

This article was downloaded by: [Texas A&M University Libraries]

On: 20 November 2014, At: 16:20

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Materials Research Letters

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/tmrl20>

### Repetitive Ultra-low Stress Induced Nanocrystallization in Amorphous Cu–Zr–Al Alloy Evidenced by in situ Nanoindentation

Y. Liu<sup>a</sup>, J. Jian<sup>b</sup>, J.H. Lee<sup>b</sup>, C. Wang<sup>cd</sup>, Q.P. Cao<sup>cd</sup>, C. Gutierrez<sup>e</sup>, H. Wang<sup>ab</sup>, J.Z. Jiang<sup>cd</sup> & X. Zhang<sup>ae</sup>

<sup>a</sup> Department of Materials Science and Engineering, Texas A&M University, College Station, TX 77843, USA

<sup>b</sup> Department of Electrical Engineering, Texas A&M University, College Station, TX 77843, USA

<sup>c</sup> International Center for New Structured Materials, Zhejiang University, Hangzhou 310027, People's Republic of China

<sup>d</sup> Laboratory of New Structured Materials, Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China

<sup>e</sup> Department of Mechanical Engineering, Texas A&M University, College Station, TX 77843, USA

Published online: 12 May 2014.

To cite this article: Y. Liu, J. Jian, J.H. Lee, C. Wang, Q.P. Cao, C. Gutierrez, H. Wang, J.Z. Jiang & X. Zhang (2014) Repetitive Ultra-low Stress Induced Nanocrystallization in Amorphous Cu–Zr–Al Alloy Evidenced by in situ Nanoindentation, Materials Research Letters, 2:4, 209-216, DOI: [10.1080/21663831.2014.911778](https://doi.org/10.1080/21663831.2014.911778)

To link to this article: <http://dx.doi.org/10.1080/21663831.2014.911778>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Versions of published Taylor & Francis and Routledge Open articles and Taylor & Francis and Routledge Open Select articles posted to institutional or subject repositories or any other third-party website are without warranty from Taylor & Francis of any kind, either expressed or implied, including, but not limited to, warranties of merchantability, fitness for a particular purpose, or non-infringement. Any opinions and views expressed in this article are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor & Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Terms & Conditions of access and use can be found at <http://www.tandfonline.com/page/terms-and-conditions>

It is essential that you check the license status of any given Open and Open Select article to confirm conditions of access and use.

## Repetitive Ultra-low Stress Induced Nanocrystallization in Amorphous Cu–Zr–Al Alloy Evidenced by *in situ* Nanoindentation

Y. Liu<sup>a</sup>, J. Jian<sup>b</sup>, J.H. Lee<sup>b</sup>, C. Wang<sup>c,d</sup>, Q.P. Cao<sup>c,d</sup>, C. Gutierrez<sup>e</sup>, H. Wang<sup>a,b</sup>, J.Z. Jiang<sup>\*c,d</sup> and X. Zhang<sup>\*a,e</sup>

<sup>a</sup>Department of Materials Science and Engineering, Texas A&M University, College Station, TX 77843, USA;

<sup>b</sup>Department of Electrical Engineering, Texas A&M University, College Station, TX 77843, USA; <sup>c</sup>International Center for New Structured Materials, Zhejiang University, Hangzhou 310027, People's Republic of China;

<sup>d</sup>Laboratory of New Structured Materials, Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China; <sup>e</sup>Department of Mechanical Engineering, Texas A&M University, College Station, TX 77843, USA

(Received 7 March 2014; final form 1 April 2014)

Supplementary Material Available Online

Stress driven nucleation of nanocrystals in amorphous alloys has been a subject of intensive debate in the past decade. It has long been postulated that nanocrystals form succeeding the occurrence of shear bands in deformed amorphous alloys. In this study, we show, via *in situ* nanoindentation of amorphous Cu<sub>44</sub>Zr<sub>44</sub>Al<sub>12</sub> alloy in a transmission electron microscope that the formation of nanocrystals occurred at an ultra-low stress of 0.25 GPa in the elastic deformation regime, accompanied by load-drops without evidence of shear bands. Furthermore, during successive loading, repetitive nanocrystal nucleation events were observed, and the stress required for nucleation kept on increasing to ~0.54 GPa, implying the occurrence of a 'hardening' effect in the amorphous alloy. This study provides direct evidence to advance our understanding on deformation-induced nanocrystallization of amorphous alloys.

