperatures than at high temperatures. Such a trend is in accord with the general criterion of free volume model.6,8) The kinetics of volume relaxation was well described by a SER-function with the relaxation time, τα, and the Kohlrausch exponent, βα, as below.

ΔV/V0 = (∆V/V0)0[1 − exp(−t/τα)βα]  \( (1) \)

The relaxation times and the Kohlrausch exponents are summarized in Table 2. The relaxation time is plotted against the annealing temperature, T, in Fig. 2(a), where the relaxation time of BMG heavily pre-annealed at 673 K for 1.8 × 10^4 s is shown for comparison.5) Hence, the result of enthalpy relaxation is due to Qiao.9) The relaxation time of heavily pre-annealed BMG (at 673 K) is much longer than those of the as-cast BMG and the weakly pre-annealed BMG (at 715 K), and the difference becomes more pronounced at lower temperatures. We previously fitted the relaxation time of the heavily pre-annealed BMG to the VFT equation, τα = τα0 exp[D*/T0V/(T − T0V)], with a pre-factor τα0 = 1.1 × 10^{-14} s, a fragility parameter D* = 44.2, a VT temperature T0V = 311 K.5) Also, using these parameters, the fragility, m = d(log τa)/d(T/T0V)|τa=τa ≈ 29 was determined, where T = T0V[1 + D*/ln{2 − log τa0}]/T0V ≈ 685 K is the specific temperature that gives τa of 100 s. On the other hand, the temperature dependence of the relaxation times for the as-cast and weakly pre-annealed BMGs (at 715 K) cannot be fitted by a VFT equation and/or an Arrhenius equation. The Kohlrausch exponent, βα, is plotted as a function of T in Fig. 2(b). The temperature dependence of βα is appreciable for the pre-annealed BMGs and the trend is analogous to the result for the static α-relaxation as reported elsewhere.5,6,9–11) However, the as-cast BMG exhibits an interesting feature that the exponent retains a low value, approximately 0.5, even at
Fig. 1 Volume changes, $\Delta V/V_{as}$ and $\Delta V/V_g$ of (a) as-cast, (b) pre-annealed (715 K) Zr$_{55}$Cu$_{30}$Ni$_{5}$Al$_{10}$ BMGs during isothermal structural annealed (715 K) and blue (673 K-pre-annealed) solid circles. Also, Kohlrausch exponents, $\beta$'s, are fitted to red straight line (as-cast BMGs) and black line (pre-annealed BMGs).

Fig. 2 (a) Relaxation time, $\tau$, and (b) Kohlrausch exponent, $\beta$, of as-cast and pre-annealed Zr$_{55}$Cu$_{30}$Ni$_{5}$Al$_{10}$ BMGs, where results of enthalpy relaxation are according to Ref. 9 (solid triangle). Also, Kohlrausch exponents, $\beta$'s, which are modified by Narayanaswamy-Tool-Moyinham method, are denoted by red (as-cast), green (715 K-pre-annealed) and blue (673 K-pre-annealed) solid circles. $\beta$'s were fitted to eq. (6) and the result is shown in red solid lines. The black solid circle indicates $\beta$ calculated by eq. (7) for 673 K-pre-annealed BMGs.

Fig. 3 (a) $\tau$'s and (b) $\beta$'s of as-cast Zr$_{55}$Cu$_{35}$Al$_{10}$, Zr$_{55}$Cu$_{35}$Pd$_{3}$Al$_{10}$, Zr$_{55}$Cu$_{35}$Ti$_{3}$Al$_{10}$, Zr$_{55}$Cu$_{35}$Ni$_{15}$Al$_{5}$, and Zr$_{55}$Cu$_{35}$Ni$_{15}$Al$_{5}$ and Zr$_{55}$Cu$_{35}$Ni$_{15}$Al$_{10}$ BMGs together with pre-annealed Zr$_{55}$Cu$_{35}$Al$_{10}$ and Zr$_{55}$Cu$_{35}$Ni$_{15}$Al$_{10}$ BMGs. $\tau$'s are fitted to red straight line (as-cast BMGs) and black line (pre-annealed BMGs).

