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Nanoindentation analysis of time-dependent deformation in as-cast and annealed Cu–Zr bulk metallic glass

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ABSTRACT

The room-temperature time-dependent deformation of a Cu–Zr binary bulk metallic glass was investigated by performing nanoindentation creep experiments. Experimental results show that creep is much more pronounced in the as-cast sample than in the annealed sample. In both cases, the amount of creep displacement was found to increase with the loading rate. From the results, the influence of structural state and indentation rate on the creep behavior is discussed. Additionally, the stress exponent for the steady-state creep is estimated from the curve of creep displacement vs. holding time.

1. Introduction

The plastic deformation of bulk metallic glasses (BMGs) occurs in either homogeneous or inhomogeneous way, depending on temperature and stress [1–3]. While homogeneous deformation is dominant at high temperature (above $\sim 0.7T_g$ where T_g is the glass transition temperature), plastic deformation at room temperature takes place mostly in an inhomogeneous way: plastic strain is highly localized into narrow shear bands [2,3].

For the last decade, the instrumented indentation test (IIT), especially nanoindentation, has been widely applied to the assessment of both inhomogeneous and homogeneous deformation in metallic glasses (see review articles [4,5]). In addition to the simple and easy procedure of the test, the IIT has two important merits in application to the BMG study. First, while the producible volumes of the BMGs are still not sufficiently large for conventional mechanical testing, IIT requires only a small volume of the testing material. Second, BMGs often show very limited plasticity during uniaxial test, whereas IIT can provide load–displacement information during the entire loading and unloading sequences.

While many indentation studies have been carried out on BMGs to analyze their instantaneous elastic–plastic behavior under quasi–static loading (such as hardness, Young's modulus, and inhomogeneous 'serrated' flow), a limited number of investigations have been devoted to their time-dependent deformation (i.e., creep) that occurs mostly in a homogeneous way. The indentation creep study of amorphous alloys can be helpful not only for solving scientific curiosity, but also for obtaining practical engineering information about small-size contact that can occur during various possible applications of BMGs (e.g., device for micro-electro-mechanical system, MEMS).

Since creep is expected to occur mainly at high reduced temperature (T/T_g) where deformation is homogeneous, nanoindentation creep experiments at room temperature have been mostly conducted on BMGs with a low T_g (and thus room temperature is about $0.7–0.75T_g$) such as Ce-, La-, and Mg-based BMG. For example, Wei and colleagues [6–9] reported the room-temperature indentation creep of Ce- and La-based BMGs and argued that their viscoelastic behavior could be described by the well-known Kelvin model. Also, Castellero et al. [10] analyzed the room-temperature creep of two Mg–Cu–Y metallic glasses. Very recently, Huang et al. [11,12] attempted to extend the room-temperature creep analysis to Fe- and Ti-based BMGs whose T_g is not so low. Nevertheless, the influence of structural state on the room-temperature indentation creep of BMG is not yet fully understood.

With this in mind, here we investigated the room-temperature creep behavior of as-cast and annealed Cu–Zr binary BMG during indentation and how it is influenced by intrinsic material condition

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(initial free volume) and extrinsic testing condition (loading rate). Although there is considerable literature on the effects of these conditions on various mechanical properties of BMG (including tensile/compressive strength, plastic strain, toughness, etc.; for example, see [13–15]), few efforts have been given for analyzing their effects on the room-temperature creep. The examined material in the present work was $Cu_{50}Zr_{50}$ BMG having probably the largest amount of free volume (or the lowest atomic packing density) among the various bulk-forming Cu–Zr binary alloys [16]. Very recently, Park et al. [17] reported that this BMG exhibited obvious room-temperature creep under uniaxial compression, even though its T_g is about 693 K and thus room temperature is only about $0.43T_g$.

