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# Deformation-induced change in the structure of metallic glasses during multistep indentation

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The perplexing controversy of whether deformation-induced hardening/softening is intrinsic or extrinsic remains an outstanding fundamental problem in the low-temperature rheology and dynamics of metallic glasses. In this Brief Report, by manipulating nanoscale plastic deformation in a multistep instrumented indentation process, we *in situ* characterize and definitively elucidate the deformation-driven structural changes in metallic glasses via their strengthening or softening effect on consecutive mechanical behavior.

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Plastic deformation of crystalline materials is well known to be accomplished by multiplication and exhaustion of dislocations and the change in dislocation density during deformation can lead to noticeable strain hardening or softening.[1] In principle, such a dislocation-mediated hardening and softening is not operative in amorphous solids, such as metallic glasses, because of lack of dislocations.[2–6] Surprisingly, recent studies demonstrate that macroscopic strength change caused by deformation can take place in bulk metallic glasses (BMGs).[7–13] Nevertheless, the experimental results are perplexing: both strain hardening and softening have been discordantly reported. Moreover, the interpretations are also controversial. From intrinsic material behavior such as deformation-induced excess dilatation[7] and crystallization[10] to extrinsic factors of testing machine and sample surface conditions[12] have accordingly been proposed. The evidence of deformation-induced structure changes and thereby strain softening or hardening within or in the close vicinity of the shear bands are extremely scarce. Despite a long desire to its explication, the strain-induced structure changes and their impact on mechanical properties of BMGs are considerably difficult to experimentally characterize because of technical difficulties to measure hardness/strength directly on shear bands with a width of tens of nanometers. Accordingly, the intrinsic nature of strain hardening and softening in BMGs have not been definitively elucidated by experiment to date, which remains an unsolved fundamental problem in rheology and dynamics of glasses. In this Brief Report, by manipulating nanoscale plastic deformation during multistep instrumented indentation, we report on *in situ* identification of deformation-induced structure changes in BMGs and their corresponding influence on succeeding mechanical behavior.

Four glassy alloys, namely, $Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$, $Pd_{40}Ni_{40}P_{20}$, $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$, and $Fe_{57.6}Co_{14.4}B_{19.2}Si_{4.8}Nb_4$, were prepared in form of rods by copper-mold casting and were metallographically polished to a mirror finish surface. The amorphicity of all the four samples was verified by x-ray diffractometry and transmission electron microscopy (TEM). A dynamic ultramicro-hardness tester (Shimadzu W201S), equipped with a Berkovich diamond indenter, was employed to carry out the multistep indentation tests. Cyclic load-unload instrumented indentation tests were conducted at a constant force rate to impress the specimens in 5 up to 20 cycles at maximum test forces ranging from 10 to 200 mN. By manipulating the incremental load, $\Delta F$, hence the plastic deformation volume increment underneath the indenter, $\Delta V_{def}$, between contiguous load-unload cycles $N$ and $N+1$, the possible hardening/softening induced by intrinsic structural change in the predeformed region can be purposely "zoomed in" in the mechanical response with aid of deformation discontinuity between cycles. The hardness values are calculated using Oliver-Pharr approach.[13,14] The indentation topographies were characterized and analyzed using atomic force microscope (Veeco Instruments Inc., CP-50-OL) in tapping mode and the WSXM™ and IGOR™ software. The microstructure of the deformed volumes was investigated by TEM (JEOL, JEM-2100F). The TEM samples were prepared by multibeam focused ion-beam system (JEOL, JIB-4600F).