**Keywords:** Amorphous Alloy, *In situ* Nanoindentation, Nanocrystallization, Stress, Hardening

### Highlights

- First *in situ* observation of ultra-low stress-induced nanocrystallization of amorphous alloys without evidence of shear bands.
- Successive loading leads to repetitive nucleation events, but nucleation requires increasing stress, i.e. a hardening effect is observed in deformed amorphous alloys.

Since the discovery of amorphous Au–Si [1] in 1960, amorphous alloys (also referred to as metallic glasses) have been investigated intensively.[2,3] Recent reviews have covered glass-forming ability,[4] mechanical properties,[5–7] and the microstructure–property relationship.[8] Compared with crystalline materials, amorphous alloys often exhibit close to theoretical strength and a large elastic strain,[9,10] good corrosion and wear resistance.[11,12] However, a major drawback

of these alloys is their limited room temperature ductility and toughness because of shear localization in discrete shear bands.[13,14] There are two major atomic-scale mechanisms in the literature on shear localization or shear band formation: deformation-induced dilatation or free volume production [15,16]; and local events of cooperative shearing of atomic clusters, referred to as shear transformation zones (STZs).[17–19]

Numerous mechanisms have been proposed to improve the ductility and toughness of amorphous alloys, including shear band interaction and multiplication,[20–22] nanocrystallization,[23] and shear band–nanocrystal interaction.[24] Das et al.[25] showed substantial work hardening, and compressive strain can be achieved in amorphous CuZrAl compared with amorphous CuZr, owing to nanocrystallization. Liu et al.[26] discovered superplastic deformation in ZrCuNiAl bulk metallic glass (BMG) under compression due to the introduction of structural heterogeneity which prohibits catastrophic

\*Corresponding authors. Emails: [zhangx@tamu.edu](mailto:zhangx@tamu.edu); [jiangjz@zju.edu.cn](mailto:jiangjz@zju.edu.cn)

failure. Dalla Torre et al.[27] observed a sharp drop in viscosity (shear softening) in deformed glassy ZrTiCuNiAl, where the appearance of serrated plastic flow was ascribed to the facilitation of additional flow in shear bands.

As the formation of nanocrystals in or along shear bands in amorphous alloys could potentially improve their ductility, stress-induced nanocrystallization has raised significant attention. Yoo et al.[28] observed indentation-induced nanocrystals on Zr-based metallic glasses by both Berkovich and cube-corner indenters. Chen et al.[29] observed nanocrystals in shear bands through a bending experiment, and ascribed nanocrystallization to a large strain accumulated in shear bands. Kim et al.[30] found (through post-indentation microscopy) nanocrystals in shear bands surrounding *ex situ* indented zone in Zr-based amorphous alloys and the authors attributed nanocrystallization to flow dilatation that radically enhanced atomic diffusional mobility inside shear bands. Jiang and Atzmon [31] reported that nanocrystals can form in shear bands only on the compressive side but not on the tensile side of bended amorphous alloys. Chen et al.[32] explained the tension–compression asymmetry of crystallization in amorphous alloys. These classical post-deformation studies deem shear bands necessary (as precondition) for nanocrystallization.

As most of the previous studies focused on post-deformation microstructural analysis, some major issues remain poorly understood. (1) What is the nucleation stress for nanocrystallization? (2) Do nanocrystals form preceding or succeeding the formation of shear bands? (3) How do nanocrystals contribute to work hardening of amorphous alloys? Techniques such as *in situ* deformation in a transmission electron microscope have recently been used to directly probe the structure–property relationship in metallic materials.[33–37] *In situ* tension studies on amorphous alloys revealed: large elastic strain limit,[9] remarkable ductility,[38] and nanocrystal-induced delocalization of shear bands and blunting of crack tips.[24] *In situ* nanoindentation studies on Zr-based metallic glass pillars revealed significant load-drops (when applied stress exceeded yield strength) accompanied by the formation of large shear bands.[39,40]