$T_g = 680$ K, which is comparable with those obtained from the dynamic mechanical analysis (DMA) just below and above $T_g$. To further examine this point, we conducted the volume relaxation experiments just below $T_g$ for the as-cast BMGs with compositions of Zr$_{55}$Cu$_{35}$Al$_{10}$, Zr$_{55}$Cu$_{35}$Al$_{10}$, Zr$_{55}$Cu$_{35}$Pd$_{3}$Al$_{10}$, Zr$_{55}$Cu$_{35}$Ti$_{3}$Al$_{10}$, Zr$_{55}$Cu$_{35}$Ni$_{15}$Al$_{5}$ and Zr$_{55}$Cu$_{35}$Ni$_{15}$Al$_{5}$ BMGs. Also, regarding the Zr$_{55}$Cu$_{35}$Al$_{10}$ glass, the as-cast glass was pre-annealed at 691 K (10 K below $T_g$) for 1.8 x $10^3$ s to examine pre-annealing effects. The values of $\tau$ and $\beta$ of these BMGs are presented in Figs. 3(a) and (b) as a function of $T/T_g$, together with those of the Zr$_{55}$Cu$_{35}$Ni$_{15}$Al$_{10}$ glass. The data on $\tau$'s largely overlap irrespective of alloy compositions with some scatter. On the other hand, the data on $\beta$'s follow two separate straight lines, for the as-cast BMGs and the pre-annealed BMGs. Thus, we conclude that the weak temperature dependence and the small values of $\beta$ are generally observed for the static relaxation of the as-cast Zr-based BMGs in a temperature region close to $T_g$, which is similar to the DMA result.

3.2 Maximum volume change during relaxation

The maximum volume change, $\Delta V/V_{as}$, was determined from the volume relaxation curves as shown in Fig. 1, where $V_{rel}$ indicates the volume at room temperature for the relaxed sample. Figure 4 presents $\Delta V/V_{as}$, as a function of the temperature difference, $T-T_g$. $\Delta V/V_{as}$ becomes smaller (negatively larger) as $T$ deviates from $T_g$, which seems to represent a trend except for Zr$_{57}$Cu$_{30}$Pd$_{3}$Al$_{10}$
and Zr70CuNi16Al8 glasses, where regarding the Zr55Cu30Ni5Al10 glass the mean values calculated with the as-cast and pre-annealed samples are plotted. Figure 5 schematically shows the volumes of glasses and supercooled liquids in a range from room temperature, \( T_r \), up to around the fictive temperature, \( T_f \), of the as-cast BMG. Each curve defines the thermal expansion coefficient, \( \alpha_{g,as} \), \( \alpha_{g,rel} \), \( \alpha_l \), where the coefficient of the as-cast glass is assumed to be equal to that of the relaxed glass, i.e. \( \alpha_{g,as} \approx \alpha_{g,rel} = \alpha_g \) and \( \alpha_l \) is the coefficient of a supercooled liquid. When the as-cast sample is held at a given temperature, \( T \), below \( T_f \), it could relax to a state near the volume curve of the supercooled liquid. If \( \alpha_g \) and \( \alpha_l \) are the same for all the alloy systems studied, \( \Delta V/V_{\text{as}} \) could be scaled as a function of \( T - T_f \). The information about \( T_f \) is limited, so far, whereas we alternatively used \( T - T_g \) in Fig. 4. Assuming that the thermal expansion coefficient, \( \alpha = (\partial \ln V/\partial T)_p \), has negligible temperature dependence under constant pressure, the volumes of glasses and supercooled liquid can be expressed as, \( \bar{V}_{\text{g},as}(T) = \bar{V}_g(T) \exp[\alpha_g(T - T_P)] \). \( \bar{V}_{\text{g},rel}(T) = \bar{V}_g(T) \exp[\alpha_g(T - T_{Pf})] \approx \bar{V}_g(T) \). In addition, the relation, \( V_f(T) = \bar{V}(T) \exp(\alpha(T - T_P)) \), is available, where \( V_f(T) \) denotes the specific volume of a supercooled liquid at \( T_f \). With simple mathematical consideration, \( \Delta V/V_{\text{as}} = [V_{\text{rel}}(T_f) - V_{\text{as}}(T_f)]/V_{\text{as}}(T_f) \) is derived as follows.