Figures 1(a) and 1(b) show typical force vs depth ($P$-$h$) curves of Pt-based BMG by multistep instrumented indentation at load increments of 1.0 and 4.0 mN/step, respectively. Conventional "single-step" $P$-$h$ curves are also obtained for comparison with multistep results to highlight possible altering in the mechanical response by deformation-induced structural evolution.[15] In the cases of large load increments (e.g., 4.0 mN/step), all load-unload cycles in the $P$-$h$ curve can be distinctly identified with remarkable increment in plastic deformation at a higher peak load level than that in the preceding unloading, whereas negligible difference is found between global mechanical response of single-step and multistep tests [Fig. 1(b)]. In the cases of small load increments (e.g., 1.0 mN/step), some adjacent unload-reload steps are found to overlap with each other at later stage of deformation, displaying an elastic load step despite of the increase in peak indentation load upon reloading. For example, in a multistep test with load increment of 1.0 mN/step, only 11 out of 15 applied unload-reload steps can be visually distinguished in the $P$-$h$ plot [Fig. 1(a)]. As a result of these unusual elastic load cycles, a global strengthening in multistep experiment, viz., a less total indentation depth [Fig. 1(a)] and higher hardness [Fig. 1(c)] than those in a single-step experiment at the same maximum load level comes about. Similar results are also recurrently observed in the Pd-based BMG (not shown). By contrast, this global strengthening by multistep indentation is not observed in the Zr-based and Fe-based BMGs. Nevertheless, it can be clearly seen in Fig. 2(a) that multistep instrumented indentation of Zr-based BMG renders a larger indentation depth than single-step one as an incremental load smaller than 10 mN/step, displaying an-

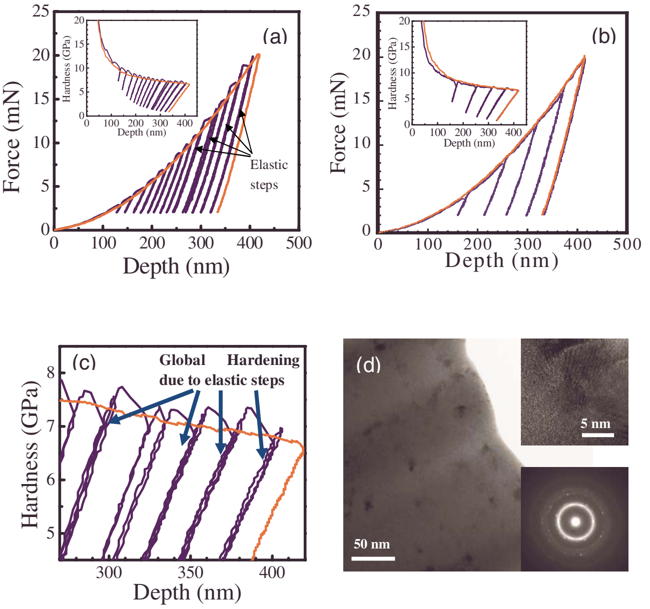

FIG. 1. (Color online) Typical *P-h* curves (dark color) of ductile monolithic $Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$ BMG by multistep nanoindentation at various load increments and load steps: (a) 1.0 mN/step, 20 steps and (b) 4.0 mN/step, 5 steps. Elastic load-unload steps (indicated by arrows) are clearly seen (a) in the cases of small load increments but (b) not in the cases of large ones. Corresponding single-step *P-h* curves (the light gray curves in print, or in red online) are also shown as reference. When compared to single-step results, an overall "hardening," i.e., a less indentation depth at the same maximum load level, comes about as a result of these elastic steps in multistep experiments. (c) Closeup of corresponding hardness vs depth curves of (a) to highlight this global hardening phenomenon. (d) A density of nanocrystallites can be clearly seen in the deformed volume right underneath the indent tip. The diffraction pattern and high-resolution images in the inset also unambiguously confirm the presence of crystallites.