2. Experimental

Rod-typed $Cu_{50}Zr_{50}$ BMG samples with a diameter of 1 mm were prepared using a Cu mold casting. For comparison with the as-cast state, some samples were annealed at 673 K for 20 min. Because the annealing temperature was below T_g ($\sim$693 K), structural relaxation might have occurred instead of crystallization, and thus the free volume in the BMG would have been reduced. No crystalline peak was detected in the X-ray diffraction (XRD) spectra of the annealed specimen (not shown here). Nanoindentation creep tests were performed at various loading rates using a Nanoindenter-XP (Nano Instruments Inc., Oak Ridge, TN) with a typical Berkovich indenter.

3. Results and discussion

Fig. 1 compares the compressive stress–strain curve of the as-cast sample to that of the annealed sample. The as-cast sample exhibits a large plasticity (i.e., high plastic strain prior to failure), which is rare for a metallic glass. As mentioned above, this is conceivably due to the very large amount of initial free volume of the BMG (perhaps the largest among various bulk-forming Cu–Zr binary amorphous alloys [16]). Since the amount of the initial free volume can be significantly reduced by structural relaxation, the annealed sample shows much less plasticity and higher yield strength than the as-cast one.

There have been many efforts to estimate the uniaxial creep behavior by using instrumented indentation tests, and two different methods are possible: the constant displacement method (also called the load–relaxation method) and the constant load method. Because it is relatively difficult to keep the indentation depth constant, we adopted the constant load method in the present work. During the test, the load was increased up to a peak load of 50 mN under various loading rates (0.1, 0.5, 2.5 mN/s) and then held constant for 400 s. Fig. 2 shows the testing sequence schematically.

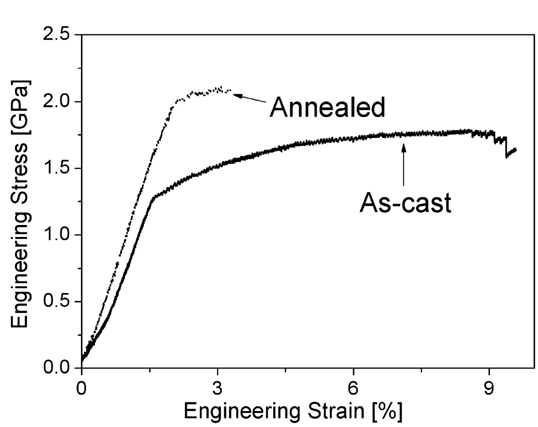

Fig. 1. Compressive stress–strain curve of the as-cast and annealed $Cu_{50}Zr_{50}$ BMG.

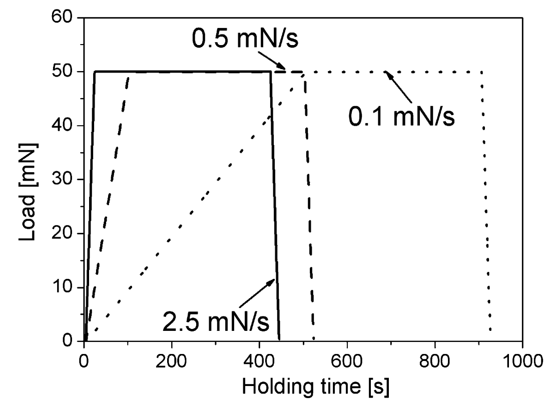

Fig. 2. Schematic illustration of the testing sequence.

Fig. 3 shows representative examples of nanoindentation load–displacement (P–h) curves obtained at three different loading rates ($dP/dt = 0.1, 0.5, 2.5$ mN/s). At a given rate, the as-cast sample showed a larger peak–load displacement than the annealed sample, which means that annealing-induced structural relaxation enhanced the static strength of the BMG. This strengthening by sub-T_g annealing has been well known for many metallic glasses (for example, see [18,19]).

