Crystallization-aided extraordinary plastic deformation in nanolayered crystalline Cu/amorphous Cu-Zr micropillars

J. Y. Zhang, G. Liu & J. Sun

State Key Laboratory for Mechanical Behavior of Materials, Xi’an Jiaotong University, Xi’an, 710049, P.R. China.

Metallic glasses are lucrative engineering materials owing to their superior mechanical properties such as high strength and great elastic strain. However, the Achilles’ heel of metallic amorphous materials — low plasticity caused by instantaneous catastrophic shear banding, significantly undercut their structural applications. Here, the nanolayered crystalline Cu/amorphous Cu-Zr micropillars with equal layer thickness spanning from 20–100 nm are uniaxially compressed and it is found that the Cu/Cu-Zr micropillars exhibit superhigh homogeneous deformation (≈30% strain) rather than localized shear banding at room temperature. This extraordinary plasticity is aided by the deformation-induced devitrification via absorption/annihilation of abundant dislocations, triggering the cooperative shearing of shear transformation zones in glassy layers, which simultaneously renders the work-softening. The synthesis of such heterogeneous nanolayered structure not only hampers shear band generation but also provides a viable route to enhance the controllability of plastic deformation in metallic glassy composites via deformation-induced devitrification mechanism.

The widespread enthusiasm for research on metallic glasses (MGs)1–3 is driven by both a fundamental interest in the structure and properties of disordered and nonequilibrium materials and their unique promise for structural and functional applications, in particular for small-scale applications, such as nano- and micro-electro-mechanical systems (NEMS and MEMS)4–6. Although many bulk MGs exhibit high strength and show substantial fracture toughness, they lack tensile ductility and fail in an apparently brittle manner in unconstrained loading geometries2. For instance, some bulk MGs exhibit significant plastic deformation in compression or bending tests, but all exhibit negligible plasticity (<0.5% strain) in uniaxial tension1–3. To overcome brittle failure in tension, introducing an additional crystalline phase into a MG matrix is capable of suppressing such shear failure, resulting in enhanced global plasticity by forming multiple shear bands (SBs) and SB patterns8–10. Another effective approach to suppress the catastrophic failure of MGs is synthesizing crystalline/amorphous (C/A) nanolaminates with tensile strength ~1–3 GPa and tensile ductility of ~3–14% via integrating crystalline and amorphous layers11–12.

Since MGs are not in thermodynamic equilibrium, supplying such alloys with sufficient energy can promote a phase transformation from an amorphous to a more stable crystalline phase. Mechanical energy in the form of plastic deformation thus can trigger the formation of nanocrystals from the glassy phases, which is well known as deformation-induced devitrification (DID)13–18. For monolithic MGs, DID can effectively improve their ductility due to the propagation of SBs can be inhibited by the crystallites13–19, implying the high controllability of the plastic flow of MGs can be achieved. However, the underlying physical mechanism of DID and how this unique phenomenon influences the mechanical behaviors of MGs matrix composites and/or C/A nanolaminates remains shrouded in much mystery. Here, the interplay between the amorphous layers and crystalline layers as well as their mutual effects on mechanical behavior was revealed by investigating the extraordinary plastic deformation in nanolayered crystalline Cu/amorphous Cu-Zr pillars under compression condition at low strain rate and room temperature.

Results

Microstructure of C/A micropillars. The XRD patterns of as-deposited C/A Cu/Cu-Zr multilayers reveal a strong (111) peak in Cu, which broadens with decreasing layer thickness (h). The peak intensity of glassy Cu60Zr40...
is quite low in all of the C/A multilayers, which agrees well with the observed weak amorphous humps in monolithic amorphous films in the diffraction angle range (2θ) of 35–45°. The typical cross-sectional TEM images of h = 20 and 50 nm C/A multilayers unveils drastic contrast differences between nanocrystalline Cu and amorphous Cu-Zr layers, as respectively shown in Fig. 1(a) and (c), from which one can clearly see the modulated layered structure as well as internal amorphous structure in glassy Cu-Zr layer. The selected area diffraction pattern (SADP) shown in the inset of Fig. 1(a) and (c) also exhibited a diffuse amorphous ring, as is verified by the HRTEM observations in Fig. 1(b) and (d). In all of the C/A multilayers, the interfaces of C/A multilayers (CAIs) are quite distinguishable, see Fig. 1(b) and (d). Detailed descriptions about the microstructure of multilayers have been described elsewhere20,21.

