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Correlation between structural relaxation and shear transformation zone volume of a bulk metallic glass

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The effect of structural relaxation on shear transformation zones (STZs) in a $Zr_{70}Ni_{16}Cu_6Al_8$ glassy alloy is evaluated. Upon annealing, the measured STZ size dramatically decreases with moderate augment of mass density caused by the increase of icosahedra short-range orders. The greater atomic packing density gives rise to involvement of lesser atoms in the formation of STZs and thereby degradation of ductility. This study demonstrates that STZ volume is a key parameter reflecting the intrinsic relationship between atomic structure and mechanical properties of metallic glasses. *© 2009 American Institute of Physics*. [doi:10.1063/1.3246151]

The physical processes responsible for the dynamics and rheology of bulk metallic glasses (BMGs) at temperatures far below their glass transition points have long been of intense scientific and engineering interests.[1–4] Owing to the pioneering work by Argon,[5] the low-temperature deformation of metallic glasses is known to associate with shear transformation zones (STZs) that spontaneously and cooperatively reorganize in aid of free volumes when subjected to shear stress.[6–10] A benchmark of mechanical yielding of metallic glasses is that the potential-energy barrier to a mechanical instability of STZs approaches to zero with aid of shear stress.[4,7,9] The statistically averaged potential barrier is dependent on, in addition to stress and strain, the average volume of STZs.[4,6] Recently, following Johnson–Samwer cooperative shearing theory[7] and rate-jump nanoindentation technique,[11] we have developed a model to experimentally characterize the STZ volumes of BMGs.[10] The measured STZ volumes display an intrinsic correlation with the ductility, i.e., a BMG with larger STZ volume tends to be more ductile, which bestows an implication that STZ volume may be a key parameter to bridge atomic structure and mechanical behavior for establishing the structure-properties correlations of BMGs.

Owing to their nonequilibrium state, metallic glasses are subjected to intrinsic structural relaxation during annealing, which is a major factor to cause degradation of mechanical properties such as loss of plasticity.[4] On the other hand, structural relaxation by annealing at a temperature below glass transition point has been used to investigate the role of free volume in mechanical behavior of BMGs.[12,13] In this letter, we report on our observations that upon structural relaxation, the STZ volume of a hypoeutectic BMG decreases accompanied by increase in mass density and decrease of plasticity.

A quaternary hypoeutectic $Zr_{70}Ni_{16}Cu_6Al_8$ alloy was selected as the example alloy because of its excellent tensile ductility and detectable degradation in mechanical properties by annealing.[14] A $Zr_{70}Ni_{16}Cu_6Al_8$ coupon was fabricated in a shape of rod by arc-tilt-casting technique, preparation details of which can be found elsewhere.[14] Specimens with diameter of 3 mm and thickness of approximately 4 mm were cut from the as-cast rod and were subsequently annealed at 543 K (~0.9 Tg) for various time, viz. 0, 1800, and 7200 s (hereafter denoted as Zr-1, Zr-2, and Zr-3, respectively), prior to polishing the surfaces to mirror finish. The amorphicity of all the three samples was verified by x-ray diffractometry and high-resolution transmission electron microscopy. A commercial depth-sensing indentation apparatus, MTS™ G200 NanoIndenter, equipped with a Berkovich indenter was employed to characterize the STZ size. The mass density of the samples was measured by Archimedes method with a Shimadzu Accupyc 1330 gas pycnometer. Synchrotron x-ray scattering experiments were carried out at BL04B2 of SPring-8, Japan, with a 61.6 keV incident x-ray beam.