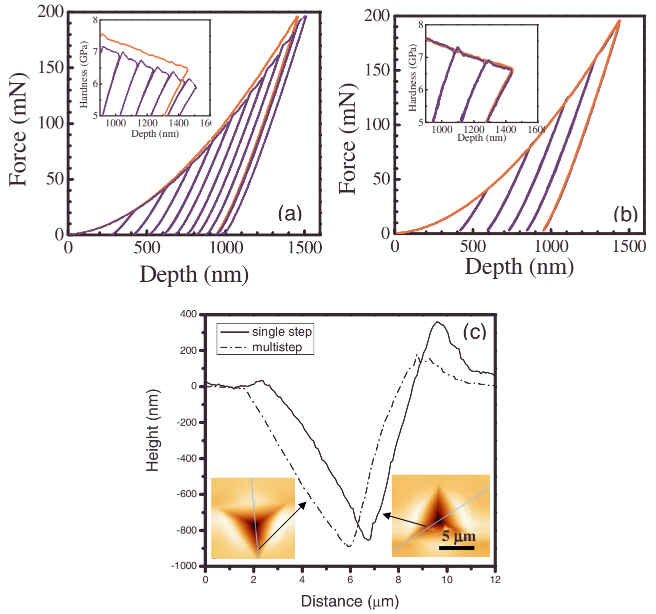

FIG. 2. (Color online) Typical *P-h* curves of $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ BMG by multistep instrumented indentation at (a) 19.6 mN/step, 10 steps and (b) 39.2 mN/step, 5 steps. When compared to single-step results, an overall "softening," i.e., a larger indentation depth at the same maximum load level as shown in the line scan profiles of indentations in (c), comes about. The corresponding hardness vs depth curves are given in the insets of (a) and (b). Furthermore, a lower pileup-to-indent volume ratio indicates a softer deformed volume by multistep load-unload than that by single-step one.

other atypical scenario of global softening in BMGs under indentation. This softening phenomenon, however, decays quickly upon increase in the incremental load and disappears at an incremental load of 40 mN/step [Fig. 2(b)].

Upon unloading in a load-unload cycle, residual stresses are expected to pertain, which possibly influence the ensuing mechanical response and measured hardness stemming from the large elastic limit of BMGs.[16,17] To investigate the significance of this potential effect, an Fe-based BMG that has a similar elastic limit as Pt-, Pd-, and Zr-based BMGs is tested in the same manner. As examples shown in Figs. 3(a) and 3(b), the single-step response of the Fe-based sample exhibits a perfect match with multistep ones, neither global strengthening nor softening was observed at a variety of load increments, ruling out possible influences of residual stresses as well as instrumental or experimental artifacts on our above observations of hardening in Pt-/Pd-based BMGs and softening in Zr-based BMG. Therefore, the underpinning processes of the above-mentioned global hardening or softening must originate from the unique deformation features of these glassy alloys.

In an earlier study, Yang and Nieh[18] reported a hardening and recovery phenomenon in a Zr-based BMG under multistep instrumented indentation. The accumulation and annihilation of free volume in the deformation volume[19–21] were proposed to be responsible for the hardness disparity.[18] In this work, it is indeed evidenced that besides the indentation size effect in measured hardness as in the single-step plot,[22] the hardness value of all the samples undergoes a slight yet discernible increase followed by a gradual drop to a stable value when reloaded to a load level higher than the peak load of the previous unloading, leading to negligible discrepancy in the global mechanical behavior [for instance, Fig. 2(b)]. However, the global strengthening in this work is intrinsically different from the localized hardening and recovery reported by Yang and Nieh,[18] given the apparent difference between the nature of deformation in the two phenomena and the dissimilar effect on the global mechanical response.

It has been reported that nanocrystallites form as a result of deformation in Al-, Ti-, and Zr-based metallic glasses.[23–25] Recently, a high-resolution electron microscope investigation on deformed ductile $Zr_{50}Cu_{50}$ BMG suggests that extensive nanocrystallization along shear bands can dramatically increase the strength of the shear regions since the viscosity of semisolid glass slurries depends exponentially on the fraction of solid nanocrystals.[10,26] Likewise, an intense density of nanoparticles that did not exist in the as-cast Pt-based BMG sample was observed in the indented volume, confirming the deformation-induced origin of these nanoparticles [Fig. 1(d)]. Nevertheless, such nanocrystallites were not observed in the postdeformation volume of Zr- and Fe-based BMG

