Influence of *In-Situ* Nanoprecipitation on Constant Load Deformation in the Glass Transition Region of a $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ 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 $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ (at %) bulk metallic glass (BMG). The experimental curves showed the characteristics, softening and subsequent recovering phenomena which have been observed in a 'stable' Zr-based BMG and also hardening through whole deformation process due to the *in situ* nanoprecipitation in the glass matrix. These characteristics are fairly reproduced by the fictive stress model extended by the Johnson-Mehl-Avrami (JMA) equation and mixture rule for respectively expressing influences of the Newtonian viscosity and of Young's modulus and critical stress on volume fraction of the nanoprecipitates.

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1. Introduction

A number of bulk metallic glasses (BMGs) have been formed by a copper mould casting technique in Mg-Ln-TM,¹⁾ Ln-Al-TM,²⁾ Zr-Al-TM,³⁾ Zr-(Ti, Nb, Pd)-Al-TM,⁴⁾ Zr-Ti-TM-Be,⁵⁾ Fe-(Al, Ga)-(P, C, B, Si),⁶⁾ Pd-Cu-Ni-P,⁷⁾ (Fe, Co, Ni)-(Zr-, Nb, Ta)-B,⁸⁾ Fe-Co-(Zr, Nb)-(Mo, W)-B⁹⁾ and Co-Fe-Ta-B¹⁰⁾ alloy systems, and some of them have already gained application fields. In order to open up new application fields of the BMG, many efforts were done for designing its composite materials. One of the composite designs, glass matrix and nanocrystalline particle mixed structure alloy has been prepared by the copper mould cast technique with subsequent heat treatment at the supercooled liquid region (SLR) to induce devitrification.¹¹⁾ This composite sometimes shows higher fracture strength or plasticity at room temperature than the monolithic BMG without annealing.^{11,12)} Because this composite is prepared using devitrification in the SLR of the cast monolithic BMG, the viscous flow at the SLR with the *in situ* devitrification is useful for manufacturing its products. In this process, the material is prone to be subjected to extreme high strain rates or high stresses, and the viscosity becomes the non-Newtonian state. Therefore, understanding of the transition between the Newtonian-non-Newtonian viscous flows of a supercooled liquid of BMGs influenced by the *in situ* devitrification is of both scientific and technological importance.

In this paper, we intend to investigate experimentally mechanical response (*e.g.*, stress, strain and viscosity) of a $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ BMG¹³⁻¹⁶⁾ during nonlinear viscoelasticity influenced by the *in situ* nanocrystallization under constant load compression at T_g , and also to reproduce it by a calculation model based on the fictive stress model.¹⁷⁾

2. Experimental

For compressive tests, cylindrical samples, 2.5 mm in diameter and 5 mm in length (aspect ratio 2.0), were cut from $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ cast rods. The glass transition temperature, T_g ,

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 $T = 708 \text{ K}$ ($= T_g$) in a purified argon atmosphere by an Instron type machine. The samples were inserted between Al_2O_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 $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ BMG at as cast state and nanocrystallization by isothermal annealing at T_g

Figure 1 shows a bright-field TEM image of a $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ BMG as cast state. The sample consists of two phases, glassy matrix and homogeneously dispersing particles in an average diameter of $\sim 10 \text{ nm}$. 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 nanoparticle phases are respectively determined to be $\text{Cu}_{44.0}\text{-Zr}_{45.6}\text{Ti}_{10.4}$ and $\text{Cu}_{70.5}\text{Zr}_{24.3}\text{Ti}_{5.2}$ (hereafter Cu-rich phase). The nanoparticle is unknown phase therefore its volume fraction, ϕ_Q , can not be estimated directly.

Figures 2(a) and (b) shows DSC curves and the corresponding XRD patterns of the $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ BMGs annealed isothermally at $T = 708 \text{ K}$ for various times. Isothermal annealing at $T = 708 \text{ K}$ ($= T_g$) enhances phase transformation of the first exothermic peak in the DSC curve. But no apparent peak diffracted from the new phase is observable and it just influences the half width of the halo peak around 2θ of 40 degrees in XRD patterns in Fig. 2(b). Figure 3 shows a

Fig. 1 Bright field transmission electron microscopic (TEM) image of an as-cast $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ bulk metallic glass. Its electron diffraction pattern is inserted in Fig. 1.