In Fig. 3, two trends of indentation creep are obvious. First, the indentation creep phenomenon (that is, the increase in penetration depth during the load-holding segment) is much more pronounced in the as-cast sample than in the annealed sample. This implies that the structural relaxation enhanced not only the static

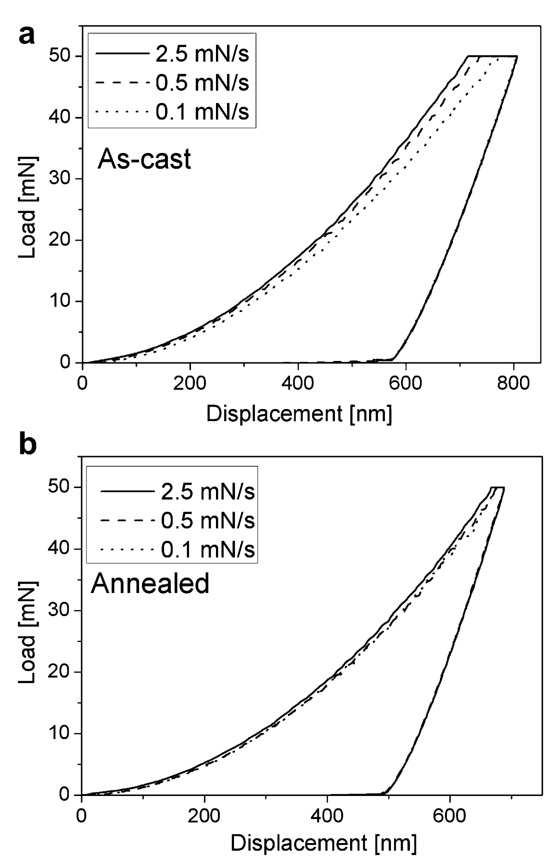

Fig. 3. Representative load–displacement curve obtained at three different loading rates (0.1–2.5 mN/s); (a) as-cast and (b) annealed sample.

room-temperature strength (i.e., resistance to inhomogeneous instantaneous deformation) but also the creep strength (i.e., resistance to homogeneous time-dependent deformation). A similar result was reported in the study of a Zr-based BMG by Van Steenberge et al. [20], though their peak-load holding was not made for the creep evaluation but for thermal drift correction. Although the detailed mechanism remains unsolved yet, it can be convinced from the above results that the amount of initial free volume (that can be reduced by structural relaxation) seriously affects indentation creep. Note that, for metallic glasses, a single mechanism can be applied irrespective of the macroscopic deformation mode (i.e., homogeneous or inhomogeneous); the most popular one is 'shear transformation zone (STZ)' model [2,21]. A larger amount of initial free volume can result in the occurrence of more STZs. Thus, whether the macroscopic deformation mode at a given temperature is homogeneous or inhomogeneous, the structurally relaxed BMG (having a relatively low free volume) would exhibit higher resistance to any mode of deformation (i.e., higher hardness and creep-resistance together) than the as-cast one.

Second, the creep behavior in Fig. 3 shows a strong rate dependency. This becomes clearer if the creep behavior observed in the as-cast sample is re-plotted as the creep displacement against the holding time, as shown in Fig. 4(a). The maximum creep displacement recorded during peak-load holding shows a strong dependency on the loading rate, i.e., a faster loading corresponds to a larger creep displacement. For each rate condition, the creep displacement rapidly increases at an early stage and then the increasing rate reaches steady-state in the range of $t > \sim 100$ s. This is somewhat analogous to the two-stage behavior observed in standard uniaxial creep experiments at a constant stress state; the primary (transition) creep and the secondary (steady-state) creep.