Deformation morphologies and mechanical response of C/A micropillars. The typical FIB/SEM images taken before and after uniaxial compression of nanolayered micropillars with h = 50 nm were shown in Fig. 2(a) and (b), respectively. It appears that the deformed pillar at strain ~ 20% shows plastic barreling instead of shear banding and extrusion of material from the individual Cu layers, as proved by the point energy analysis20. Further cross-sectional FIB/SEM observations revealed that no shear fracture occurred in glassy layers in ~ 20% strained C/A pillars with h = 50 nm, even if the maximum strength of C/A pillars (~2.3 ± 0.1 GPa) sharply overwhelm the yield strength of amorphous Cu60Zr40 (~1.7 ± 0.05 GPa), as shown in Fig. 2(c).

The representative true stress-strain curves of the C/A pillars with three different layer thicknesses are shown in Fig. 2(d). It is found that the C/A pillars exhibit smooth plastic flow, supporting the absence of shear banding events often associated with monotonic MGs. This is in sharp contrast with the jerky true stress-strain response of amorphous pillars (see inset in Fig. 2d). Moreover, it is noteworthy that in Fig. 2(d) the maximum strength of C/A pillars monotonically increases from ~ 1.7 ± 0.05 to 2.3 ± 0.1 GPa as h decreases from 100 to 20 nm. In other words, the size-driven strength appears to increase in a “smaller is stronger” fashion. Another intriguing feature is that the true stress-strain response of C/A pillar gradually shifts from initial strain hardening (at low plastic strain εp < 10%) to work softening (at high plastic strain εp > 10%).

In particular, the h = 100 nm pillars exhibit weak even no strain hardening, while the smaller h pillars present stronger hardening behavior. The increased strain hardening capability with reducing h is caused by more glide dislocation-interface interactions20,22,23. In contrast, there is a propensity that smaller h pillars exhibit more pronounced softening behavior owing to more CAIs acting as dislocation sinks exist in the smaller h pillars12,20.

Internal structure features of compressed C/A micropillars. To further explore the nanoscaled mechanical properties of the as-deposited C/A multilayers and unveil the underlying physical mechanisms of their extraordinary plasticity, TEM samples were fabricated by FIB from the 30% deformed C/A pillars to observe the detailed deformation features, using a trenching and lift-out technique. Fig. 3(a) is the typical cross-sectional FIB/SEM images of the 30% deformed h = 50 nm C/A pillars, from which one can see the wavy CAIs, non-uniform reduction in layer thickness and broken amorphous layers, radically different from the homogeneity in deformation in the 20% compressed C/A pillars. This means that the heterogeneity in the layer thickness reduction and the fragmentation of amorphous layer is only apparent under such severe deformation (~30% strain). Further TEM observations and EDX analysis of the deformed C/A pillars through-thickness cross-sections are shown in Fig. 3(b–d). We summarize our observations based on TEM observations and EDX analysis as follows: (i) In spite of the non-uniform thickness reduction, there was no interfacial delamination, implying good strain compatibility of CAIs. (ii) There were no traces of fracture or microcracks in nanocrystalline Cu and amorphous Cu-Zr layers, indicating extraordinary homogeneous flow in glassy layers and high compressive deformability of nanolayered Cu/Cu-Zr pillars (> 30% strain) can be achieved without sacrificing strength. (iii) Neither heavy dislocations storage nor abundant planar defects such as stacking faults and deformation twins in the crystalline Cu (and crystalline Cu-Zr phase) layers were observed (see Fig. 3b), implying the nucleated dislocations can be...
and the SB propagation stress are comparable, the propagation of SBs is rather than the SBs in the glassy layers were frequently observed, suggesting the DID could occur during plastic deformation. (v) The deformation-induced nanophase is orthorhombic $\text{Cu}_{10}\text{Zr}_7$ phase because the chemical composition of amorphous $\text{Cu}_{60}\text{Zr}_{40}$ is quite close to that of $\text{Cu}_{10}\text{Zr}_7$, indicating a possible structural affinity of the $\text{Cu}_{10}\text{Zr}_7$ phase and the glass on a short range order length scale$^{24}$. absorbed by the opposite CAIs and/or glassy layers. (iv) The amorphous Cu-Zr layers were almost fully crystallized (localized residual amorphous phase can still be found at the junction of grain boundaries (GBs) and CAIs, see Fig. 3c and d). This renders the nanosized crystallites with a wide size range of $\sim 10–50$ nm rather than the SBs in the glassy layers were frequently observed, suggesting the DID could occur during plastic deformation. (v) The deformation-induced nanophase is orthorhombic $\text{Cu}_{10}\text{Zr}_7$ phase because the chemical composition of amorphous $\text{Cu}_{60}\text{Zr}_{40}$ is quite close to that of $\text{Cu}_{10}\text{Zr}_7$, indicating a possible structural affinity of the $\text{Cu}_{10}\text{Zr}_7$ phase and the glass on a short range order length scale$^{24}$. Absorption of dislocations nucleated from crystalline phase by amorphous layers is accompanied with localized shearing flow, the questions natural arise are why DID occurs under high compressive strain at room temperature, and why the amorphous layers are almost fully crystallized at nanoscale ($\sim 20–100$ nm). It has been reported that both the mass transportation and the temperature rise within SBs and their vicinity produced by significant plastic flow can cause nanocrystallization in the narrow SBs$^{16,17,33,32}$. However, the fact that crystalline CuZr phase almost has the same composition as the parent glass suggests that there is no significant mass transportation occurred during plastic deformation. Moreover, the microcompression tests were performed at ambient temperature far below the glass transition points of amorphous $\text{Cu}_{60}\text{Zr}_{40}$ and the deformation volume is largely confined, which minimizes the temperature rise contributing to DID. In particular, there is no shear banding occurred avoided directly the consequence of the inevitable dynamic flow dilatation in the actively deforming bands (without any substantial increase in temperature during plastic flow) and of the attendant dramatic enhancement in atomic diffusional mobility$^{36}$. Therefore, we can exclude that the precipitation of the $\text{Cu}_{10}\text{Zr}_7$ nanocrystals during deformation originates from a temperature rise as well as mass transportation. Instead, we believe that stable plastic flow of the material leads to atomic displacements or arrangements, which directly results in crystallization.

