Correlation of dynamic and quasistatic relaxations: The Cox–Merz rule for metallic glass

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The correlation of quasistatic and dynamic relaxations was discussed in a typical strong $Zr_{55}Al_{10}Ni_5Cu_{30}$ metallic glass from room temperature to T_g. The quasistatic relaxation behavior, investigated by high temperature compressive testing at a constant strain rate, was compared with dynamic tensile relaxation behavior. A correlation equation of the dynamic frequency and quasistatic strain rate was successfully deduced, and then its validity was experimentally confirmed in a fragile metallic glass. Using this correlation, the Cox–Merz rule, derived for correlating the steady-state and dynamic viscosities of the polymers, is found to be applicable to metallic glasses. © *2009 American Institute of Physics*. [doi:10.1063/1.3272922]

In the glassy state, metallic glass exhibits a relaxation phenomenon, an essential nature of thermodynamically nonequilibrium glassy materials. This relaxation phenomenon is known to dominate the mechanical properties (elastic modulus, yield stress, and toughness[1–4]) of the glasses. In a mechanical approach, the relaxation behavior of metallic glass has been investigated by the static stress relaxation with constant strain,[5] creep with constant stress,[6] the quasistatic deformation with constant strain rate,[7–10] or the dynamic vibration with cyclic sinusoidal stress or strain.[11–14] Because the elastic and viscous properties can be deduced individually from the phase difference between the stress and strain cycles, the frequency and temperature dependence of these properties can be easily obtained through frequency and temperature scans. Thus, the dynamic method is useful for investigating the relaxation behavior. This method provides information on the relaxation variation and distribution caused by the glass transition (α), as well as various kinds of sub-T_g relaxations (β, γ, etc.). Linking the information from the dynamic method to that from the (quasi) static method can provide information for further discussions on the quasistatic mechanical properties in metallic glasses, e.g., yielding, fracture, and stress-overshoot, with the dynamic relaxation characteristics. However, few reports have combined information from these modes. In this study, we investigate the temperature dependence of the quasistatic relaxation behavior from the room temperature (T_{RT}) to T_g in a typical strong $Zr_{55}Al_{10}Ni_5Cu_{30}$ bulk metallic glass, and then compare it with the dynamic relaxation behavior to deduce a correlation equation for the quasistatic strain rate and dynamic angular frequency in metallic glass.

A master ingot of $Zr_{55}Al_{10}Ni_5Cu_{30}$ (at. %) was prepared by the arc-melting technique in a purified argon atmosphere. The metallic glassy rod and ribbon were prepared by copper mold casting and melt spinning techniques, respectively. X-ray scattering, using a Cu-Kα radiation, confirmed the glassy structure of both samples. For the quasistatic high temperature compressive test, the cast rods were cut into pieces (2 mm in diameter and 4 mm in length) and their upper and lower planes were polished in parallel. High temperature compressive tests were carried out with a Servo Parser EHF-EA25 (Shimadzu Co. Ltd.) with a chamber filled with purified argon. For dynamic measurements the glassy ribbon (0.03 mm thick) was cut into ~40 mm long sections. Tensile dynamic tests were carried out with a Solid Analyzer RSA-II (Rheometrics, Inc.). In the present study, a sinusoidal dynamic tensile strain is applied and the replying stress is recorded. Strain amplitude is kept less than 10^{-5} in the linear viscoelastic state during tests.

Figure 1 shows the true compressive stress-strain (S-S) curves in $Zr_{55}Al_{10}Ni_5Cu_{30}$ bulk metallic glass at various isothermal testing temperatures (T_t) from T_{RT} to the calorimetric glass transition temperature (T_g=684 K at a heating rate of 0.67 K/s) under a constant strain rate ($\dot{\varepsilon}$) of 1×10^{-3} s^{-1}. With increasing T_t, the fracture stress (σ_f) decreased gradu-

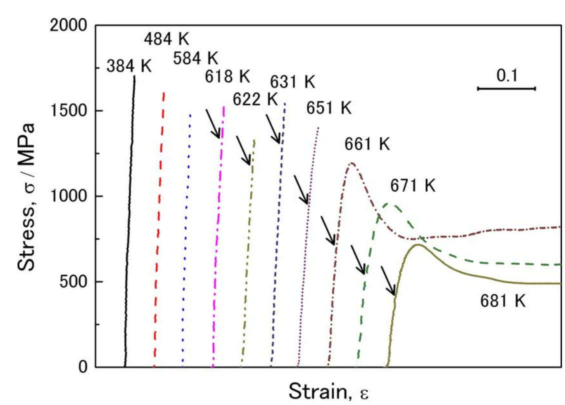

FIG. 1. (Color online) True compressive S-S curves of a $Zr_{55}Al_{10}Ni_5Cu_{30}$ bulk metallic glass at various isothermal testing temperatures (T_t) varied from room temperature (T_{RT}) to glass transition temperature (T_g=684 K at 0.67 K/s). The test strain rate is ~1×10^{-3} s^{-1}. The arrows on the curves indicate the yield points. The nonlinear part observed in curves up to ~200 MPa is due to incomplete contact between the sample and the die.