In this study, *in situ* nanoindentation in a transmission electron microscope was conducted on a traditional amorphous  $\text{Cu}_{44}\text{Zr}_{44}\text{Al}_{12}$  alloy which exhibited a large compressive strain and work-hardening behavior in the plastic regime.[25] Our *in situ* nanoindentation study on sputtered amorphous films shows clear evidence of ultra-low stress ( $\sim 15\%$  of yield strength) induced nanocrystallization accompanied by discrete load-drops. Shear bands were not observed during indentation. Successive loading of the films (at the same location) reveals that a substantial increase in stress is necessary to continue triggering nucleation of nanocrystals.

Thin films were deposited on Si wafers in a DC magnetron sputtering system (DCMS, JZCK-400) by using a crystalline  $\text{Cu}_{45}\text{Zr}_{48}\text{Al}_7$  target. The composition of the films examined by electron-dispersive X-ray spectroscopy in a field-emission scanning electron microscope (FE-SEM, Hitachi S-4800) was  $\text{Cu}_{44}\text{Zr}_{44}\text{Al}_{12}$ . The amorphous microstructure was confirmed by X-ray diffraction (XRD, PANalytical X'Pert PRO), and synchrotron radiation XRD at beamline BL14B1 of the Shanghai Synchrotron Radiation Facility at a wavelength of 0.12398 nm. The glass transition temperature  $T_g$  (716 K) and peak crystallization temperature  $T_x$  (795 K) were measured by high-precision differential scanning calorimetry (DSC) on a Netzsch DSC-404 instrument. Metallic glass ribbons with the same composition were fabricated by the melt-spinning technique and examined in DSC for comparison. As shown in Supplementary Figure S1, the metallic glass ribbons had similar  $T_g$  (718 K) and slightly lower  $T_x$  (784 K). The film density was measured to be 6.652 g/cm<sup>3</sup>, nearly identical to that of metallic glass ribbons. Indentation modulus of the amorphous film measured by *ex situ* nanoindentation with a Berkovich tip is 91 GPa, nearly identical to that of bulk amorphous alloys with similar compositions, 89 GPa in amorphous  $\text{Cu}_{46}\text{Zr}_{46}\text{Al}_8$  measured by uniaxial tension studies.[41] *In situ* nanoindentation was performed by using a transmission electron microscopy (TEM) sample holder manufactured by NanoFactory Inc. on a JEOL 2010 transmission electron microscope operated at 200 kV with a point-to-point resolution of 0.23 nm.

During *in situ* nanoindentation, a spherical shape nanoindenter tip was used with a tip radius of  $\sim 1,500$  nm. Indentation stress was estimated using the Hertzian contact estimation for the spherical tip [42] (see supplementary information for the calculation method in detail). TEM specimen thickness at the edge was measured to be  $\sim 30$  nm by using cross-section scanning electron microscopy (SEM) micrographs (Supplementary Figure S2).

Evidence of *in situ* nanoindentation-induced nanocrystallization in amorphous  $\text{Cu}_{44}\text{Zr}_{44}\text{Al}_{12}$  film was observed by comparing the microstructure of as-deposited and indented films. The bright field (BF) TEM micrograph and the selected area diffraction (SAD) pattern inserted in Figure 1(a) shows that as-deposited film was fully amorphous. Dark field (DF) TEM micrographs (by selecting different portions of the diffuse diffraction ring) in (a-1) and (a-2) show no evidence of nanocrystals. After indentation, the diffraction ring in Figure 1(b) remains diffuse. However, DF-TEM micrographs taken from the deformed specimen ((b-1) and (b-2)) reveal the formation of numerous nanocrystals,  $\sim 5$  nm in diameter. The high-resolution TEM (HRTEM) micrograph in Figure 1(c) shows lattice fringes from several nanocrystals as delineated by dotted lines in the deformed specimens. The