Fig. 1 and Table I illustrate that a moderate ~0.6% densification of the sample from 6.405 to 6.444 g/cm^3 is achieved after annealing at 543 K for 7200 s, indicating a widely observed densification effect of structural relaxation on the atomic packing density.[15] To explore the structure change corresponding to the density increase, the atomic structure of the three samples were investigated by synchrotron x-ray diffraction. The structural factors, $S(q)$, for $Zr_{70}Ni_{16}Cu_6Al_8$ under various annealing history indicate that, in lieu of the expected shift toward high q of the first main

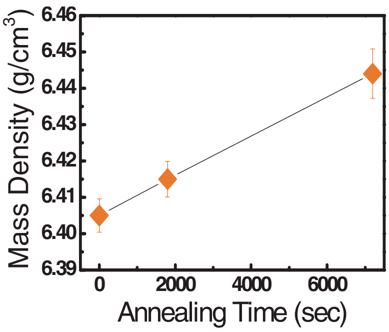

FIG. 1. (Color online) Dependence of mass density on annealing time. It can be unambiguously seen that the mass density increases with increasing annealing time at 543 K, indicating a widely observed densification effect of structural relaxation of metallic glasses by annealing.

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TABLE I. Measured STZ volume and mass density of $Zr_{70}Ni_{16}Cu_6Al_8$ annealed at 543 K for 0, 1800, and 7200 s.

Annealing time (s)	Hardness (GPa)	Strain rate sensitivity	STZ volume (nm^3)	Mass density (g/cm^3)
0 (as-cast)	5.01 ± 0.01	0.00282 ± 0.00055	15.70 ± 3.85	6.4045 ± 0.0046
1800	5.03 ± 0.01	0.00441 ± 0.00011	10.65 ± 0.21	6.4147 ± 0.0049
7200	5.64 ± 0.02	0.00582 ± 0.00013	7.60 ± 0.21	6.4443 ± 0.0068

peak (q_1) in conformity with the densification upon annealing,[16] a constant first sharp peak at $q_1 = 2.55$ Å^{-1} is observed for all the three samples [Fig. 2(a)]. Accordingly, with an average atomic volume $v_a = 20.55$ Å^3/atom for $Zr_{70}Ni_{16}Cu_6Al_8$, the power-law correlation function proposed by Ma *et al.*[17] is found to be satisfied within the medium-range length scale: $q_1 \cdot v_a^{0.433} = 9.44$. Moreover, for all the three samples, a shoulder (q_{22}) develops on the right-hand side of the second peak (q_{21}), indicative of an icosahedra short-range order (ISRO).[18,19] Actually, by fitting the second peak and its shoulder with two overlapping Gaussians, we found a constant $q_{21}/q_1 = 1.714 \pm 0.006$ whereas q_{22}/q_1 ratio increases from 1.941, 1.961, to 1.983 for Zr-1, Zr-2, and Zr-3, respectively. These values are well consistent with theoretical ones $q_{21}/q_1 = 1.71$ and $q_{22}/q_1 = 2.04$ for ISRO. The shift in q_{22} originated from the structural relaxation, albeit small, can be viewed as a proof for the enhanced dense packing by increase in ISRO,[19,20] which suggests atomic-scale origins of the structural relaxation and densification of the glassy $Zr_{70}Ni_{16}Cu_6Al_8$ alloy. In contrast with noticeable change in the ISRO, the reduced atomic pair distribution functions (RPDF), $G(r)$, for Zr-1, Zr-2, and Zr-3 show nearly no difference in both the first and second neighbor shell distances.[20] Beyond the second shell ($r > 6.78$ Å), on the other hand, more obvious fluctuations in the RPDF curve are observed, which endorses the change in the medium-range order caused by the increase of ISRO in association with free volume density during annealing.