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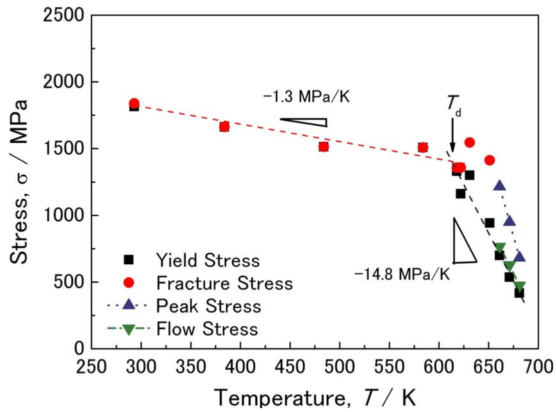

FIG. 2. (Color online) Temperature dependence of the yield stress (σ_y), fracture stress (σ_f), peak stress (σ_p), and steady-state viscous flow stress (σ_s) of a $Zr_{55}Al_{10}Ni_5Cu_{30}$ bulk metallic glass at a strain rate of $1 \times 10^{-3}\ s^{-1}$ at various isothermal testing temperatures varied from room temperature (T_{RT}) to the glass transition temperature (T_g). The standard deviation on the stress is estimated to be $\sim 8\%$.

ally. However, when T_t reached 651 K, which is 95% of T_g, an obvious yielding point, at which the S-S curve departed from the initial linear trend, began to appear. Stress and strain at the yield point and the initial linear slope are defined as yield stress (σ_y), yield strain (ε_y), and apparent Young's modulus (E_{ap}), respectively, in this study. Compressive plastic elongation increased with increasing T_t. When T_t reached 661 K, which is 96% of T_g, the glassy sample did not fracture any more, and the "stress-overshoot" phenomenon, followed by a steady-state non-Newtonian viscous flow, appears in the S-S curves.[7–10] This overshoot tends to decrease with further increasing T_t, and then almost disappears in the vicinity of T_g. In the condition determined by T_t and $\dot{\varepsilon}$, the steady-state Newtonian viscous flow, which is independent of $\dot{\varepsilon}$, appeared with the steady-state flow stress (σ_s).[7–10] Figure 2 demonstrates the T_t dependence of σ_y, and σ_f in addition to the peak stress (σ_p) and σ_s at $T_t \geq 661$ K. σ_y initially decreases gradually with increasing T_t, with a slope of -1.3 MPa/K from T_{RT}, then drastically with a slope of -14.8 MPa/K up to T_g. The cross point of these linear slopes, which is considered to indicate the ductility improvement temperature (T_d) by thermal activation, is estimated to be 613 K ($\sim 0.90\ T_g$). The difference between σ_f and σ_y increases with increasing T_t, up to 651 K, while that between σ_p and σ_y tends to decrease with T_t. Note that σ_y has almost the same value as σ_s; stress returns and equilibrates finally at σ_y after the stress peak. When σ exceeds the yield point, the stress-induced structural relaxation of the glass to viscous liquid starts to be driven by a stress gap (σ-σ_y).[9,10] If the relaxation time (τ) becomes dynamically short enough to complete the whole stress-induced relaxation process ($\tau \ll \dot{\varepsilon}^{-1}$) before fracture, the viscoelastic glassy solid succeeds in transforming into a steady-state non-Newtonian viscous liquid. However, if τ is comparable or rather longer than $\dot{\varepsilon}^{-1}$, a catastrophic localized shear fracture disturbs the completion of the relaxation process after showing a little plastic elongation. Thus, using a relaxation function, σ_y can be expressed by[15]

$$\sigma_y = E_{ap}\varepsilon_y \approx \sigma_s = E_u \dot{\varepsilon} \tau \left\{ 1 - \exp\left[- \frac{1}{\left(\frac{\dot{\varepsilon}}{\varepsilon_y}\right)\tau} \right] \right\}, \tag{1a}$$

where, E_u, is the unrelaxed Young's modulus measured by the dynamic (ultrasonic) vibration, the frequency of which is significantly higher than the inverse of the relaxation time of the glass.[1] ε_y is recognized in the polymer science field as the critical strain at which the initial glassy structure becomes further disordered dynamically. From Eq. (1a), E_{ap} can be expressed by

$$E_{ap} \approx E_u \left(\frac{\dot{\varepsilon}}{\varepsilon_y}\right) \tau \left\{ 1 - \exp\left[- \frac{1}{\left(\frac{\dot{\varepsilon}}{\varepsilon_y}\right)\tau} \right] \right\}. \tag{1b}$$

