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Structural inhomogeneity and anelastic deformation in metallic glasses revealed by spherical nanoindentation

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In this letter, the anelastic deformation of a Zr-based metallic glass (MG) at ambient temperature is revealed through spherical nanoindentation. A general rheological model, which is linked with the atomic structure of MGs, is proposed to explain the observed anelasticity. The experimental and theoretical results clearly indicate the existence of structural inhomogeneity intrinsic to MGs, which causes the anelastic deformation upon mechanical loading under high loading rates before shear banding. The outcome of the current research provides an important insight into the property-structure relation of MGs. © *2010 American Institute of Physics*. [doi:10.1063/1.3532968]

Since the advent of metallic glasses (MGs) in the 1960s, understanding their inelastic deformation at ambient temperature has been the issue of intense research efforts.[1–9] Over the past decades, a variety of deformation models have been proposed to rationalize the observed deformation phenomena in MGs,[1–4,9] which were almost built on the same notion that MGs possess intrinsic structural inhomogeneity at the atomic scale which governs their overall mechanical properties.[1–4,9] Despite the wide use of these models, however, it is still obscure how the inelastic deformation occurs in the apparent elastic deformation regime. The answer to this question is not trivial and related to the atomic packing in MGs, which is a challenging issue even today for materials scientists to resolve.[10,11] In view of these, studying the subcritical inelastic deformation events that carry structural "fingerprints" may help us decode the nature of atomic packing in MGs.

To unveil the preyielding inelastic deformation mechanism, a spherical nanoindentation approach is proposed in this study. A Zr-based MG sample, which has the chemical composition of $Zr_{55}Pd_{10}Cu_{20}Ni_5Al_{10}$ (in at. %), was selected as the model material. Prior to the nanoindentation, the amorphous nature of the MG was confirmed using x-ray diffraction analyses (not shown here) and the sample surface was mechanically polished to a mirror finish. The nanoindentation experiments were subsequently performed with the low-load NanoIndenter system (Hysitron Inc., Minneapolis, MN) with a 5-μm spherical nanoindenter, which possesses the resolutions of ~1 nm in displacement and ~1 μN in load. Owing to its ultrafast data acquisition rate (~10 000 points per second), unusually high loading rates can be programmed and applied during nanoindentation. With the built-in nanodynamic mechanical analysis (nanoDMA) module, the damping factor of the whole system was characterized to be around ~0.014 kg s^{-1} before nanoindentation. Such a machine damping factor will result in an 'artificial' viscosity of about ~0.05 MPa s when deforming the material with a microscopic dimension, which, however, is negligibly small and would not affect the experimental results as can be seen later.

As shown in Fig. 1(a), a trapezoidlike loading profile was programmed for the nanoindentation experiments, which consists of three segments, namely, loading, holding and unloading, as in usual nanoindentation experiments. The loading time, t_L, was systematically varied to amplify the inelastic response of the MG, while the unloading time, t_U, was fixed at ~0.1 s to warrant the full recovery of the delayed elastic deformation. In doing so, any residual plastic deformation can be detected after the unloading. The holding time, t_H, was set at a somewhat arbitrary value of ~0.1 s for monitoring the material's transient dynamic response.

Figure 1(b) displays the typical load-displacement curves obtained by indenting the Zr-based MG at a constant load of 800 μN and varying t_L, from which it can be seen

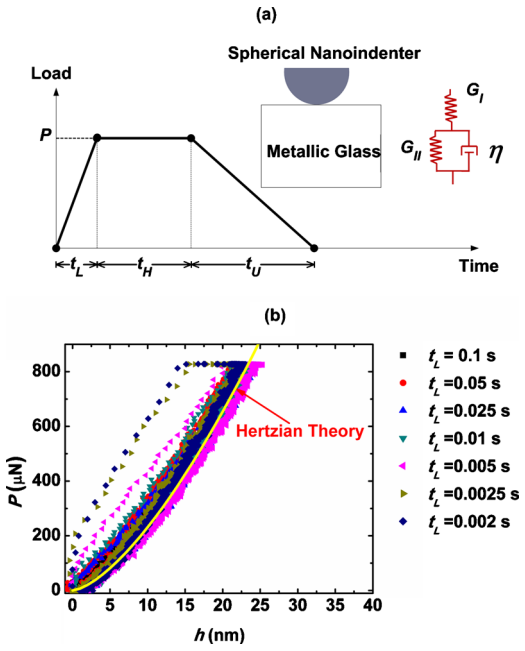

FIG. 1. (Color online) (a) The sketch of the indentation loading profile [the insets: the sketch of the spherical nanoindenter and MG sample (left) and the three-parameter rheological model for MGs (right)], and (b) the indentation load-displacement curves which show anelastic deformation occurring at fast loading rates (the quasistatic Hertzian response corresponds to a indenter tip radius of ~5 μm, a material's Young's modulus of ~76 GPa and a Poisson's ratio of ~0.365).