To understand the underlying mechanism of DID, we follow the footsteps of Lu$^{33}$ and Lee et al$^{36}$ in light of the viewpoints of
thermodynamics and kinetics associated with two different stress states imposed on the samples, i.e., hydrostatic compression and shear. When the uniaxial compression of \(-2\) GPa (corresponding to the maximum strength of present C/A samples) is applied to the sample, it is decomposed into hydrostatic compression (\(-1\) GPa) and shear stress (\(-1\) GPa) at the maximum shear plane\(^{38}\). The hydrostatic compressive stress can reduce the energy barrier for nucleation; while the shear stress can lower the energy barrier for diffusion and induce the atoms to migrate along the shear direction, promoting an increase in the local free volume associated with atomic dilatation\(^{18,24}\). Analogous to the single-atom squeezing in Spaepen’s model\(^{34}\), the local shear transformations, or the motion of STZs, around free-volume sites can lead to the pushing apart of surrounding atoms along activation paths, resulting in an activation dilatation and thereby lowering the local viscosity and energy barrier for atomic diffusion in localized regions\(^{18,39,40}\). Therefore, the simultaneous action of hydrostatic compression and shear stress via uniaxial compression induces an enhancement of the nucleation rate, which promotes crystallization to accommodate the external compressive stress by reducing the volume of the amorphous phase through crystallization at room temperature.

Based on HRTEM observations of the deformed sample in Fig. 3, the nanocrystallites formed during deformation is orthorhombic Cu\(_{10}\)Zr\(_{7}\) phase. In this DID process the independent STZs which begin as small regions where the local atomic structure is capable of inelastic rearrangements under an applied stress, could take an important role as the nuclei for the nanocrystallization\(^{37,38}\). The STZ-mediated activities, namely cooperative shearing of unstable STZs activated by shear stresses, are the underlying reason to achieve the homogeneous-like flow as well as the amorphous-to-crystalline transition in Cu-Zr layers\(^{38,39}\). The cooperative shearing model of STZs\(^{38}\) correlated the structure of MGs with their energetics by introducing the concept of potential-energy landscape (PEL) in combination with STZs and thus allows one to interpret their deformation behavior at the atomistic scale and the DID process is kinetically favored.