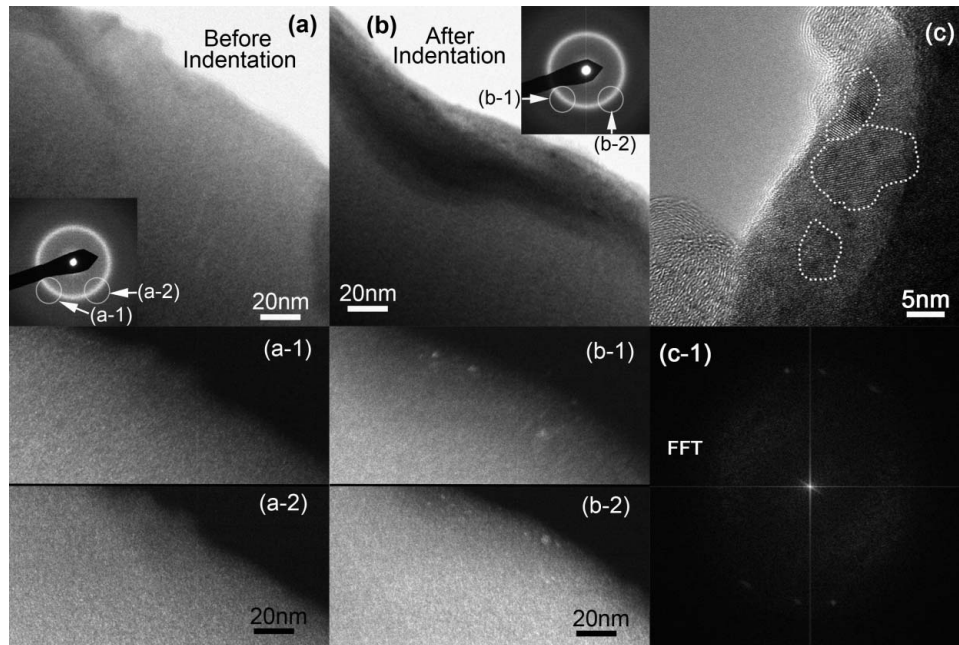


Figure 1. Evidence of *in situ* nanoindentation-induced nanocrystallization in the amorphous Cu–Zr–Al film. (a) As-deposited film was fully amorphous as shown in the BF TEM micrograph and confirmed by the inserted SAD pattern. The corresponding DF TEM micrographs (a1 and a2) show no evidence of nanocrystals before indentation. (b) BF TEM micrograph shows the formation of nanocrystals after *in situ* nanoindentation. The maximum applied stress was  $\sim 0.6$  GPa. The inserted SAD pattern did not show noticeable variation in intensity. However, the corresponding DF-TEM micrographs (b1 and b2) clearly reveal the formation of numerous nanocrystals in the deformed region. (c) HRTEM and corresponding FFT (c1) of the image show the evidence of nanocrystals (outlined by dotted lines) with grain size of several nm on deformed surface.

fast Fourier transform (FFT) of the micrograph in (c-1) reveals distinctive diffraction dots. No evidence of shear bands was observed during or after indentation through an extensive microscopy survey over a much broader area of indented specimens.

During the first loading cycle (L1) in Figure 2(a), the indentation stress–displacement curve reveals two consecutive load-drop events (labeled as a-2 and a-3) at  $\sim 0.25$  GPa. The corresponding DF-TEM micrographs in Figure 2(a2)–(a3) captured the formation of nanocrystals during each load-drop (Supplementary video S1 and Figure S3(a)). The location of the indenter is outlined in Figure 2(a1). A similar load-drop event was observed during the second loading cycle (L2) in Figure 2(b). The load-drop labeled as b-2 took place at  $\sim 0.3$  GPa, accompanied by the formation of nanocrystals as shown in Figure 2(b-2) (Supplementary video S2 and Figure S3(b)). The concurrent load-drop and the formation of nanocrystals were also confirmed by *in situ* nanoindentation experiments under the BF-TEM mode (Supplementary video S3 and Figure S4).

