Influence of *In-Situ* Nanoprecipitation on Constant Load Deformation in the Glass Transition Region of a Cu$_{60}$Zr$_{30}$Ti$_{10}$ Bulk Metallic Glass

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Nonlinear viscoelasticity influenced by an *in situ* nanocrystallization under constant load compression at the glass transition temperature, $T_g$, is investigated with a Cu$_{60}$Zr$_{30}$Ti$_{10}$ (at %) bulk metallic glass (BMG). The experimental curves showed the characteristics, softening and onset crystallization temperature, $T_x$, were determined to be 708 K and 740 K, respectively using a differential scanning calorimeter (Seiko DSC 6300) at a heating rate of 0.33 K/s. The high temperature compression tests were conducted isothermally at $T = 708$ K ($= T_g$) in a purified argon atmosphere by an Instron type machine. The samples were inserted between Al$_2$O$_3$ plates toughened by ZrO$_2$ in the machine, and were heated to the test temperature at a heating rate of 0.33 K/s and hold for 180 s for thermal equilibrium, then, compressive tests were started. Transmission electron microscopy (TEM) was carried out using a JEOL-JEM3000F microscope operating at 300 kV. Samples for the TEM observation are prepared by an ion-polishing technique.

3. Results and Discussion

3.1 Structure of a Cu$_{60}$Zr$_{30}$Ti$_{10}$ BMG at as cast state and nanocrystallization by isothermal annealing at $T_g$

Figure 1 shows a bright-field TEM image of a Cu$_{60}$Zr$_{30}$-Ti$_{10}$ BMG as cast state. The sample consists of two phases, glassy matrix and homogeneously dispersing particles in an average diameter of $\sim$10 nm. By selected area electron diffraction (SAED) pattern taken at 300 kV inserted in Fig. 1, the particles have a fcc-structure with lattice parameter of 4.15 nm. And by nano beam EDX analysis, average compositions (at %) of the matrix metallic glass and the nano-particle phases are respectively determined to be Cu$_{44.0}$-Zr$_{24.6}$Ti$_{10.4}$ and Cu$_{70.5}$Zr$_{23.3}$Ti$_{5.2}$ (hereafter Cu-rich phase). The nanoparticle is unknown phase therefore its volume fraction, $\phi_0$, can not be estimated directly.

Figures 2(a) and (b) shows DSC curves and the corresponding XRD patterns of the Cu$_{60}$Zr$_{30}$Ti$_{10}$ BMGs annealed isothermally at $T = 708$ K for various times. Isothermal annealing at $T = 708$ K ($= T_g$) enhances phase transformation of the first exothermic peak in the DSC curve. But no apparent peak differed from the new phase is observable and it just influences the half width of the halo peak around 2$\theta$ of 40 degrees in XRD patterns in Fig. 2(b). Figure 3 shows a...
bright-field image of Cu$_{60}$Zr$_{30}$Ti$_{10}$ BMG annealed isothermally at $T = 708$ K for 7.8 ks. In addition to the nanoparticles of the Cu-rich phase which have already existed at as-cast state, one can easily see finer particles in average diameter of ~5 nm precipitated around the Cu-rich phase. The new phase cannot be identified by the SAED pattern inserted in Fig. 3, therefore it is considered to be unknown nanocrystalline phase. The phase transformation of the first exothermic peak in DSC curve is nanocrystallization from the matrix metallic glass around the Cu-rich phase. The transition kinetics from the glassy matrix phase to the nanocrystalline phase was examined in the crystallization reaction during isothermal
nanocrystallization originated by inhomogeneous nucleation at \( T = 708 \text{ K} \). The \( n \) and \( K \) are the Avrami exponent and a fitting parameter, respectively.

The parameters, \( K \) and \( n \), are determined to \( 1.04 \times 10^{-3} \) and 0.78, respectively. The \( n \) value ranges from 2 to 3 in a previous report on other metallic glasses. With comparing them, the \( n \) value of the present work is low and means the nanocrystallization originated by inhomogeneous nucleation sites mainly around the quenched-in particles. Considering the lower present annealing temperature of \( T_g \), other works, this behavior seems to be fair.