Next, we will illustrate the underlying reasons for the lack of residual defects (such as dislocations, stacking faults and deformation twins) and mainly focus on the mechanism of atomic arrangements in the DID behavior from the following atom-scale viewpoint. Most recently, Arman et al.\(^{26}\) performed large-scale molecular dynamics simulations to investigate plasticity in Cu/Cu\(_{49}\)Zr\(_{51}\) glass nanolaminates under uniaxial compression. It is revealed that (leading and trailing) partials/full dislocations are observed in the Cu layers and screw dislocations are seen near the CAIs. Further experimental observations and simulations demonstrate that the nanoscale amorphous layer (or the CAI) not only exhibits an extraordinary capacity to act as dislocation sources/sinks but also as effective barrier for dislocations, and do interact with dislocations (including interface-induced screw dislocations), enabling absorption of free volume and free energy transported by the dislocations through CAIs\(^{37,26}\). When the incoming dislocations transmit cross the CAI and propagate inside the Cu layer, they will be absorbed by the
Methods

Multilayer synthesis and microstructure characterization. The ~ 2 μm-thick Cu/Cu-Zr C/A multilayers with equal layer thickness (h) varying from 20 to 100 nm and monotonous Cu60Zr40 amorphous films were deposited on Si (100) substrates by direct current (DC) magnetron sputtering at room temperature. Cu (99.999%) and Zr (99.99%) targets were used to produce alternating layers of nanocrystalline pure Cu and amorphous Cu60Zr40 (atomic fraction). The internal structure features of as-deposited Cu/Cu-Zr and Cu60Zr40 films were characterized by X-ray diffraction and transmission electron microscopy (TEM). High resolution transmission electron microscopy (HR-TEM) and energy dispersive X-ray (EDX) analyses to identify the elemental composition and the interface integrity of the specimens were performed on an FEI Tecnai 2000 TEM, with Fischione a ultra-high resolution high-angle annular dark field detector (0.23 nm resolution in STEM image mode) and Oxford instruments EDX detector with a spatial resolution of ~1 nm for chemical analysis. Detailed descriptions about the preparation of multilayers have been described elsewhere.

Flat punch compression test of nanolayered micropillars. To further explore their micro-scaled mechanical properties, the small tapered (~2–4 μm) nanolayered Cu/Cu-Zr micropillars with diameter (~750 nm) were fabricated from the as-deposited multilayers using a Helios Nano Lab 600i dual-beam focused ion beam (FIB) system, which also allows scanning electron microscopy (SEM) imaging. To minimize the potential damage from ion irradiation due to the Ga ion beam and to clean any newly-deposited materials from the pillar surface, the final FIB fine milling step was performed under a lowered voltage (15 kV) and current (15 pA). For comparison reasons, the φ = 950 nm Cu60Zr40 amorphous pillars were also prepared and then compressed at the same condition as mentioned above.

All the pillars were then uniaxially compressed in a Hystron T6 950 with a 10 μm flat-plate quadrilateral cross-section diamond indenter at a constant strain rate of 2 × 10−4 s−1 up to ~20–30% strain. Force-displacement data were continuously recorded, and the initial geometry of the pillar was measured from the SEM images. True stress-strain curves were calculated using a constant volume and homogeneous deformation assumption model to characterize the deformation behaviors.

Because of the amount of time required to conduct the vast majority of compression experiments, considerable efforts have been devoted to correcting for thermal drift to improve the reliability and accuracy of the present nanoscale deformation measurements. In the present work, the allowable-drift-rate was set at 0.005 nm s−1, which is 20 times smaller than the typical value (0.1 nm s−1) used in the testing of micromicropillars such that the effect of thermal drift could be minimized and neglected. More details about the micropillars preparation procedures, testing methods and true stress-strain curve calculation procedure can be found in Ref.