Successive loading was performed at the same location up to 12 cycles. As shown in Figure 3(a), load-drops were observed repetitively for the first nine loading cycles, after which the load-drop phenomenon was absent. The stress at the onset of the load-drop increased gradually from 0.25 to 0.54 GPa (Figure 3(b)). Meanwhile the displacement at the occurrence of the

load-drop increased rapidly during the first few initial loading cycles, reached a plateau ( $\sim 40$  nm) during the fourth to eighth cycle, and increased again for the ninth indentation cycle. To rule out the possibility that amorphous films were at very different glassy state compared with casted metallic glasses, we performed numerous *in situ* nanoindentation experiments on melt-spun metallic glass ribbons of identical compositions. These studies (Supplementary video S4, Figures S5 and S6) show a very similar phenomenon: low stresses can trigger nanocrystallization.

Load-drop events were frequently identified in our *in situ* nanoindentation study. During deformation of brittle BMG, shear softening (a sudden drop of viscosity) typically occurs due to the existence of fine shear bands (10 nm thick), and highly localized deformation in shear bands may lead to consequent catastrophic failure of BMG.[13] Shear softening may be explained by the excess free volume model [15,16] or STZ mechanisms.[19] In ductile BMG, serrated plastic flows observed on the compressive stress–strain curves and during *ex situ* nanoindentation were attributed to shear band formation and propagation events.[7] In the current study, nanocrystals were formed during *in situ* nanoindentation in the elastic deformation regime and no shear bands were detected. The load-drop may be associated with the local variation of specific density. It is well adopted that amorphous alloys have excess free