Fig. 3 Bright field transmission electron microscopic (TEM) image of a $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ bulk metallic glass isothermally annealed at $T = 708$ K for 7.8 ks. Its electron diffraction pattern is inserted in Fig. 3.

Fig. 2 Differential scanning calorimetric (DSC) curves at a heating rate of 0.33 K/s (a) and X-ray diffraction (XRD) patterns (b) of $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ bulk metallic glasses isothermally annealed at $T = 708$ K for 0 (= as-cast), 1.2, 5.4, 7.8 and 21.6 ks. Peaks at 2θ of 28 and 36 degree are diffracted from a sample holder.

bright-field image of $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ 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

Fig. 4 Dependence of the normalized heat release, H/H_{total} , which corresponds to the first exothermic peak in the DSC curve of a $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ bulk metallic glass on annealing time, t_a , isothermally at $T = 708$ K. The n and K are the Avrami exponent and a fitting parameter, respectively.

annealing at $T = 708$ K ($\sim T_g$). Figure 4 shows change in the normalized enthalpy, H/H_{total} , with various annealing times, t_a , where H and H_{total} are respectively enthalpies of the first exothermic peak of annealed and as-cast samples. By fitting with the Johnson-Mehl-Avrami (JMA) equation,¹⁸⁾

$$\frac{H}{H_{\text{total}}} = \exp(-K \cdot t_a^n), \quad (1)$$

the parameters, K and n , are determined to 1.04×10^{-3} and 0.78, respectively. The n value ranges from 2 to 3 in a previous paper¹⁹⁾ 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 , than other works, this behavior seems to be fair.

3.2 Compressive constant load deformations of the $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ BMG at T_g

In the strict sense, the as-cast $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ 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 ~ 30 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 influence of the *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

Fig. 5 Experimental strain-time ($\log \varepsilon$ - $\log t$) (a) and viscosity-time ($\log \eta$ - $\log t$) (b) of a $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ bulk metallic glass under various constant compressive loads, F , of 50 kgf (= the initial applied stress, $\sigma_0 = 100$ MPa), 100 kgf (200 MPa), 200 kgf (400 MPa), 250 kgf (500 MPa) and 300 kgf (600 MPa) at $T = 708$ K.

($\log \varepsilon$ - $\log t$) curves taken under various constant loads, F , of 50 kgf (the initial applied stress, $\sigma_0 = 100$ MPa), 100 kgf (200 MPa), 200 kgf (400 MPa), 250 kgf (500 MPa) and 300 kgf (600 MPa) at $T = 708$ K. The true strain, ε , was calculated with $\varepsilon = \Delta l/l_0 \cdot (1 + \Delta l/l_0)$, where l_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 σ_0 is less than a critical stress, σ_c (~ 150 MPa at $t = 0$ s), at a condition of the Newtonian flow prevails, e.g., $\sigma_0 = 100$ MPa, the strain, $\log \varepsilon$, 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 $F = 300$ kgf ($\sigma_0 = 600$ MPa), the $\log \varepsilon$ increases linearly for $t \leq 5$ 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

Fig. 6 Experimental viscosity-time ($\log \eta$ - $\log t$) curves under a constant compressive load of 400 kgf (the initial applied stress, $\sigma_0 = 800$ MPa) of $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ bulk metallic glasses previously annealed isothermally at $T = 708$ K for 0 (= as-cast), 1.2, 1.8, 3.0 and 5.4 ks.

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 $\text{Zr}_{55}\text{Al}_{10}\text{Ni}_{15}\text{Cu}_{30}$ 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 $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ 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.*¹⁷⁾ This model is based on two hypotheses below,

- (1) For an applied stress, there exists an equilibrium structure of liquid.
- (2) Structure of liquid is disordered (inducing free vol-

umes) 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 mode²⁰⁻²²⁾ and softening/recovering phenomena under constant compressive-load mode,^{20,24)} of the stable liquid were successfully reproduced. The relationship between an applied stress, σ_f , and viscosity of the corresponding equilibrium structure, η , is expressed by,

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

where η_N , β and σ^* are respectively the Newtonian viscosity, an 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,

$$\frac{d\sigma_f}{dt} = \frac{\sigma - \sigma_f}{\lambda_f}, \quad (3)$$

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

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

where ε , E and τ_f respectively are strain, Young's modulus and stress relaxation time, the fictive stress model calculation can be conducted. In this work, λ_f is considered to be the same value with τ_f .