1. Wang, W. H. The elastic properties, elastic models and elastic perspectives of metallic glasses. Progress in Materials Science 57, 487–656 (2012).
2. Cheng, Y. Q. & Ma, E. Atomic-level structure and structure–property relationship in metallic glasses. Progress in Materials Science 56, 379–473 (2011).
3. Trexler, M. M. & Thadhani, N. N. Mechanical properties of bulk metallic glasses. Progress in Materials Science 55, 759–839 (2010).
4. Ashby, M. F. & Greer, A. L. Metallic glasses as structural materials. Scripta Materialia 54, 321–326 (2006).
5. Greer, A. L. Metallic glasses. Science 267, 1947–1953 (1995).
6. Demetriou, M. A damage-tolerant glass. Nature Mater. 10, 123–128 (2011).
7. Schuh, C. A., Hufnagel, T. C. & Ramamurty, U. Mechanical behavior of amorphous alloys. Acta Materialia 55, 4067–4087 (2007).
8. Das, J. et al. ‘Work-hardenable’ ductile bulk metallic glass. Physical Review Letters 94, 205501 (2005).
9. Hofmann, D. C. et al. Designing metallic glass matrix composites with high toughness and tensile ductility. Nature 451, 1085–1089 (2008).
10. Hays, C. C., Kim, C. P. & Johnson, W. L. Microstructure controlled shear band pattern formation and enhanced plasticity of bulk metallic glasses containing in situ formed ductile phase dendrite dispersions. Physical Review Letters 84, 2901–2904 (2000).
11. Kim, J. Y., Jang, D. C. & Greer, J. R. Nanolaminates Utilizing Size-Dependent Homogeneous Plasticity of Metallic Glasses. Advanced Functional Materials 21, 4550–4554 (2011).
12. Wang, Y. M., Li, J., Hanrau, A. V. Y. & Barbee, J. T. W. Ductile crystalline-amorphous nanolaminates. Proceedings of the National Academy of Sciences of the United States of America 104, 11155–11160 (2007).
13. He, Y., Shiflet, G. J. & Poos, S. I. Nanoindentation-induced nanocrystallization in aluminum-based metallic glasses. Acta Metallurgica et Materialia 43, 83–91 (1995).
14. Guo, F. Q. & Lu, K. Formation of a single α-Fe nanophase during mechanically driven crystalization of an Fe50Mn50 bulk metallic glass. Nanosciencetecht 7, 509–517 (1996).
15. Wang, K. et al. Micromechanisms of serrated flow in a Ni50Pd50P20 bulk metallic glass with a large compression plasticity. Acta Materialia 56, 2834–2842 (2008).
16. Kim, J. I., Choi, Y., Suresh, S. & Argon, A. S. Nanocrystallization During Nanindentation of a Bulk Amorphous Metal Alloy at Room Temperature. Science 295, 654 (2002).
17. Chen, M. Extraordinary plasticity of ductile bulk metallic glasses. Physical Review Letters 96, 245502 (2006).
18. Lee, S. W., Huh, M. Y., Fleury, E. & Lee, J. C. Crystallization-induced plasticity of Cu–Zr containing bulk alloy. Acta Materialia 54, 349–355 (2006).
19. Chen, M. Crystalline Mechanical Behaviour of Bulk Metallic Glasses. Microscopic Understanding of Strength and Ductility. Annu Rev Mater Res 38, 445–469 (2008).
20. Zhang, J. Y., Liu, G., Lei, S. Y., Niu, J. J. & Sun, J. Transition from homogeneous-like to shear-band deformation in nanolayered crystalline Cu/amorphous Cu–Zr micropillars: Intrinsic vs. extrinsic size effect. Acta Materialia 60, 7173–7196 (2012).
21. Zhang, J. Y. et al. Mechanical properties of crystalline Cu/Zr and crystal-amorphous Cu/Cu–Zr multilayers. Materials Science and Engineering: A 552, 392–398 (2012).
22. Zhang, J. Y. et al. Length scale-dependent deformation behavior of Cu/Zr micropillars. Acta Materialia 60, 1610–1622 (2012).
23. Zhang, J. Y. et al. Intrinsic and extrinsic size effects on deformation in nanolayered Cu/Zr micropillars: From bulk-like to small-volume materials behavior. Acta Materialia 60, 4054–4064 (2012).
24. Lee, S. W., Huh, M. Y., Chae, S. W. & Lee, J. C. Mechanism of the deformation-induced nanocrystallization in Cu-based bulk metallic amorphous alloy under uniaxial compression. Scripta Materialia 54, 1349–1444 (2006).
25. Liu, M. C., Lee, C. J., Lai, Y. H. & Huang, J. C. Microscale deformation behavior of amorphous/nanocrystalline multilayered pillars. Thin Solid Films 518, 7295–7299 (2010).
