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

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The correlation of quasi-static and dynamic relaxations was discussed in a typical strong Zr55Al10Ni5Cu30 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 non-equilibrium glassy materials. This relaxation phenomenon is known to dominate the mechanical properties (elastic moduli, yield stress, and toughness) of the glasses. In a mechanical approach, the relaxation behavior of metallic glass has been investigated by the static stress relaxation with constant strain, creep with constant stress, the quasistatic deformation with constant strain rate, or the dynamic vibration with cyclic sinusoidal stress or strain. 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 behavior and distribution caused by the glass transition, as well as various kinds of sub-\( T_g \) relaxations. 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 Zr55Al10Ni5Cu30 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 Zr55Al10Ni5Cu30 (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.

In a typical strong metallic glass, a relaxation phenomenon, an essential nature of thermodynamically non-equilibrium glassy materials. This relaxation phenomenon, 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.
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 ($\sigma_y$), yield strain ($\varepsilon_y$), 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.\textsuperscript{7–10} This overshoot tendency decreases 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 ($\sigma_f$).\textsuperscript{7–10} Figure 2 demonstrates the $T_t$ dependence of $\sigma_y$ and $\sigma_f$ in addition to the peak stress ($\sigma_p$) and $\sigma_f$ at $T_t\approx661$ K. $\sigma_y$ 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 ($\approx0.90 T_g$). The difference between $\sigma_f$ and $\sigma_y$ increases with increasing $T_t$, up to 651 K, while that between $\sigma_p$ and $\sigma_f$ tends to decrease with $T_t$. Note that $\sigma_f$ has almost the same value as $\sigma_y$; stress returns and equilibrates finally at $\sigma_f$ after the stress peak. When $\sigma$ exceeds the yield point, the stress-induced structural relaxation of the glass to viscous liquid starts to be driven by a stress gap ($\sigma-\sigma_y$).\textsuperscript{9,10} If the relaxation time ($\tau$) becomes dynamically short enough to complete the whole stress-induced relaxation process ($\tau<\dot{\varepsilon}^{-1}$) before fracture, the viscoelastic glassy solid succeeds in transforming into a steady-state non-Newtonian viscous liquid. However, if $\tau$ 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, $\sigma_y$ can be expressed by\textsuperscript{15}

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

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.\textsuperscript{1} $\varepsilon_y$ 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

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

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\textsuperscript{16}

$$
|E''| = \sqrt{\left(E''\right)^2 + (E'^{\prime})^2} = E_u \frac{\omega \tau}{(1 + \omega^2 \tau^2)^{1/2}}, \quad (2)
$$

where $E'$, $E''$, and $\omega$ 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,\textsuperscript{15}

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

Equation (2) yields

$$
|E''| \approx E_u \omega \tau \left[ 1 - \exp \left( -\frac{1}{\omega \tau} \right) \right]. \quad (4)
$$

The approximation by Eq. (3) works well in both $\omega \tau \ll 1$ and $\omega \tau \gg 1$, and causes a maximum error of $\approx10\%$ around $\omega \tau \sim 2$. Considering the physical meaning of $|E''|$ ($=E'$ when $T_t<T_g$), this value equals $E_{ap}$, although the deformation mode is different, i.e., dynamic and quasistatic modes,

$$
|E''| = E_{ap}. \quad (5)
$$

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

$$
\omega = \frac{1}{\dot{\varepsilon}/\varepsilon_y}. \quad (6)
$$

Although $\varepsilon_y$ shows a little $T_t$ dependence, especially in $T > T_d$, for convenience, we assume $\varepsilon_y \approx 0.02$ 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 $\sigma_y$ (see Fig. 2). From Eq. (6), $\omega$, which effectively corresponds to $\dot{\varepsilon}$, is estimated at $\approx5 \times 10^{-3}$ 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$_{40}$P$_{20}$ metallic glass.\textsuperscript{17} In both typically
strong and fragile metallic glasses, $E^\prime$ is in good agreement with $E'_\infty$; this experimentally confirms that Eq. (6) can adequately bridge between the dynamic and quasistatic relaxations in metallic glass with $\epsilon_y \sim 0.02$.

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

$$|\eta^\prime| = \frac{|E^\prime|}{3\omega}.$$  

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

$$\eta^\prime \equiv \frac{E_\infty\omega}{3|\eta^\prime|} \left[ 1 - \exp\left(-\frac{1}{\omega\tau}\right) \right]$$

$$\approx \frac{E_\infty\tau}{3} \left[ 1 - \exp\left(-\frac{1}{(e_y\tau)}\right) \right] \approx \eta_y,$$  

where, $\eta_y$ is the steady-state flow viscosity. In polymer science, Eq. (8) is well known as the Cox–Merz rule,\(^{18}\) $|\eta^\prime| = \eta_y$ when $e_y$ is on the order of one for polymer melts, and $10^3$ for polymer glasses.\(^{15}\) The present work shows that the Cox–Merz rule is applicable for metallic glasses with $\omega = 50\dot{\epsilon}$, from Eq. (6).

In this study, the quasistatic relaxation behavior in a Zr$_{35}$Al$_{10}$Ni$_5$Cu$_{30}$ 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 $\sim 0.02$ 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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