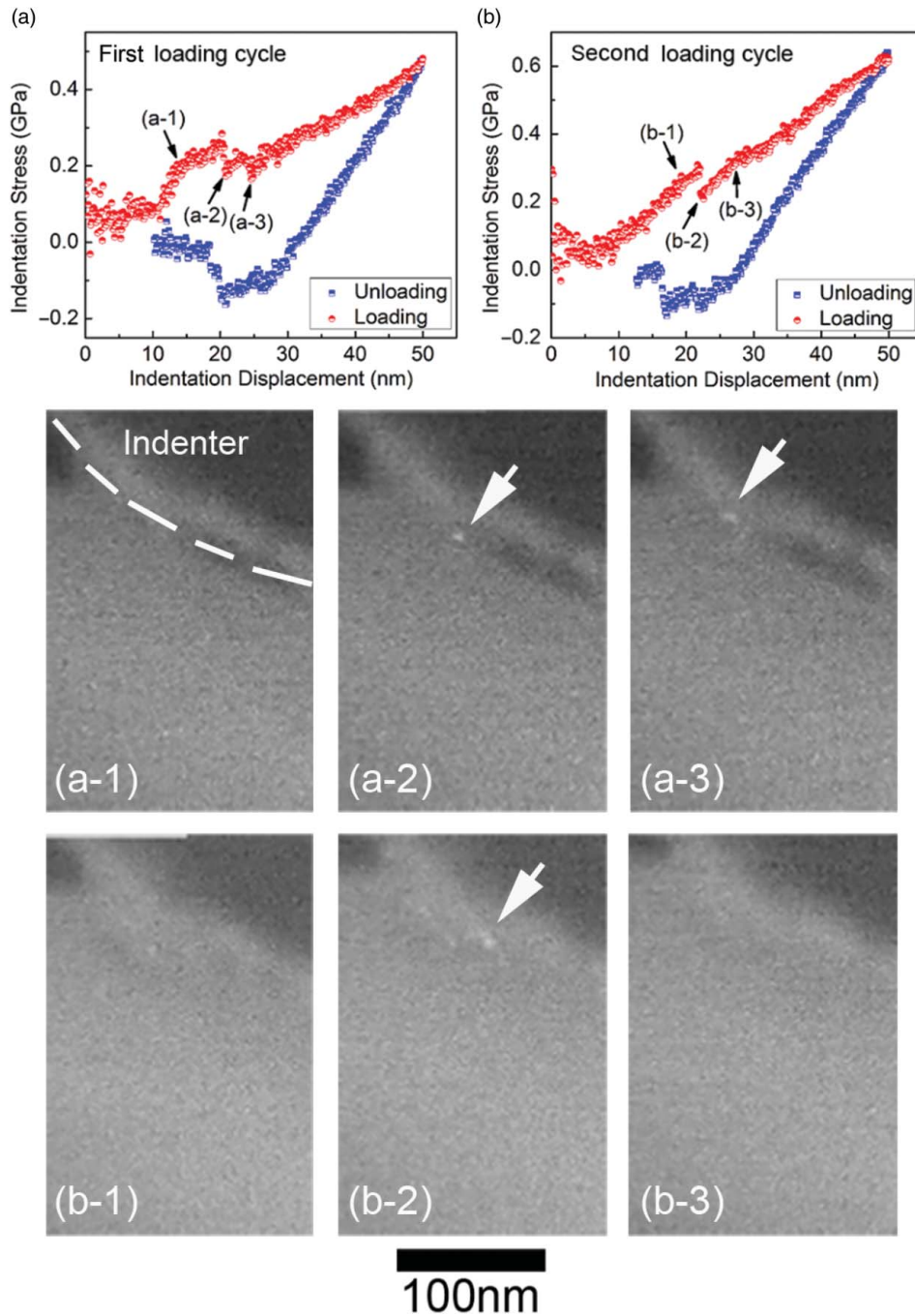


Figure 2. Stress–displacement plots recorded during (a) the first and (b) the second *in situ* nanoindentation cycles show multiple load-drops at low stresses during loading process. (a1–a3) Snapshots captured in the DF TEM mode show the formation of two different nanocrystals during the first loading cycle, corresponding to two distinct load-drop events labeled as a-2 and a-3 in (a) at a stress level of  $\sim 0.25$  GPa (see Supplementary Figure S2(a) and video S1). (b1–b3) Similarly during the second loading cycle, another nanocrystal was identified coinciding with the load-drop (b-2) as indicated in (b) when reaching a stress of  $\sim 0.3$  GPa. These snapshots show simultaneous formation of nanocrystals and occurrence of load-drops (see Supplementary Figure S2(b) and video S2).

volume and lower density than their crystalline counterparts. Thus, when atoms transform from short or medium range order (amorphous state) to long range order (crystalline state) during indentation, a load-drop event is captured.

Stress-induced nucleation of nanocrystals has previously been observed in amorphous alloys by *ex situ* bending,[29] indentation,[10,30] and compression.[31] Churyumov et al.[43] reported *ex situ* observation of crystallization in Zr-based BMG subjected to cyclic

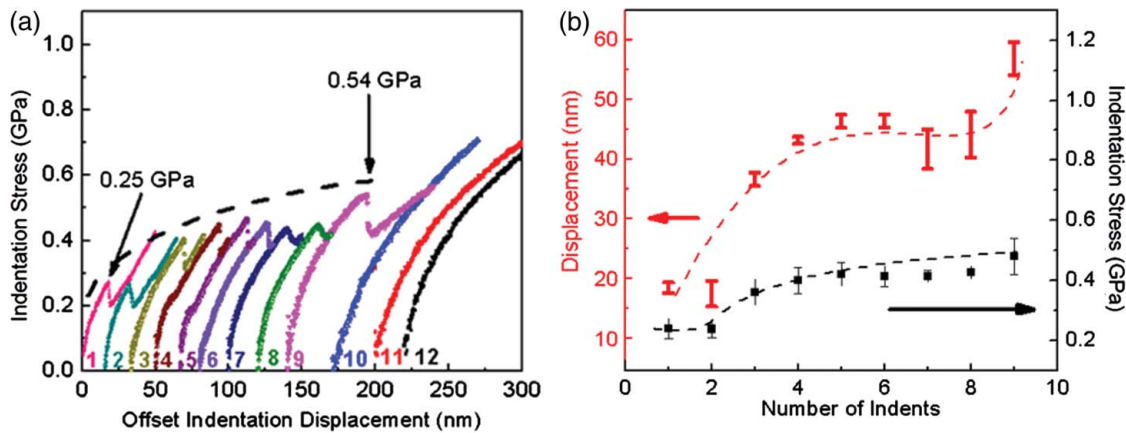


Figure 3. Repetitive loading cycles (up to 12 cycles) to probe *in situ* nanoindentation-induced nanocrystallization. (a) Load-drop was identified repetitively during the first nine loading cycles. After nine cycles, load-drops appeared absent in succeeding cycles. (b) The stress at the onset of load-drop increased gradually from 0.25 to 0.54 GPa. The displacement at the occurrence of load-drop increased gradually during the first few loading cycles, reached a plateau ( $\sim 40$  nm), and eventually increased again to  $\sim 55$  nm.