The viscoelasticity of a glassy solid has been well measured by various dynamic methods because the viscous effect causes a phase shift between the sinusoidal strain and stress waves. The dynamic complex modulus (E^*) of the Maxwell element, which is sometimes used for predicting the viscoelastic behavior of metallic glasses, can be expressed by[16]

$$|E^*| = \sqrt{(E')^2 + (E'')^2} = E_u \frac{\omega\tau}{(1+\omega^2\tau^2)^{1/2}}, \tag{2}$$

where E', E'', and ω are the storage modulus corresponding to the elastic energy, the loss modulus corresponding to the energy spent as heat or a phase or structural change in a dynamic cycle, and the angular frequency (rad s^{-1}), respectively. If we use an approximation,[15]

$$\frac{1}{[1+\omega^2\tau^2]^{1/2}} \cong 1 - \exp\left(-\frac{1}{\omega\tau}\right). \tag{3}$$

Equation (2) yields

$$|E^*| \cong E_u \omega\tau \left[1 - \exp\left(-\frac{1}{\omega\tau}\right) \right]. \tag{4}$$

The approximation by Eq. (3) works well in both $\omega\tau \ll 1$ and $\omega\tau \gg 1$, and causes a maximum error of $\sim 10\%$ around $\omega\tau \sim 2$. Considering the physical meaning of $|E^*|$ ($\approx E'$ when $T_t < T_g$), this value equals E_{ap}, although the deformation mode is different, i.e., dynamic and quasistatic modes,

$$|E^*| = E_{ap}. \tag{5}$$

Therefore, we finally obtain a correlation of ω and $\dot{\varepsilon}$ by comparing Eqs. (1b) and (4),

$$\omega = \frac{1}{\varepsilon_y}\dot{\varepsilon}. \tag{6}$$

Although ε_y shows a little T_t dependence, especially in $T > T_d$, for convenience, we assume $\varepsilon_y \sim 0.02$ in Eq. (6) for $T_{RT} \leq T_t \leq T_g$. Figure 3(a) demonstrates T_t dependence of E_{ap} at $\dot{\varepsilon} = 1 \times 10^{-3}\ s^{-1}$ obtained from Fig. 1. E_{ap} decreases gradually up to T_d, then drastically with increasing T_t in the same manner as σ_y (see Fig. 2). From Eq. (6), ω, which effectively corresponds to $\dot{\varepsilon}$, is estimated at $\sim 50 \times 1 \times 10^{-3} = 5 \times 10^{-2}$ rad s^{-1}. Using a melt-spun ribbon of the same metallic glass, E^* at $\omega = 5 \times 10^{-2}$ rad s^{-1} is measured from T_{RT} up to T_g, then compared with E_{ap} in Fig. 3(a). Figure 3(b) also demonstrates E^* and corresponding E_{ap} in a typical fragile $Pd_{40}Ni_{10}Cu_{30}P_{20}$ metallic glass.[17] In both typically

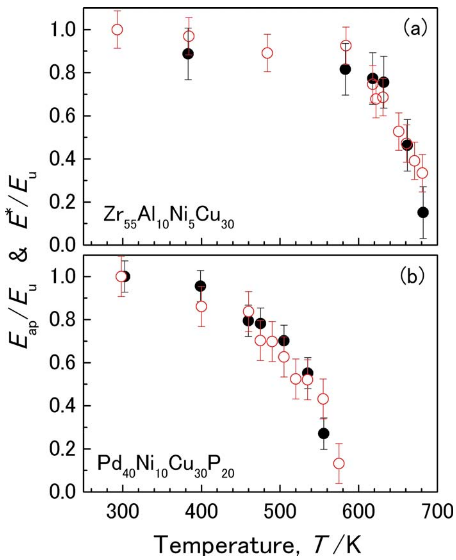

FIG. 3. (Color online) Isothermal testing temperature dependence of the apparent Young's modulus (E_{ap}) at a quasistatic strain rate of 1×10^{-3} s^{-1} and of the complex modulus (E^*) at a dynamic angular frequency of 5×10^{-2} rad s^{-1} from room temperature (T_{RT}) to the glass transition temperature (T_g) in a strong $Zr_{55}Al_{10}Ni_5Cu_{30}$ metallic glass ($T_g\sim684$ K at 0.67 K/s) (a) and in a fragile $Pd_{40}Ni_{10}Cu_{30}P_{20}$ metallic glass ($T_g\sim575$ K at 0.67 K/s) (b). The strain rate and angular frequency satisfy Eq. (6) with $\varepsilon_y=0.02$. Open and solid symbols indicate data for the quasistatic apparent Young's modulus and dynamic complex modulus both of which are normalized by the Young's modulus at T_{RT}.

strong and fragile metallic glasses, E^* is in good agreement with E_{ap}; this experimentally confirms that Eq. (6) can adequately bridge between the dynamic and quasistatic relaxations in metallic glass with $\varepsilon_y\sim0.02$.