\[
\left( \frac{\Delta V}{V_{\text{as}}} \right)_{\text{eq}} = \frac{\exp[\alpha_g(T - T_f)] - \exp[\alpha_l(T - T_l)]}{\exp[\alpha_l(T - T_l)]}
\]

\[
= \exp[\alpha_g(T - T_f)] \left[ \exp(\Delta \alpha(T - T_f)) - 1 \right]
\]

where the difference in the thermal expansion coefficient is defined as \( \Delta \alpha = \alpha_l - \alpha_g \). The fitting procedure for the as-cast and pre-annealed Zr55Cu30Ni5Al10 glasses gave, \( \Delta \alpha \approx 1.3 \times 10^{-5} \text{K}^{-1} \) and \( T_f \approx 738 \text{K} \), and the solid line in Fig. 4 denotes the calculation. We previously reported that \( T_f \) was approximately 720 K for the Zr55Cu30Ni5Al10 glass used.\(^6\)

Then \( T_f \) was defined as a crossing point between the atomic volume curve of the as-cast glass, \( \bar{V}_{\text{g},as}(T_f) \approx \bar{V}_g[1 + \alpha_g(T - T_f)] \), with \( \alpha_g \approx 3.2 \times 10^{-5} \text{K}^{-1} \) and the corresponding liquid curve, \( \bar{V}_l(T) \). The liquid volume per atom, \( \bar{V}_l(T) \approx \bar{v}_l + \nu \bar{v}_g(T) \), was given with the free volume, \( \bar{v}_l(T) = \bar{v}_m(T - T_r) + \left( \bar{t}_m(T_r) - 1 \right) \left( T_m(T) \right)^{1/2} / 2B \), and parameters, \( \bar{v}_m = 1.84 \times 10^{-23} \text{cm}^3 \), \( T_m = 605 \text{K} \), \( \nu = \bar{v}_m / 2B = 6.42 \times 10^{-28} \text{cm}^2 / \text{K} \). The \( \bar{v}_l(T) \) was measured by electro-levitation and volume relaxation experiments. Using this formula for \( \bar{v}_l(T) \), \( \alpha_l(738) \approx 6.0 \times 10^{-5} \text{K}^{-1} \) was calculated and this value is close to the experimentally determined one, \( \alpha_l = 4.5 \times 10^{-5} \text{K}^{-1} \). As seen in Fig. 4, the volume change of the Zr55Cu30Pd3Al10 glass is larger than those of other glasses. Although a large volume change of the Zr57Cu30Pd3Al10 glass is phenomenologically explained by a consideration that \( \Delta \alpha \) may be larger than for other alloy systems, its origin is not identified so far. Regarding the Zr70CuNi16Al8 glass, its somewhat small volume change may be caused by the structural peculiarity in comparison with the Zr60Cu30Al10 glass system, which may be related to the fact that the Zr70CuNi16Al8 glass causes the precipitation of a quasi-crystal phase instead of a crystalline phase.\(^12\)

4. Discussion

4.1 Moynihan, Narayanaswamy-Tool-Moynihan methods

The relaxation function, \( \Phi(t) \), is generally defined as, \( \Phi(t) = \int_0^\infty g(t) \exp(-t/\tau)d\tau \), where \( g(t) \) is the distribution function of relaxation time \( \tau \). Moynihan proposed that when the isothermal relaxation is executed near the thermal equilibrium, the mean relaxation time, \( \tau_M \), could be used to describe the relaxation kinetics.\(^13\) We can obtain easily the mean relaxation time, \( \tau_M \), as, \( \Phi(t)dt = \int \tau g(\tau)d\tau = \tau_M \). Furthermore, when the \( \Phi(t) \) is approximated as \( \Phi(t) \approx \exp(-(t/\tau_M)^\beta) \), \( \tau_M \) is given as,

\[
\tau_M = \tau_M \Gamma(1/\beta)/\beta = \tau_m l(\beta)
\]