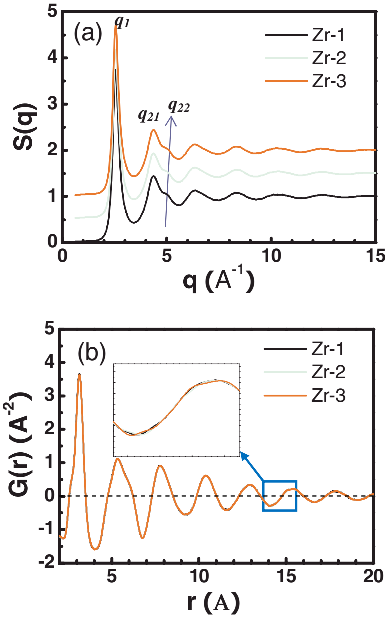

FIG. 2. (Color online) (a) The structural factor $S(q)$ of the $Zr_{70}Ni_{16}Cu_6Al_8$ alloy annealed at 543 K for 0, 1800, and 7200 s. Detectable difference was seen in the shoulder of second $S(q)$ peaks of Zr-1, Zr-2, and Zr-3, which indicates that the structural relaxation by annealing brings about the increase of ISRO in the hypoeutectic $Zr_{70}Ni_{16}Cu_6Al_8$. (b) Corresponding reduced pair distribution functions $G(r)$ showing negligible difference in the first and second shell distance. Closer inspection on higher-order peaks evidences the change in medium-range order, as the example shown in the inset.

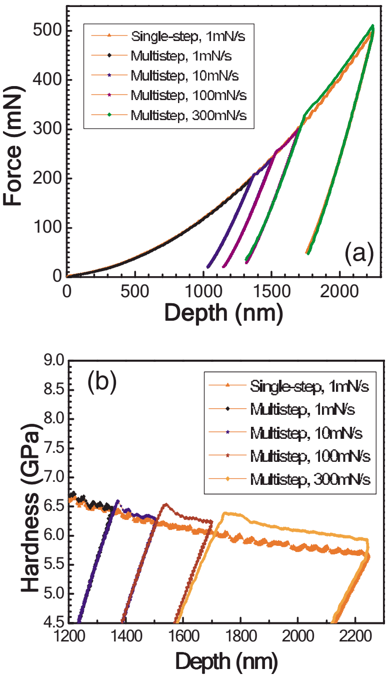

FIG. 3. (Color online) (a) Example *P-h* and (b) corresponding hardness vs depth curves of Zr–3 by rate-jump nanoindentation testing at a variety of loading rates ranging from 1 to 300 mN/s.

Typical force versus depth curves of Zr-3 by rate-jump nanoindentation are shown as examples in Fig. 3(a), whereas the corresponding hardness versus depth curves are consequently calculated,[21] as shown in Fig. 3(b). The fast approaching of hardness to a stable value upon straining provides an implication of negligible contribution of softening by dilatation upon straining to mechanical response at this ‘steady flow’ stage owing to the unique deformation features of depth-sensing indentation technique by which the plastic deformation is accomplished by continuously involving new undeformed volume underneath the diamond indenter.[22] Four loading rates, viz. 1, 10, 100, and 300 mN/s, were adopted to measure the hardness, H and strain rate sensitivity (SRS), m, for characterizing their STZ volumes.[10] At the same loading rates, the hardness of the BMG increases with annealing time [Fig. 4(a)], demonstrating that denser structure has a higher hardness. It can be clearly seen that the hardness of all three samples displays a weak yet discernable dependence on loading rates, which enables measurement of SRS of $Zr_{70}Ni_{16}Cu_6Al_8$ with various thermal history. However, as over the applied loading rate range the low SRS yields only a few percent difference in hardness that may be comparable to that induced by indentation size effect,[23,24] a conventional one-step instrumented indentation experiment is also conducted, which is used as reference to minimize the size effect in the measured SRS by normalizing the measured hardness in rate-jump experiments [Fig. 3(b)].[11] In consequence, strain rate sensitivities of Zr-1, Zr-2, and Zr-3 were shown in Fig. 4(a). Upon determination of hardness and SRS, the STZ volume, Ω, is calculated as $\Omega = kT/C'mH$,[10] where k is Boltzmann constant, T is temperature, and C' is a material-dependent constant.