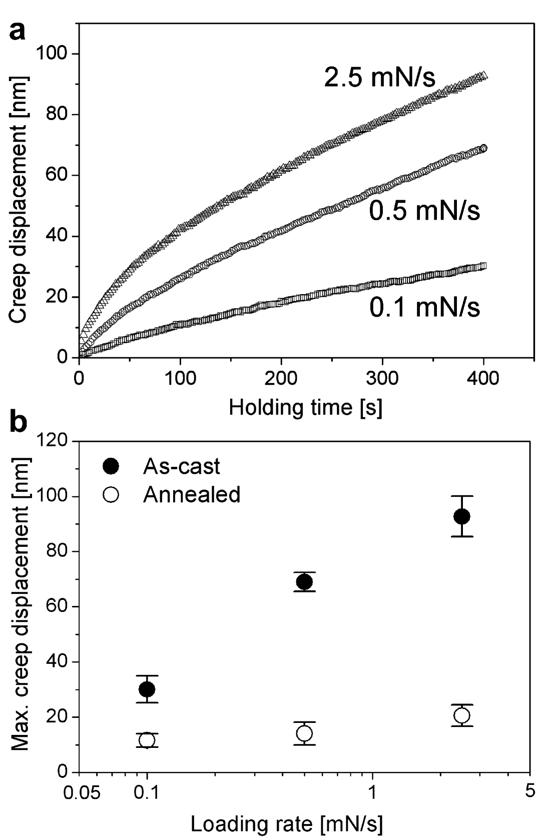

Fig. 4. Creep displacement during the load-holding sequence (a), and the variation in maximum creep displacement with respect to loading rate (b).

Fig. 4(b) summarizes the measured values of the maximum creep displacement as a function of loading rate. The maximum creep displacement for both the as-cast and annealed samples exhibits an almost linear increase with the loading rate, though the as-cast sample shows a much stronger rate dependency than the annealed sample.

The rate dependency of the indentation creep (i.e., the larger creep according to the faster loading) might be explained from two different (structural and phenomenological) viewpoints. From a structural viewpoint, the rate dependency is conceivably related to the excess free volumes that can be created during deformation. Based on Spaepan's free volume theory [1], de Hey et al. [22] verified that it is reasonable to assume that the production rate of free volume during deformation is proportional to the strain rate. Although it is difficult to directly convert the indentation loading rate (dP/dt) to the indentation strain rate [$d\varepsilon/dt = h^{-1}(dh/dt)$], a material indented at a higher loading rate will surely experience a higher strain rate than one at a lower loading rate. Therefore, faster indentation generates a larger amount of excess free volume during the loading sequence. As mentioned above, a BMG having a greater amount of free volume can generate more STZ, and thus can be less resistant to time-dependent deformation.

From a phenomenological viewpoint, the rate dependency seems to be related to the fact that the contribution of the deformation during the loading sequence to the total deformation (that can be represented by h_0/h_t where h_0 and h_t are the displacement recorded at the starting and ending point of holding sequence, respectively) is increasing with decreasing loading rate. It can be analyzed in two different ways. The first way focuses on the case of slow loading, as Ma et al. suggested in their study on nanocrystalline Ni [23]. For slow loading, more time is needed to reach the peak load, providing the possibility for the occurrence of creep deformation during the loading sequence, which is somewhat analogous to the phenomenon called 'dynamic creep.' Conversely, the second way is more focusing on the case of fast loading; at higher loading rate, the plastic flow (that was not produced during the loading) can be delayed and occur during the holding sequence. This may be in agreement with the results by Concustell et al. [24] who observed a strong rate dependency of creep displacement during a very short holding (only for 2 s) in their nanoindentation study on a Pd–Cu–Ni–P bulk metallic glass. This dependency might be partly attributed to an artifact related to the delayed plastic deformation.