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that all curves return to the zero displacement after unloading, implicative of the elastic nature of the material's response. For $t_L > 0.01$ s, the loading and unloading curves overlap and obey the classic Herztian theory [Fig. 1(b)]. In contrast, the loading curves deviate significantly from the Herztian theory for $t_L < 0.01$ s. During the holding time, the material "creeps" all the way to the corresponding Herztian point and then follows the Herztian response in unloading. Based on the work of Packard *et al.*,[12] the yielding load for typical Zr-based MGs can be estimated around ~4000 μN when they are indented with a 5-μm spherical tip, which is consistent with our experimental results.

Recent simulations and experiments suggest that MGs be a mixture of solid- and liquidlike atomic clusters.[8–11,13,14] Even in the apparent elastic deformation regime, their deformation still consists of the uncorrelated inelastic deformation of the liquidlike atomic clusters with the solidlike ones deforming elastically.[9,13] According to Ma *et al.*,[15] the solidlike atomic clusters responsible for the short-range order in MGs form a percolating network. In line with this finding, it is reasonable to propose that the solidlike atomic clusters generally encage the liquidlike ones. As such, the atomic structure of a MG can be simplified as a rheological three-parameter model [the inset of Fig. 1(a)]. The dashpot in the Kelvin unit is equivalent to the liquidlike atomic clusters, while the spring to the encaging solidlike ones. Furthermore, a second spring connected in series to the Kelvin unit is also assumed, which physically corresponds to those solidlike atomic clusters, if there were any, not interacting with any liquidlike clusters. Note that there may be other rheological models available for anelastic solids; however, in the literature, the three-parameter model was found to have the widest range of applications.[16] Since the essence of the underlying physics has been captured by the current model, we would keep our analysis within the analytic framework of the three-parameter model for simplicity.

For an elastic Hertzian contact, the load-displacement relation can be expressed as $h^{3/2} = 3P(1-\nu)/8GR^{0.5}$, where h is the indent depth; P is the indentation load; ν is the material's Poisson's ratio, G is the shear modulus and R is the indenter tip radius. For an anelastic solid as shown by the inset of Fig. 1(b), the loading curve can be derived from the Hertzian solution using the integral transform method,[17]

$$h(t)^{3/2} = h_0(t)^{3/2} - \frac{3\dot{P}(1-\nu)t_c}{8\sqrt{R}G_{II}}\left[1 - \exp\left(-\frac{t}{t_c}\right)\right], \qquad (1)$$

where $\dot{P}$ is the loading rate; G_{II} is the shear modulus of the spring in the Kelvin unit; t_c is the material's relaxation time and equals η/G_{II} with η being the viscosity of the dashpot; and $h_0(t)$ is the Hertzian solution $h_0(t)^{3/2} = 3P(t)(1-\nu)/8\sqrt{R}(1/G_I + 1/G_{II})$, where G_I is the shear modulus of the spring connected with the Kelvin unit in series. Note that Eq. (1) is valid only for the loading curve due to the limitation of the integral transform method.[17] For simplicity, a constant Poisson's ratio is assumed for both springs in deriving Eq. (1).

Treating G_I, G_{II}, and t_c as the three unknowns, their values can be extracted from the experimental data through nonlinear data fitting. Note that Eq. (1) is a viscoelastic solution; however, any nonlinearity in the material's behavior can be detected if the obtained t_c or η differs at different loading or

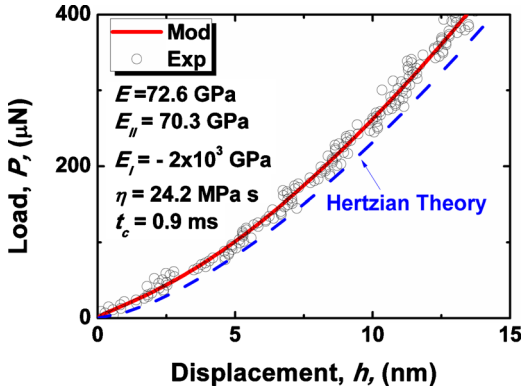

FIG. 2. (Color online) The comparison of the loading curves obtained from the experiment and theory corresponding to the loading time of 0.03 s (note that the Hertzian response corresponds to $E = 72.6$ GPa).