where \( \Gamma \) is the gamma function and \( \tau_m \) is equivalent to the isothermal relaxation time, \( \tau_M \), in the present study. The function \( l(\beta) \) monotonously decreases with increasing \( \beta \). The modification on \( \tau_m \) is more efficient for smaller \( \beta \), for instance,
Thus we conjecture, dependence of Kohlrausch index methods. Secondly, we conclude that a strong temperature upon the Moynihan or Narayanaswamy-Tool-Moynihan is summarized in Table 3 together with including the as-cast and pre-annealed ones, and the result determined. Although the different depends on the thermodynamic state reached at $T_0$, the NTM method accounts for the thermal history of the glass and derived the formula,

$$\frac{T_t - T}{T_0 - T} = \frac{P_f(t) - P_{T,\infty}}{P_{T,0} - P_{T,\infty}} = \Psi_f(t)$$

where $\Psi_f(t)$ is the value of physical property at time $t$, and $P_{T,0}$ and $P_{T,\infty}$ correspond to its initial and saturated values at $T$, respectively. The concept behind this method is that the change in the short-range order, $T_0$, of glass structure during isothermal annealing is proportional to the corresponding change in the physical property. The relaxation function, $\Psi_f(t)$, at $T$ is expressed as,

$$\Psi_f(t) = \exp\left[-\left(\int_0^t \frac{1}{\tau_0} + \varepsilon\right)\right]$$

$$\tau_0 = A \exp[x \Delta_h/RT + (1 - x) \Delta h/RT]$$

where $A$, $x$, $\Delta h$ and $\varepsilon$ are disposal parameters consistently determined by fitting operation, where $T_0$ depends on itself through eq. (5). The relation $T_t = T$ is generally satisfied in the supercooled liquid region. Then the relaxation time is reduced to $T_0 = A \exp[\Delta h/RT]$ under the assumption of the Arrhenian behavior of the relaxation kinetics, and the relaxation function is reduced to the conventional form, $\Psi_f(t) = \exp[-t/\tau_0]$. The relaxation time, $\tau_\text{NTM}$, was calculated by numerically integrating the optimized relaxation function from $t = 0$ to infinity. We estimated $\tau_\text{NTM}$ and $\beta_\text{NTM}$ with volume relaxation data for several BMGs including the as-cast and pre-annealed ones, and the result is summarized in Table 3 together with $A$, $x$, and $\Delta h$ determined. Although the $x$ (≈ 1.07) in the case of $T = 653$ K is slightly beyond the limitation, $x = 1$, this is due to experimental uncertainty. The isothermal relaxation time, $\tau_0$, becomes larger after NTM correction and $\tau_\text{NTM}$ is compatible with $\tau_0$ as shown in Fig. 6. Meanwhile $\beta_\text{NTM}$ is compatible with $\beta_0$'s of 673 K-pre-annealed BMGs as shown in Fig. 2. Thus we conjecture, first, that the isothermal relaxation time of BMGs exhibit the modification effect for raw data based upon the Moynihan or Narayanaswamy-Tool-Moynihan methods. Secondly, we conclude that a strong temperature dependence of Kohlrausch index $\beta_0$ is an inherent property common to pre-annealed BMGs, and it is unchanged even after the modification due to the NTM method.

### 4.2 Temperature dependence of the Kohlrausch exponent, $\beta_0$

It was revealed by the present study that the as-cast BMG exhibits a weak temperature dependence of the $\beta_0$ in accordance with the trend indicated by DMA. The small $\beta_0$ means that the relaxation time is widely distributed. The $\alpha$-relaxation is regarded as a collective thermal activation process caused by surmounting potential energy barriers between atoms. Thus the randomness of potential barrier height, in other word, the topological short-range order directly connects to the distribution of relaxation times. The as-cast BMG surely possesses a smaller amount of topological short-range order than the pre-annealed BMG, resulting in a wider relaxation time spectrum. Stillinger examined the temperature dependence of $\beta_0$ in terms of the concept of the potential energy landscape (PEL) and derived the formula,