stress,  $1,000 \pm 200$  MPa, slightly below the typical yield strength,  $\sim 1.6$  GPa.[44] Crystallization was observed after 100 cycles of fatigue tests. This observation is consistent with previous *ex situ* studies of stress-induced crystallization.[29,30] However, these observations mostly showed the coexistence of shear bands and nanocrystallites. A recent *in situ* nanoindentation study on pillars ( $\sim 200$  nm in diameter) of the Cu–Zr–Al amorphous alloy of nearly identical composition (yield strength of 2 GPa) showed that load-drop occurred at  $\sim 1$ – $2$  GPa stress level, concurrently with the generation of shear off-sets (shear bands).[40] In another *in situ* nanoindentation study of Zr-based metallic glass pillars (200 nm in diameter), the stress for shear-band-induced load-drop is also  $\sim 2$  GPa (comparable to yield strength).[39] It has long been postulated that nanocrystals form succeeding the formation of shear bands, which contain significantly localized plastic deformation. Furthermore, the nucleation stress for nanocrystals is unknown. Our study shows that the nucleation stress of nanocrystals on virgin amorphous films is very low,  $\sim 0.25$  GPa, compared with the yield strength of typical Cu–Al–Zr amorphous alloys ( $\sim 1.8$  GPa).[25] Thus, nanocrystallization occurs during the elastic deformation regime, preceding the formation of shear bands, in large contrast to the well-adopted concept. The low stress required for nanocrystallization is to some degree consistent with the observation of simple bending-induced crystallization on the compressive side of metallic glass ribbons.[29]

To understand the activation of nanocrystallization under such a low nucleation stress, we start from the thermodynamics point of view. Fernandez et al.[45] studied amorphous  $(\text{Cu}_{50}\text{Zr}_{50})_{100-x}\text{Al}_x$  ( $x = 0$ – $10$  at%). The crystallization temperature of these amorphous alloys was estimated to be 750–800 K. The kinetic energy

(provided by heating) of an atom needed to overcome the amorphous-to-crystalline transition energy barrier at room temperature ( $T_R$ ) is estimated to be  $k \cdot (T - T_R) = (770 - 300 \text{ K}) \times 8.6 \times 10^{-5} \text{ eVK}^{-1} \approx 40 \text{ meV}$ , where  $k$  is the Boltzmann constant and  $T$  is the absolute temperature of crystallization. Under stress during *in situ* nanoindentation of amorphous  $\text{Cu}_{44}\text{Zr}_{44}\text{Al}_{12}$  alloy, the activation energy barrier for nucleation of nanocrystals could be reduced. Lee et al.[46] have studied thermodynamics of the nucleation of nanocrystal in an amorphous matrix under hydrostatic compression. Their analyses showed that the applied hydrostatic pressure could enhance the formation of nanocrystals as free energy required to produce a critical nucleus size decrease with increasing pressure.

Shear softening (stress-induced reduction of viscosity), a frequently observed event, may occur during indentation of our films. The reduction in viscosity may facilitate the local rearrangement of atoms. Shuffling of atoms may eliminate excess free volume locally and thus achieve medium–long range order in neighboring atoms and, consequently, the formation of nanocrystals. Such a hypothesis could be validated by molecular dynamics simulations.