The dynamic complex viscosity $[\eta^*(\omega)]$ is defined by

$$|\eta^*| = \frac{|E^*|}{3\omega}. \tag{7}$$

From Eqs. (1a) and (4), Eq. (7) yields

$$\begin{aligned}|\eta^*| &\cong \frac{E_u\omega\tau}{3\omega}\left[1-\exp\left(-\frac{1}{\omega\tau}\right)\right] \\ &\approx \frac{E_u\tau}{3}\left\{1-\exp\left[-\frac{1}{\left(\dfrac{\dot{\varepsilon}}{\varepsilon_y}\right)\tau}\right]\right\} = \eta_s,\end{aligned} \tag{8}$$

where, η_s is the steady-state flow viscosity. In polymer science, Eq. (8) is well known as the Cox–Merz rule,[18] $|\eta^*| = \eta_S$ when ε_y^{-1} is on the order of one for polymer melts, and 10^1 for polymer glasses.[15] The present work shows that the Cox–Merz rule is applicable for metallic glasses with $\omega\approx50\dot{\varepsilon}$, from Eq. (6).

In this study, the quasistatic relaxation behavior in a $Zr_{55}Al_{10}Ni_5Cu_{30}$ metallic glass was observed through the elastic modulus and stress, measured by high temperature compressive tests. Based on the results that the yield stress is comparable to the steady-state flow stress, and the yield strain at which the linear viscoelasticity breaks down into the nonlinear state maintaining an almost constant value of ~0.02 from T_{RT} to T_g, a correlation equation of the dynamic angular frequency and quasistatic strain rate was successfully deduced, and then confirmed by experimental results with both fragile and strong metallic glasses. This correlation is expected to enhance further understanding of the relaxation phenomenon of metallic glasses and the mechanical properties or viscous workability from the scientific and engineering viewpoints, respectively.

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[1]T. Ichitsubo, S. Kai, H. Ogi, M. Hirao, and K. Tanaka, Scr. Mater. **49**, 267 (2003).
[2]H. Kato, H. Igarashi, and A. Inoue, Mater. Lett. **62**, 1592 (2008).
[3]R. Raghavan, P. Murali, and U. Ramamurty, Intermetallics **14**, 1051 (2006).
[4]P. A. Hess and R. H. Dauskardt, Acta Mater. **52**, 3525 (2004).
[5]O. P. Bobrov, K. Csach, V. A. Khonik, K. Kitagawa, S. N. Laptev, and M. Yu Yazvitsky, Scr. Mater. **54**, 369 (2006).
[6]O. P. Bobrov, V. A. Khonik, S. A. Lyakhov, K. Csach, K. Kitagawa, and H. Neuhauser, J. Appl. Phys. **100**, 033518 (2006).
[7]H. Kato, Y. Kawamura, A. Inoue, and H. S. Chen, Appl. Phys. Lett. **73**, 3665 (1998).
[8]J. Lu, G. Ravichandran, and W. L. Johnson, Acta Mater. **51**, 3429 (2003).
[9]H. S. Kim, H. Kato, A. Inoue, and H. S. Chen, Acta Mater. **52**, 3813 (2004); H. S. Kim, H. Kato, A. Inoue, H. S. Chen, and S. I. Hong, Mater. Trans. **45**, 1228 (2004).
[10]H. Kato, A. Inoue, and H. S. Chen, Acta Mater. **54**, 891 (2006).
[11]D. N. Perera and A. P. Tsai, J. Phys.: Condens. Matter **11**, 3029 (1999).
[12]Z. F. Zhao, P. Wen, C. H. Shek, and W. H. Wang, Phys. Rev. B **75**, 174201 (2007).
[13]P. Rosner, K. Samwer, and P. Lunkenheimer, Europhys. Lett. **68**, 226 (2004).
[14]Q. Wang, J. M. Pelletier, H. Xu, L. Xia, X. H. Tan, and Y. D. Dong, J. Mater. Sci. **40**, 4795 (2005).
[15]S. Matsuoka, *Relaxation Phenomena in Polymers* (Oxford University Press, New York, 1992).
[16]J. D. Ferry, *Viscoelastic Properties of Polymers*, 3rd ed. (Wiley, New York, 1980).
[17]H. Kato, T. Wada, M. Hasegawa, J. Saida, A. Inoue, and H. S. Chen, Scr. Mater. **54**, 2023 (2006).
[18]W. P. Cox and E. H. Merz, J. Polym. Sci. **28**, 619 (1958).