$$1/\beta_0 = 1 + (\gamma + 1/k_B T)/\eta$$

where $\eta$, $\gamma$ are regarded as the material-specific positive parameters, and $k_B$ is the Boltzmann’s constant. The eq. (6) is applied to $\beta_0$ of the pre-annealed and as-cast BMGs as shown in Fig. 2. Although the fitting is apparently good, negative $\gamma$ is obtained and this is in disagreement with Stillinger’s prediction. Vilgis derived another equation to explain the temperature dependence of Kohlrausch exponent based upon the concept of PEL, which predicts the $\beta_0$ at temperature $T_g^*$ as,

$$\beta_0(T_g^*) = 1 - \frac{T_0^V}{T_g^*} \sqrt{D^*}$$

where $D^*$ and $T_0^V$ are the VFT parameters mentioned in the previous section. The $\beta_0$ ($T_g^* \approx 685$) ≈ 0.93 was evaluated by the VFT parameters obtained for the isothermal relaxation times of heavily pre-annealed BMG, which was also compatible with the extrapolation from the Kohlrausch exponents obtained below $T_g$ as seen in Fig. 2. Equation (7) quantitatively predicts the magnitude of the Kohlrausch exponent at $T_g^*$, which includes various static relaxation studies reported for Zr-Be based BMGs and $\beta_0$ ($T_g^*$)'s of 0.84~0.91 are calculated with reported VFT parameters. However, the effectiveness of Vilgis’s prediction is limited to pre-annealed or pre-stabilized BMGs and not suitable for as-cast BMG, because the VFT fitting seems to be inappropriate for as-cast BMG.

### 4.3 Consistency of the relaxation time in both supercooled liquid and glass solid

The relaxation kinetics of the supercooled liquid has been mainly investigated by dynamic mechanical analysis (DMA), because the static measurement is not capable of measuring the short relaxation time in the supercooled liquid. When the relaxation in the glassy region is induced over a sufficiently long period of time, the thermodynamic state achieved is close to the supercooled liquid state at ambient temperature. Therefore, the static measurement is suited to the long relaxation processes. The relaxation times of Zr$_{55}$Cu$_{30}$Ni$_{15}$Al$_{10}$ glasses are plotted against $T_g^*/T$ in Fig. 7 for both static result in the glassy state and dynamic one in the supercooled liquid. The static relaxation times include all $\tau_0$ and $\tau_\text{NTM}$ for samples pre-annealed at 673 K, in addition, at 653, 660, 665, and 673 K for both the as-cast and 715 K-annealed ones. The VFT fitting was performed for these relaxation times and the result is summarized in Table 4. The values of $\tau_0$, $D^*$, $T_0^V$...
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are compatible with the VFT parameters, that were estimated by Narayanaswamy-Tool-Moynihan method, and disposal parameters, A, x, AΔ determined. They predicted enhancement of atomic mobility for as-cast BMG. Moynihan and NTM methods can reduce the difference in the static relaxation in the present case, which is in accordance with the result of Yamasaki. The systematic isothermal relaxation experiments for the present BMG in the supercooled liquid state are compatible with the VFT parameters for isothermal relaxation time, τ_a, open symbols. They exhibited shorter relaxation times, τ_α, than those obtained by pre-annealed BMGs particularly in a low temperature region, which can be explained by the predicted enhancement of atomic mobility for as-cast BMG. Moynihan and NTM methods can reduce the difference in the kinetic behavior between the samples with different initial thermodynamic conditions, which is accomplished by taking into account the difference in the equilibrium viscosity of the BMG in the supercooled liquid state. The DMA results are reported for the Zr_{55}Cu_{30}Ni_{5}Al_{10} glass by Qiao, and those for the Zr_{46.75}Ti_{18.25}Cu_{7.5}Ni_{10}Be_{27.5} (Vit4) glass reported by Wen are also shown for comparison. Yamashita measured the equilibrium viscosity of the Zr_{55}Cu_{30}Ni_{5}Al_{10} BMG in the supercooled liquid state. In the supercooled liquid, the relation, τ = η/G, is satisfied between the dynamic relaxation time τ and the viscosity η under the Maxwell’s model for viscoelastic materials, where G is the shear modulus at the inﬁnite limit of frequency. In the present case, G = 8 GPa is assumed and the time, η/G, is plotted against, T_g*/T, where T_g* (= 679 K) is the speciﬁc temperature that gives η = 10^{12} Pa·s. The result of the VFT ﬁtting to the relaxation times of the supercooled liquid is summarized in Table 4 together with the fragility m, calculated. Basically, the similar kinetic behavior should be expected for the relaxation process in both supercooled liquid and the glass regions. The static relaxation in the present study exhibits the kinetic behavior slightly different from the dynamic and viscosity experiments as seen in Fig. 7. However, it should be noted that the kinetic behavior is signiﬁcantly different between the dynamic and viscosity experiments.