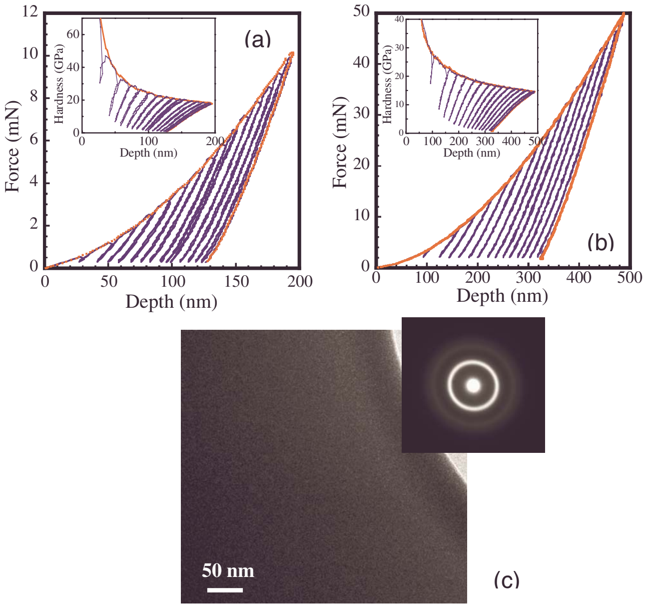

FIG. 3. (Color online) Typical *P*-*h* curves of $Fe_{57.6}Co_{14.4}B_{19.2}Si_{4.8}Nb_4$ BMG by multistep nanoindentation at (a) 0.67 mN/step, 15 steps and (b) 3.3 mN/step, 15 steps. No elastic load-unload steps are evidenced for the typical brittle Fe-based BMG. Despite of the reported local hardening upon reloading, the overall mechanical response remains identical to that of the corresponding single-step experiment. The insets are their corresponding hardness vs depth curves. (c) No detectable change in atomic structure can be found in the deformed volume right underneath the indent tip. The diffraction pattern in the inset also unambiguously confirms the full amorphicity of the deformed volume.

samples [Fig. 3(c)]. The presence of such nanoparticles in deformed Pt-/Pd-based BMGs not only alleviates the work softening caused by plastic flow of shear bands but also increases the resistance of shear band formation in consecutive deformation. As a consequence, in a multistep indentation test, *in situ* deformation-activated nanocrystallization in the Pt- and Pd-based BMGs leads to a strengthened deformed volume underneath the indenter, which detains the nucleation and/or propagation of shear bands in successive indentation while the increment of undeformed volume is small.

A systematic strain-induced softening in a Zr-based glassy alloy in which the hardness decreases linearly with increasing plastic strain and decreasing shear band spacing, whereas a shear-induced local dilatation by residual work in the glass may be the source of the observed deformation-induced softening, has been reported by Bei *et al.*[7] In this work, essentially similar to the scenario in Ref. 7, deformation-induced softening in the Zr-based BMG (same composition as the one used in Ref. 7) was evidenced in the multistep loading with the same maximum peak load as in the single-step one [Fig. 2(a)], which is verified by the difference in residual depths by multistep and single-step indentation measured from the line scan profile across the indentation [Fig. 2(c)]. Furthermore, in the case of single-step indentation, the pileup-to-indent volume ratio ($0.66 \pm 0.02$) is distinctively higher than the multistep one ($0.58 \pm 0.03$), suggesting a softer deformed volume by multistep load-unload cycles.[27–29] Based on the free volume theory by Spaepen,[18] this softening originates from the significant amount of excess free volume created by mechanical loading to accommodate the plastic deformation, which consecutively accommodates additional amount of deformation and in the meantime results in reduced pileup volume.[7,27,28] A probable reason of that this softening is much more pronounced in Zr-based BMG is that the annihilation rate of excess free volume in Zr-based BMG by self-diffusion is much lower than that in Pt-, Pd-, or Fe-BMGs, provided the diffusivity of Zr atoms well below $T_g$ is much lower as a result of its bigger atomic size than Pt, Pd, and Fe atoms.[30,31]

Akin to the composite model in Ref. 7, a composite model of deformed and undeformed volumes is herein suggested to interpret why multistep indentation is capable of capturing the strengthening/softening effect in macroscopic mechanical response. That is, the hardness of such a composite is given by

$$H = \frac{\Delta V_{def} H_{undef} + V_{def} H_{def}}{\Delta V_{def} + V_{def}}, \qquad (1)$$

where $V_{def}$ and $V_{def} + \Delta V_{def}$ are the plastically deformed volume of cycles $N$ and $N+1$ [Fig. 4(a)], respectively, and $H_{def}$ and $H_{undef}$ are hardness of the plastically deformed and undeformed volume, respectively. It is noted that $H_{undef}$ is as-