3.2 Compressive constant load deformations of the \( \text{Cu}_{60}\text{Zr}_{38}\text{Ti}_{10} \) BMG at \( T_g \)

In the strict sense, the as-cast \( \text{Cu}_{60}\text{Zr}_{38}\text{Ti}_{10} \) rod is a nanocomposite material. But as shown in Fig. 2(a), this material shows the glass transition behavior and temperature span between the onset temperatures of the glass transition and crystallization can be estimated to \( \sim 30 \text{ K} \) due to the metallic glass matrix. Therefore this material keeps good workability and deforms homogeneously with viscous flow above \( T_g \). The heating this material above \( T_g \) brings about high workability and concurrently nanocrystallization mentioned in the previous section. The nanoprecipitation must disturb the viscous flow of the matrix phase, and results in decrease in workability of the material. However, the nanoparticles enhance strength of the material at room temperature. Therefore it becomes important to investigate the influence of the \textit{in situ} nanocrystallization on viscous flow behavior at the glass transition region.

3.2.1 Dependence of viscous flow behaviors on constant applied load

Figure 5(a) shows experimental results of strain-time (log \( \varepsilon \)-log \( t \)) curves taken under various constant loads, \( F \), of 50 kgf (= the initial applied stress, \( \sigma_0 = 100 \text{ MPa} \)), 100 kgf (200 MPa), 200 kgf (400 MPa), 250 kgf (500 MPa) and 300 kgf (600 MPa) at \( T = 708 \text{ K} \). The true strain, \( \varepsilon \), was calculated with \( \varepsilon = \Delta l/\ell_0 \cdot (1 + \Delta l/\ell_0) \), where \( \ell_0 \) and \( \Delta l > 0 \) respectively are the initial sample length and displacement which is positive for compression mode. It is obvious that the larger the initial applied stress, the faster the deformation. The deformation behaviors can be divided into two modes depending on the initial applied stress. When \( \sigma_0 \) is less than a critical stress, \( \sigma_c (= \sim 150 \text{ MPa at } t = 0 \text{ s}) \), at a condition of the Newtonian flow prevails, e.g., \( \sigma_0 = 100 \text{ MPa} \), the strain, \( \varepsilon \), increases almost linearly with increasing time, \( \log t \), then the strain rate decreases due to the nanocrystallization. On the other hand, when \( 150 \text{ MPa} < \sigma_0 \leq 600 \text{ MPa} \), the flow curves show a nonlinear viscoelasticity, softening phenomenon. For example, for \( F = 300 \text{ kgf} \) (\( \sigma_0 = 600 \text{ MPa} \)), the log \( \varepsilon \) increases linearly for \( t \leq 5 \text{ s} \), then increases rapidly. This increase in the strain rate suggests a transition from the Newtonian to non-Newtonian viscous flow. This phenomenon is considered to be due to stress-induced structural disordering and is followed by a decrease in strain rate due to structural recovering caused by a decrease in true stress. These softening and recovering phenomena have been observed in constant load compressions of a \( \text{Zr}_{55}\text{Al}_{10}\text{Ni}_{5}\text{Cu}_{30} \) BMG in the glass transition region.\(^{19}\) In the present work, in addition to these phenomena, the nanocrystallization effect is overlapped in deformation behavior. As shown in Fig. 5(b), these effects can be clearly appeared in the experimental
viscosity-time (log $\eta$-log $t$) curves shown in Fig. 5(a). For $F = 300$ kgf ($\sigma_0 = 600$ MPa), the log $\eta$ drastically decreases due to the stress-induced structural disordering, then, the flow structure reaches the equilibrium state at $t = 31$ s and it begins to recover to the initial state because true stress decreases with increasing strain due to an increase in cross section of the sample. If no crystallization occurs during the deformation, e.g., in the case for the thermally stable $\text{Zr}_{55}\text{Al}_{10}\text{Ni}_{25}\text{Cu}_{10}$ BMG, the structure finally returns back to the initial Newtonian state thus the corresponding viscosity becomes a constant as same value at $t = 0$. But if crystallization occurs during deformation, viscosity increases and exceeds the initial value after the softening, e.g., curves at $F > 75$ kgf ($\sigma_0 > 150$ MPa) in Fig. 5(b).