From the indentation creep curve, one can estimate the 'creep stress exponent (n)' which has been widely used as an important measure of time-dependent deformation in a creeping solid, since the steady-state creep behavior is typically described by [25]:

$$\dot{\varepsilon} = A\sigma^n \tag{1}$$

where $\dot{\varepsilon}$ is the indentation strain rate, σ is the mean applied stress under the indenter, and A is a temperature-dependent material constant. Thus, the stress exponent can be easily estimated by the relationship, $n = \partial\ln(\sigma)/\partial\ln(\dot{\varepsilon})$. The indentation strain rate is given as $\dot{\varepsilon} = (dh/dt)h^{-1}$, and the displacement rate (dh/dt) has been often calculated by fitting the h–t curve recorded during holding at the peak load according to the following empirical law [26]:

$$h(t) = h_0 + a(t - t_0)^b + kt \tag{2}$$

where h_0 (the initial indentation depth), a, b, and k are fitting constants, and t_0 is the start time of the creep process. The mean applied stress (σ) in Eq. (1) can be estimated from the indentation hardness H (which is the same as the mean pressure) by applying Tabor's empirical relation; $H = C\sigma$ where C is a correlation factor that was assumed to be three in this study.

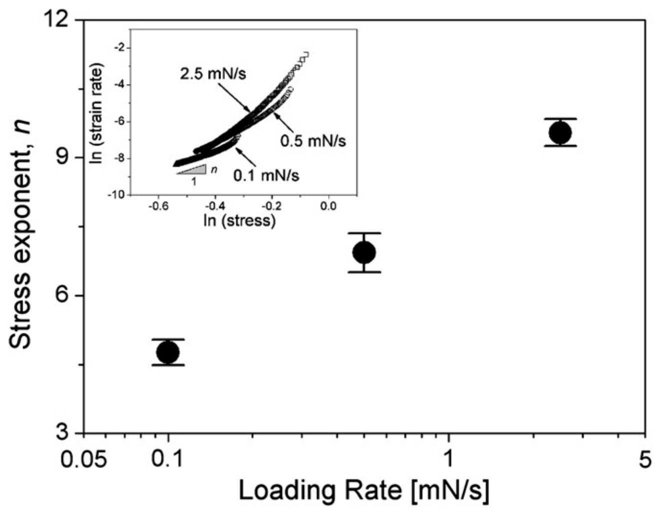

Fig. 5. Variation in the creep stress exponent with respect to loading rate. Inset image log–log plot of strain rate vs. stress.

To obtain the values of the creep stress exponent, the curves of $\ln(\dot{\varepsilon})$ vs. $\ln(\sigma)$ were drawn (see inset of Fig. 5). The slope of the curve (stress exponent) parabolically decreases with decreasing stress (i.e., with increasing holding time). In the steady-state regime (corresponding to the end of the holding period and the left-end region of the curve in the inset figure), the slope becomes constant that might indicate the stress exponent for the steady-state creep. Note that the stress exponent, n, can be directly obtained from the slope of the plot between $(\ln \dot{\varepsilon})$ and $(\ln H)$, and thus it is independent of the value of C.

Fig. 5 shows the stress exponent variation of the as-cast sample as a function of the indentation loading rate. Upon increasing the loading rate from 0.1 to 2.5 mN/s, the estimated stress exponent increases almost linearly in the range of 4–10. Interestingly, these stress exponent values are similar to that for the dislocation–creep-dominant mechanism in a crystalline material. Very limited studies on indentation creep [12,23] have reported the strong rate dependency of the stress exponent. In the studies, the trend of the stress exponent change with rate is controversial; for example, Huang et al. [12] suggested that the exponent of Fe-based BMG decreases with indentation rate, which is opposite to the present result. Whereas Ma et al. [23] reported that the exponent of nanocrystalline Ni significantly increases with the rate. The detailed mechanism for the rate-dependency of the stress exponent has not been fully understood yet and remains a subject of interest for future studies.

4. Summary

In this work, we investigated the room-temperature time-dependent deformation of the as-cast and annealed $Cu_{50}Zr_{50}$ binary amorphous alloy by performing nanoindentation creep experiments under a variety of loading rates. It was revealed that the creep of the BMG is strongly affected by both the internal condition (amount of initial free volume) and the external condition (indentation loading rate).

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