5. Conclusion

The systematic isothermal relaxation experiments for the as-cast Zr-based BMGs revealed that, first, the kinetics of the α-relaxation was characterized by slight temperature dependence of β_m, which is in accordance with the result of DMA. Secondly, they exhibited shorter relaxation times, τ_α, than those obtained by pre-annealed BMGs particularly in a low temperature region, which can be explained by the predicted enhancement of atomic mobility for as-cast BMG. Moynihan and NTM methods can reduce the difference in the kinetic behavior between the samples with different initial thermodynamic conditions, which is accomplished by taking into account the difference in the equilibrium viscosity of the BMG in the supercooled liquid state.

Table 3 Relaxation time, τ_α/s, modified by Moynihan and Narayanaswamy-Tool-Moynihan methods are shown together with isothermal relaxation time, τ_a (open symbols). Cross symbols represent the result of Moynihan method and solid circles correspond to NTM method, where red, green and blue symbol corresponds to as-cast, 715 K-pre-annealed and 673 K-pre-annealed BMGs, respectively.

Table 4 VFT parameters, τ_α, D*, T_g, m, of static, dynamic relaxation times and viscosity, and related parameters, T_m*, T_g*, m, that were determined.

Fig. 6 Relaxation times, τ_α/s, modified by Moynihan and Narayanaswamy-Tool-Moynihan methods are shown together with isothermal relaxation time, τ_a (open symbols). Cross symbols represent the result of Moynihan method and solid circles correspond to NTM method, where red, green and blue symbol corresponds to as-cast, 715 K-pre-annealed and 673 K-pre-annealed BMGs, respectively.

Fig. 7 The relaxation times of Zr_{55}Cu_{30}Ni_{5}Al_{10} BMGs (open blue circles) including isothermal, M- and NTM-modified ones are plotted against T_g*/T, together with the DMA results (Ref. 19) for Zr_{55}Cu_{30}Ni_{5}Al_{10} (green solids) and Ref. 17 for Vit4 (red solids), and calculations from viscosity (black solids) (Ref. 20). Also, solid lines denote the fitting result to VFT equations.
account of the thermal history of the sample into a
calculation. The isothermal relaxation time of as-cast sample
increased after modification and approached that of pre-
annealed sample. In order to examine the effectiveness
of modification, we compared the relaxation behavior of the
$Zr_{55}Cu_{30}Ni_{5}Al_{10}$ BMG with the dynamic and viscosity
results. Then we used the relaxation times of 673 K-
preannealed samples over the entire temperature region,
and those of the 715 K-preannealed and as-cast samples in a
temperature range between $|T - T_g| \approx 20$ K. The $\tau_\alpha(T)$ curve
was close to the relaxation times predicted from the viscosity
$\eta(T)$ curve in the supercooled liquid region, but it did not
fully agree with the result of DMA.

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REFERENCES

4) G. W. Scherer: Relaxation in Glass and Composites, (Krieger Pub
6) O. Haruyama, Y. Nakayama, R. Wada, H. Tokunaga, T. Okada, T.
7) O. Haruyama, T. Mottate, K. Morita, N. Yamamoto, H. Kato and T.
1376.
14 (1973) 122–125.
14) C. T. Moynihan, P. B. Macedo, C. J. Montrose, P. K. Gupta, M. A.
17) P. Wen, D. Q. Zhao, M. X. Pan, W. H. Wang, Y. P. Haung and M. L.
20) T. Yamazaki, S. Maeda, Y. Yokoyama, D. Okai, T. Fukami, H. M.
4732.