### 3.2.2 Dependence of constant-load deformation behaviors on pre-annealing time

Figure 6 shows the experimental viscosity-time (log $\eta$-log $t$) curves of $\text{Cu}_{60}\text{Zr}_{40}\text{Ti}_{10}$ BMGs pre-annealed isothermally at $T = 708$ K for various times, 1.2, 1.8, 3.0 and 5.4 ks. The applied load was fixed to 400 kgf ($\sigma_0 = 800$ MPa) for all curves. With increasing annealing time, the starting viscosity increases due to nanocrystallization. But all the curves once showed softening. transition to the nonlinear viscoelasticity, then followed by viscosity increase due to recovering to the linear viscoelasticity which is overlapped by the nanocrystallization effect. Here it is worth pointing out that viscosity drop due to the transition being a factor of twenty changes little with increasing the annealing time.

### 3.3 Extension of the fictive stress model to nonlinear viscoelasticity with an in situ crystallization

#### 3.3.1 Fictive stress model

For describing transition behaviors between the linear and nonlinear viscoelasticity in stable supercooled liquids, the fictive stress model was suggested by Chen et al.\textsuperscript{17} This model is based on two hypothesizes below,

1. For an applied stress, there exists an equilibrium structure of liquid.
2. Structure of liquid is disordered (inducing free volumes) with an applied stress which is larger than the critical stress, and rate of structural change to equilibrium state is dominated by relaxation time of the structure.

With the fictive stress model, some kinds of experimental nonlinear viscoelasticity, such as stress-overshoot and following stress-oscillation under constant strain rate mode\textsuperscript{20-22} and softening/recovering phenomena under constant compressive-load mode\textsuperscript{20,24} of the stable liquid were successfully reproduced. The relationship between an applied stress, $\sigma_t$, and viscosity of the corresponding equilibrium structure, $\eta$, is expressed by,

$$\frac{\sigma_t}{\sigma^*} = \frac{\eta}{\eta_N} \left[ -\ln \left( 1 - \frac{\eta}{\eta_N} \right) \right]^{-\beta}, \quad (2)$$

where $\eta_N$, $\beta$ and $\sigma^*$ are respectively the Newtonian viscosity, a stretched exponent and the maximum stress which liquid can sustain at sufficiently high shear rate and depends only slightly on temperature. By eq. (2), the flow structure and corresponding normalized viscosity is connected to the normalized stress. This stress is named the fictive stress. The hypothesis (2) is so-called stress-inducing mechanism, and is expressed by,

$$\frac{d\sigma_t}{dt} = \frac{\sigma - \sigma_t}{\lambda_t}. \quad (3)$$

where $\lambda_t$ is structural relaxation time. Using these equations and stress relaxation equation of the simple Maxwell model,

$$\frac{d\sigma}{dt} = E \cdot \frac{d\varepsilon}{dt} - \frac{\sigma}{\tau_t}, \quad (4)$$

where $\varepsilon$, $E$ and $\tau_t$ respectively are strain, Young’s modulus and stress relaxation time, the fictive stress model calculation can be conducted. In this work, $\lambda_t$ is considered to be the same value with $\tau_t$.

#### 3.3.2 Modifications for addition of an in situ crystallization effect to the Fictive stress model

1. Newtonian viscosity, $\eta_N$, to be a function of volume fraction, $\phi$, of time, $t$.
2. The maximum stress, $\sigma^*$, to be a function of volume fraction, $\phi$, of time, $t$.
3. Young’s modulus, $E$, to be a function of volume fraction, $\phi$, of time, $t$.

Modifications for (1)-(3) are explained below.

The volume fraction of nanoparticles, $\phi$, is expressed by,

$$\phi = \phi_Q + \phi_1, \quad (5)$$

where $\phi_Q$ and $\phi_1$ are respectively volume fraction of the Cu-rich phase nanoparticles and of the phase precipitated in the metallic glass matrix by annealing. The $\phi_1$ can be related to the enthalpy of the first exothermic peak, $H$, on the DSC curves shown in Fig. 2(a), thus eq. (5) is modified to,

$$\phi = \phi_Q + \left( 1 - \frac{H}{H_{\text{total}}} \right) \cdot \phi_M, \quad (5a)$$

where $H_{\text{total}}$ and $\phi_M$ are enthalpy of the whole reaction and the corresponding volume fraction of the first exothermic DSC peak.