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

- (1) Newtonian viscosity, η_N , to be a function of volume fraction, ϕ , of time, t .
- (2) The maximum stress, σ^* , to be a function of volume fraction, ϕ , of t .
- (3) Young's modulus, E , to be a function of volume fraction, ϕ , of t .

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

The volume fraction of nanoparticles, ϕ , is expressed by,

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

where ϕ_Q and ϕ_1 are respectively volume fraction of the Cu-rich phase nanoparticles and of the phase precipitated in the metallic glass matrix by annealing. The ϕ_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_{total} and ϕ_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,

$$\ln \frac{\eta}{\eta_0} = \frac{k_e \cdot \phi}{1 - \frac{\phi}{\phi_m}}, \quad (6)$$

where η , η_0 , k_e and ϕ_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, ϕ_Q , is unknown. Thus η_0 is difficult to be estimated. The relationship between η and t without η_0 is obtained by subtracting eq. (6) at $\phi = \phi_Q$ $\eta = \eta_Q$ from eq. (6), then using eqs. (1) and (5a)

$$\ln\left(\frac{\eta}{\eta_Q}\right) = \frac{k_e \phi_M [1 - \exp(-K \cdot t^n)] + k_e \phi_Q}{1 - \frac{\phi_M}{\phi_m} [1 - \exp(-K \cdot t^n)] - \frac{\phi_Q}{\phi_m}} - \frac{k_e \phi_Q}{1 - \frac{\phi_Q}{\phi_m}}, \quad (6a)$$

in the present work, $k_e = 2.5$ (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, ϕ_Q and ϕ_M are determined to be 0.26 and 0.79, respectively.

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

$$\ln \sigma^* = \phi_1 \ln \sigma_p + (1 - \phi_1) \ln \sigma_0^*, (\phi_1 \leq \phi_M), \quad (7)$$

where σ_p and σ_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, $t_a = 0, 1.2, 1.8, 3.0$ and 5.4 ks (corresponding conditions to Fig. 6) at the initial applied stress, $\sigma_0 = 800$ MPa. The true stress is calculated by $\sigma = (F/A_0) \cdot (1 - \Delta l/l_0)$, $\Delta l > 0$ for compression mode. From Fig. 7(a), a master curve at $t_a = 0$ is constructed in Fig. 7(b) with superimposing the curves of $t_a = 1.2, 1.8, 3.0$ and 5.4 ks in the initial part of recovering process to that of $t_a = 0$ ks by horizontal shift, and dependence of shift factor, a_t , on t_a is obtained in Fig. 7(b). The σ_0^* is estimated to 650 MPa at the lowest viscosity, thus highest strain rate. The maximum stress, σ^* , of the curves of $t_a = 1.2, 1.8, 3.0$ 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 σ_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,

$$\ln E = \phi_1 \ln E_p + (1 - \phi_1) \ln E_0, (\phi_1 \leq \phi_M), \quad (8)$$

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, $\dot{\epsilon} = 2.2 \times 10^{-2} \text{ s}^{-1}$ (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),²³ the

Fig. 7 Viscosity-true stress ($\log \eta$ - $\log \sigma$) curves under a constant compressive load of 400 kgf (the initial applied stress, $\sigma_0 = 800$ MPa) of $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ bulk metallic glasses previously annealed isothermally at $T = 708$ K for 0 (= as-cast), 1.2, 1.8, 3.0 and 5.4 ks. (a) Master curve at the annealing time, t_a , of 0 s of viscosity-true stress ($\log \eta$ - $\log \sigma$) curves (shown in Fig. 7(a)) (b). Dependence of the shift factor, a_t , on the annealing time, t_a , is inserted in Fig. 7(b).

E_p can be estimated to 128 GPa. Both the σ_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_g 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 nanoprecipitation 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 β 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 β

Fig. 8 Strain-time ($\log \varepsilon$ - $\log t$) (a) and viscosity-time ($\log \eta$ - $\log t$) (b) curves calculated with the extended fictive stress model calculated at the initial applied stresses of 100, 200, 400, 500 and 600 MPa at $T = 708$ K. The β , E , n and K are respectively the stretched exponent in eq. (2)), Young's modulus, the Avrami exponent and a fitting parameter in eq. (1).

becomes smaller than the initial value of ~ 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 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 $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ 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.

- (1) 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 ~ 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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