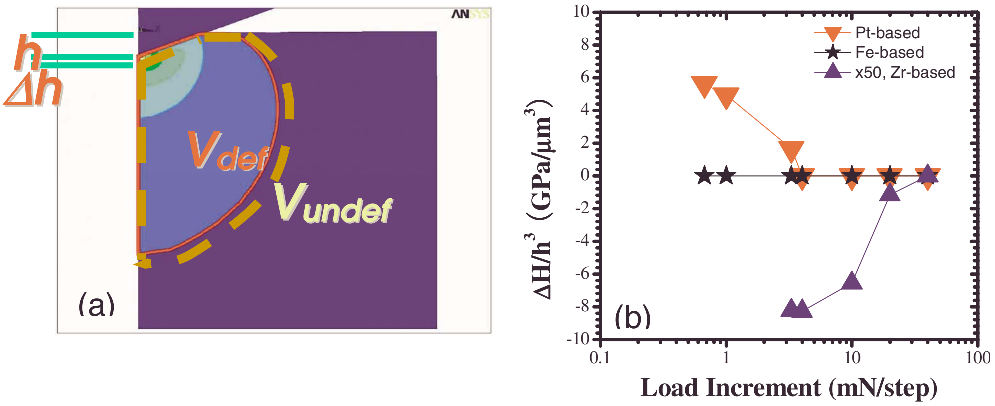

FIG. 4. (Color online) (a) Example of deformed volume underneath the indenter demonstrated in a finite-element simulation, (b) Load increment dependence of measured hardness of Pt-, Fe-, and Zr-based BMGs by manipulating the deformation amount in load steps.

sumed to be equal to the measured hardness of single-step experiment. Hence, rewriting Eq. (1)

$$H = H_{undef} + \frac{V_{def}(H_{def} - H_{undef})}{V_{def} + \Delta V_{def}}. \qquad (2)$$

The difference $H_{def} - H_{undef}$ by the hardening (nanocrystallites) or softening (local dilatation) in $V_{def}$ is assumed to be very small owing to the limited volume fraction of nanocrystallites or excess free volume in the deformed region. When the undeformed volume $\Delta V_{def}$ is only a small fraction of the deformed volume $V_{def}$, $\frac{V_{def}}{V_{def}+\Delta V_{def}} \to 1$, then $H \to H_{def}$. The hardening or softening effect in $V_{def}$ is thus highlighted. In the case of an undominative deformed volume, the contribution of term $\frac{V_{def}(H_{def}-H_{undef})}{V_{def}+\Delta V_{def}}$ in Eq. (2) may be limited so that the measured hardness may exhibit an insignificant deviation from $H_{undef}$ or the hardness measured in a single-step experiment. This composite model is thus consistent with the observation that the significance of hardening or softening effect on mechanical response decays rapidly with increase in incremental load step [Fig. 4(b)], which also explains why no obvious deviation in the global mechanical response of multistep indentation from the single-step one is observed until the later stage of deformation [Figs. 2(a) and 3(a)]. Nevertheless, in the case of single-step indentation of BMGs, the uninterrupted deformation is unable to reflect the strengthening/softening effect as the shear bands are continuously activated in the undeformed volume upon further "plowing" of the indenter into the specimen, which statistically results in a measurement of the strength/hardness of the undeformed glassy volume.

In summary, we provide an *in situ* and definitive experimental evidence of the deformation-driven structural changes in metallic glasses via their strengthening or softening effect within or near the shear bands on consecutive mechanical behavior by manipulating nanoscale plastic deformation in the proposed experimental metrology. The validity of the proposed experimental methodology has been established by a composite model of deformed and undeformed volumes underneath the indenter, which successfully interpret why multistep indentation is capable of capturing the strengthening/softening effect in macroscopic mechanical response.

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