Influence of dispersoids on viscosity of liquid, i.e., suspension, is well analyzed by the Mooney’s law,
where \( \eta, \eta_0, k_c \) and \( \phi_m \) are viscosity of the composite material, of the liquid without dispersoids, the Einstein coefficient and the maximum volume fraction of dispersoids. In the present work, as stated in section 3.1, nanoparticles (the Cu-rich phase) have already existed at as-cast state and its volume fraction, \( \phi_0 \), is unknown. Thus \( \eta_0 \) is difficult to be estimated. The relationship between \( \eta \) and \( t \) without \( \eta_0 \) is obtained by subtracting eq. (6) at \( \phi = \phi_Q \) \( \eta = \eta_Q \) from eq. (6), then using eqs. (1) and (5a)

\[
\ln \left( \frac{\eta}{\eta_Q} \right) = k_c \phi_m \left[ 1 - \exp(-K \cdot \tau^t) \right] + k_c \phi_Q \frac{1 - \exp(-K \cdot \tau^t)}{1 - \frac{\phi_Q}{\phi_m}},
\]

\[ (6a) \]

in the present work, \( k_c = 2.5 \) (for spherical particle), \( \phi_m = 1.0, K = 1.04 \times 10^{-3}, \) and \( n = 0.78 \) determined at the section 3.1. The experimental log \( \eta \)-log \( t \) curve of \( \sigma_0 = 100 \) MPa was fitted by eq. (6a) and the unknown parameters, \( \phi_Q \) and \( \phi_M \) are determined to be 0.26 and 0.79, respectively.

Because the maximum stress, \( \sigma^* \), is obtained at sufficiently high strain rate, the relaxation effect can be neglected. Therefore influence of nanoparticles on \( \sigma^* \) is considered to be approximately expressed by the mixture law,

\[
\ln \sigma^* = \phi_1 \ln \sigma_P + (1 - \phi_1) \ln \sigma^{*0}, (\phi_1 \leq \phi_M),
\]

where \( \sigma_P \) and \( \sigma^{*0} \) are particle strength and maximum stress of the starting alloy \( (t = 0) \). Figure 7(a) shows the experimental viscosity-true stress (log \( \eta \)-log \( \sigma \)) curves of \( \text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10} \) BMGs pre-annealed isothermally at \( T = 708 \) K for various times, \( t_s = 0, 1.2, 1.8, 3.0\) and \( 5.4 \) ks (corresponding conditions to Fig. 6) at the initial applied stress, \( \sigma_0 = 800 \) MPa. The true stress is calculated by \( \sigma = (F/A_o) \) (\( 1 - \Delta l/l_0 \)), \( \Delta l > 0 \) for compression mode. From Fig. 7(a), a master curve at \( t_s = 0 \) is constructed in Fig. 7(b) with superimposing the curves of \( t_s = 1.2, 1.8, 3.0 \) and \( 5.4 \) ks in the initial part of recovering process to that of \( t_s = 0 \) ks by horizontal shift, and dependence of shift factor, \( a_t \) on \( t_s \) is obtained in Fig. 7(b). The \( \sigma^{*0} \) is estimated to 650 MPa at the lowest viscosity, thus highest strain rate. The maximum stress, \( \sigma^* \), of the curves of \( t_s = 1.2, 1.8, 3.0 \) and \( 5.4 \) ks are approximately estimated to be 650, 810, 101 and 1467 MPa, respectively by \( \sigma^* = \sigma^{*0} \cdot a_t \). These values are fitted by eq. (7a), and the \( \sigma_P \) is determined to 3.8 GPa.