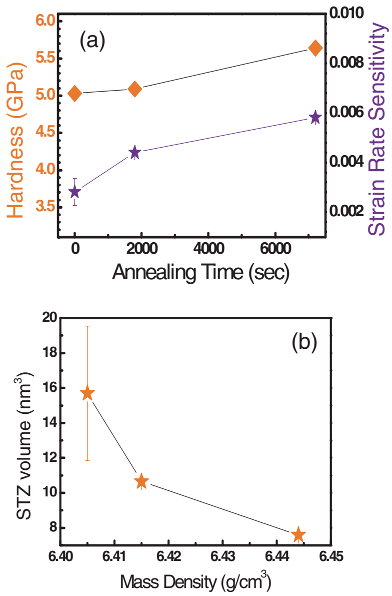

FIG. 4. (Color online) (a) Dependence of hardness and strain rate sensitivities on annealing time. (b) Correlation of the accordingly calculated STZ volume with the mass density of $Zr_{70}Ni_{16}Cu_6Al_8$ upon annealing. The STZ volume decreases dramatically in company with denser packing by structural relaxation.

As shown in Table I, the as-cast $Zr_{70}Ni_{16}Cu_6Al_8$ sample possesses a large STZ volume of 15.6 nm^3, or a characteristic size of about 2.5 nm. With increase of annealing time, the STZ volume of the $Zr_{70}Ni_{16}Cu_6Al_8$ glassy alloy decreases, approximately by half after 7200 s annealing at 543 K. Considering the changes of density and ductility with annealing, we plot the STZ volume as the function of mass density [Fig. 4(b)], which shows that denser atomic packing has smaller STZ volumes in company with lower ductility.[12] It is noteworthy that the large change in STZ volume, in contrast with an approximately 1% change in free volume,[25] implies that STZ volume may be a more direct and definitive parameter to bridge the correlation atomic structure and mechanical behavior of BMGs. Generally speaking, structural relaxation leads to either irreversible change in atomic sites rearrangement by near-T_g annealing (topological SRO) or reversible change in different atoms by annealing at temperature far below T_g (compositional SRO).[15] Since the annealing temperature of 543 K is close to 0.9T_g, the irreversible structural relaxation takes place by the annihilation of free volume due to atomic densification by the increase of ISRO as evidenced by the synchrotron x-ray scattering (Fig. 2). In general, free volume, or defective atomic packing, offers the STZ mobility required for shear deformation. The greater packing density along with the annihilation of free volume upon annealing gives rise to involvement of lesser atoms in the formation of STZs under shear stress. Moreover, the increase of the stable ISRO with low energy also leads to higher energy barriers for activation of local shear events and a lower capability for the glassy alloy to deform plastically. Therefore, structural relaxation results in degradation in ductility and augmentation in strength (hardness) as a consequence of the increased resistance for the activation of STZs.

In summary, we have systematically investigated the structural relaxation effect on the STZ volume of a hypoeutectic $Zr_{70}Ni_{16}Cu_6Al_8$ BMG. By comparing measurable changes in atomic structure and mechanical properties, we attempt to unveil the intrinsic correlation between atomic structure and mechanical behavior of BMGs by using the dynamic variable of STZ volume as the bridging parameter. It has been found that, upon structural relaxation, the atomic densification by the increase of ISRO leads to the decrease of STZ volume along with the degradation of ductility and the augmentation of hardness. The greater atomic packing density gives rise to involvement of lesser atoms in the formation of STZs and steeper potential energy barriers for activation of STZs.

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[22] It is noteworthy that the unique deformation features of instrumented indentation technique enable itself to viably characterize the STZ volume of BMGs. In an indentation test, the plastic deformation volume keeps expanding in company with increase of indentation depth, viz. upon continuous "plowing" of the indenter into the sample, the deformation zone becomes bigger by a certain amount of plastically undeformed volume getting involved in the plastic deformation process, different from a constant deformation volume in a uniaxial compression test. The deformed zone, although it may undergo possible structural change such as dilatation effect by free volume, may solely make a minor contribution to the succeeding mechanical behavior whereas the "new" plastic deformation volume is primarily responsible for the macroscopic mechanical response. Indeed, when the indentation size effect of hardness (Ref. 23) is taken into account, the contact pressure at later stage of deformation stays essentially constant upon increase of plastic strain/depth, instead of continuously softening/hardening caused by structural evolution.
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