loading rates. Figure 2 shows the comparison of the experimental loading curves with the viscoelastic model. Evidently, the current model fits the experimental results very well despite its simplicity. Interestingly, through the data fitting, it was found that $1/G_{II} \approx 1/G_I + 1/G_{II}$. As a consequence, the fitted value of G_I was either unreasonably high or even negative, manifesting the divergence of G_{II} (Fig. 2). Physically, this implies that the atomic packing in MGs does not allow for the existence of such solidlike atomic clusters that can deform without disturbing any liquid-like atomic clusters. In other words, both types of atomic clusters should be highly coupled in MGs and the liquidlike ones are well "dispersed" in the amorphous structure, frustrating any long-range order brought about by the solidlike clusters.

Considering the possible statistical inhomogeneity intrinsic to the liquidlike atomic clusters,[14,18] the average viscoelastic properties representing the whole MG alloy was finally obtained by fitting a general trend as shown in Fig. 3, which presents the variations of the indentation depth, h_p, obtained at a given indentation load, P, with the loading time, t_L. Evidently, the viscoelastic model captures the experimental trend quite well. As the loading time is shortened, the MGs appear to be "stiffer" because of the rate dependence of the liquidlike atomic clusters. The transition from the quasistatic to dynamic response occurs at the time of about ~0.01 s, which is about 10 times the average relaxation time of the MG. The fitted viscoelastic properties, such as E, η, and t_c, are tabulated in Table I, which show that the

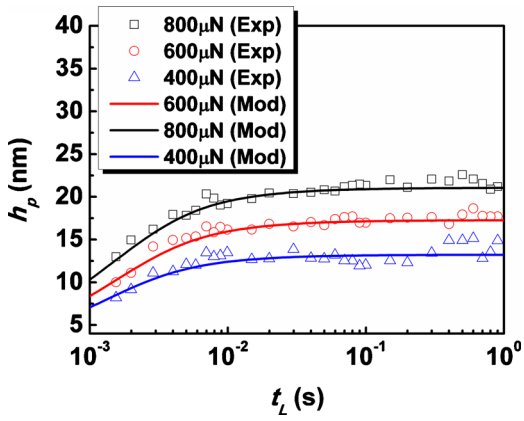

FIG. 3. (Color online) The variation of the indentation depth, h_p, with the loading time, t_L, at different indentation loads for the Zr-based MG.

TABLE I. The viscoelastic properties of the Zr-based MGs extracted by fitting the experimental data on Fig. 3.

	Zr-based MG (ν=0.365)		
Load (μN)	400	600	800
E (GPa)	76.5	76.9	76.2
t_c (ms)	0.9	1.1	1.1
η (MPa s)	25.9	31.6	31.2

overall elastic moduli and viscosity of the MG are load independent, implicative of the Newtonian flow behavior of the liquidlike atomic clusters under the current loading conditions. According to Refs. 4 and 8, the extracted viscosity, η, can be related to the concentration, χ, of the liquidlike atomic clusters, and their activation energy U_β for β relaxation, which can be simply expressed as $\eta \sim \chi \exp(U_\beta/RT)$, where R and T denote the gas constant and ambient temperature, respectively.[1,8] According to the recent work of Yu *et al.*,[19] $U_\beta \sim 26RT_g$ for MGs, where T_g is the glass transition temperature. Therefore, we can derive $\eta \sim \chi \exp(26T_g/T)$. As such, the constancy of η indicates a somewhat constant concentration of the liquidlike atomic clusters prior to shear banding.

In summary, we devised a simple nanoindentation approach in this letter to reveal and characterize the anelastic behavior of MGs. The experimental results clearly show that MGs consist of "soft" and "hard" phases at the atomic scale, which leads to the anelastic deformation behavior at the ambient temperature. As such, MGs are better to be viewed as anelastic instead of elastic solids. Such a paradigmatic shift in the theoretical modeling of the preyielding behavior may provide insights into the atomic-scale deformation mechanism of plasticity in MGs.

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