Dependence of Young’s modulus, \( E \), on volume fraction of the nanoparticle is also approximately expressed by the mixture law,

\[
\ln E = \phi_1 \ln E_P + (1 - \phi_1) \ln E_0, (\phi_1 \leq \phi_M),
\]

\[ (8) \]

where \( E_P \) and \( E_0 \) are Young’s modulus of the particle and the starting alloy \( (t = 0) \), respectively. From the slope of the experimental stress-strain curves of the samples at \( T = 708 \) K, \( \dot{\varepsilon} = 2.2 \times 10^{-2} \text{s}^{-1} \) (not shown here), Young’s modulus of the samples are determined to be 12 GPa. And from the dependence of Young’s modulus at room temperature on the volume fraction of the precipitates (not shown here),

\[ E_P \] can be estimated to 128 GPa. Both the \( \sigma_P \) and \( E_P \) are deduced as fitting parameters based on eqs. (7) and (8), respectively. The true values of them are uncertain in this work.

Using eqs. (6a), (7), (8) and ordinary equations for the fictive stress model calculation, i.e., eqs. (2)-(4), the transition behaviors between the linear and nonlinear viscoelasticity with the in situ nanocrystallization can be reproduced.

3.4 Calculation results on compressive constant load deformations of the \( \text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10} \) BMG at \( T_P \) by the extended fictive stress model

Figures 8(a) and (b) show that calculated strain-time and viscosity-time curves of the initial applied stresses of 100, 200, 400, 500 and 600 MPa, respectively. The calculated curves fairly reproduced the characteristics shown in the corresponding experimental curves in Fig. 5(b) such as the transition (softening–recovering) driven by stress, the hardening by the nanocrystallization and their dependence on initial applied stress. In addition, although the peak time of the calculated curves tends to be underestimated, their peak viscosities are almost comparable to those in the corresponding experimental curves shown in Fig. 5(b). This difference is partially due to dependence of the \( \beta \) which expresses the relaxation-time distribution during deformation on the volume fraction of the nanoprecipitates. With an increase in the volume fraction of the nanoprecipitates, the relaxation-time distribution is considered to become wider, thus the \( \beta \)
becomes smaller than the initial value of \( \sim 0.98 \). This effect results in the delay of the transition process. As another possibility of the difference between the experimental and calculated curves, one can point out the crystallization enhancement by the nonlinear viscous flow because the calculated curves, one can point out the crystallization possibility of the difference between the experimental and results in the delay of the transition process. As another possibility of the difference between the experimental and calculated curves, one can point out the crystallization enhancement by the nonlinear viscous flow because the viscous frictional loss brings about temperature raise\(^{24,26}\) of the deforming sample. Further research and investigation on the influences of the nanoprecipitation on relaxation time distribution and of the nonlinear viscous flow on nanocrystallization would be of scientific and of technological importance, and may bring about more rigid calculations of the nonlinear viscoelasticity with the in situ nanocrystallization by the extended fictive stress model.

4. Summary

Mechanical response (e.g., stress, strain and viscosity) of a Cu\(_{60}\)Zr\(_{38}\)Ti\(_{12}\) bulk metallic glass (BMG) during the nonlinear viscoelasticity influenced by the in situ nanocrystallization under constant load compression at the onset temperature of the glass transition, \( T_g \), was investigated. The stress-driven softening and subsequent recovering phenomena were observed. But this transition was strongly influenced by the hardening due to the in situ nanoprecipitation of the unknown phase of \( \sim 5 \) nm in diameter in the glassy matrix phase.

In order to add an in situ crystallization effect on calculations, the fictive stress model, which has successfully reproduced the nonlinear viscoelasticity in stable Zr-, Pd- based bulk metallic glasses, was extended with the Johnson-Mehl-Avrami method and mixture law for expressing increases in the Newtonian viscosity and in Young’s modulus and the critical stress, respectively.

The extended fictive stress model fairly demonstrated the characteristics such as the transition phenomena (softening–recovering) driven by stress, the hardening by the precipitation and their dependence on the initial applied stress under constant load compression. However, the calculated transition processes tend to be faster than those in the corresponding experimental curves. This may be due to the dependence of the relaxation time distribution on the volume fraction of the nanoparticles and also the crystallization enhancement by the nonlinear viscoelasticity.

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