Note that growth of the nucleated nanocrystals might also occur during successive loading. However, such an event was not prominent (or convincingly detected) during the current studies. In some previous studies, stress-induced grain growth has indeed been observed in nanocrystalline metals.[47,48] Under stress, grain growth typically occurs via grain rotation so that nanograins adjacent to each other might combine into larger grains. Thus, stress that induced grain growth in nanocrystalline metals is somewhat different from thermally driven coarsening of nanograins, which is mostly dominated by a diffusion process. In the current study, although stress can induce

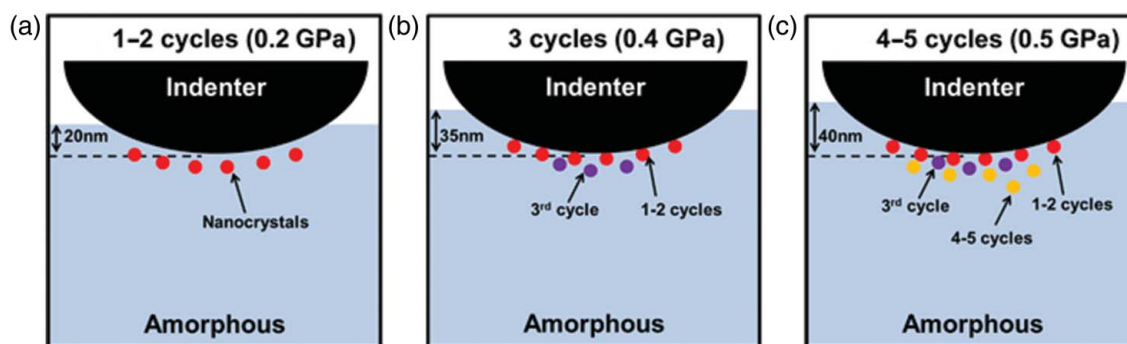


Figure 4. Schematic of stress-driven nanocrystal nucleation processes during indentation of amorphous CuZrAl. (a) In the first two loading cycles, nanocrystals are easily formed on the surface of the virgin matrix. (b) During the third loading cycle, pre-existing nanocrystals in the amorphous matrix will provide extra resistance to the nucleation of new nanocrystals. Thus, the indenter tip has to propagate deeper under greater stress to trigger nanocrystallization of new grains. A ‘hardening’ effect appears. (c) Such a process repeats in succeeding (fourth–fifth) cycles, and greater stress is required for the nucleation of nanocrystals at a deeper region in the specimens.

nanocrystals in amorphous metals, the population of these nanocrystals remains low. Hence, the probability for these nanocrystals to combine into larger grains is low. Grain growth by detaching atoms from the amorphous matrix and reattaching these atoms to nanocrystal seeds could occur during indentation, but such a diffusion process is very slow (sluggish at room temperature under stress) and hence the magnitude of the grain growth may be insignificant during the short duration of nanoindentation experiments.

Finally, we examine the ‘hardening’ effect—requirement of higher stress to trigger nucleation of nanocrystals during repetitive loading experiments. Some recent studies on wear and fatigue response of metallic glasses have shown a similar phenomenon. For instance, Packard et al.[49] reported the hardening of Fe-based metallic glass after cyclic loading at the elastic regime. Launey et al.[50,51] observed enhanced fatigue endurance strength in the same Zr-based metallic glass with less free volume, a phenomenon attributed to residual stress tailored by free volume. Packard et al.[49] reported frequent pop-in events and hardening revealed from repetitive indentation experiments on Fe-based metallic glasses. Nanocrystallization could be a plausible mechanism behind such a hardening phenomenon. However as their study was performed *ex situ*, a conclusive answer could not be arrived. Compared with *ex situ* nanoindentation, our *in situ* experiment has greater sensitivity to microstructure evolution. This is because the volume probed under the indenter tip is very small (specimen thickness is tens of nm), and hence any microstructure evolution (including nucleation of dislocations) can be accurately captured.[52] Nanocrystallization during *in situ* nanoindentation involves the formation of numerous nanocrystals with dimensions of  $\sim 5$  nm, comparable to the film thickness,  $\sim 30$  nm. Volume (and film density) change due to nanocrystallization could thus be

detected during *in situ* nanoindentation. Note that repetitive stress-drops observed in this study did not arise from the formation of shear bands as no shear bands were observed after *in situ* nanoindentation. In fact if shear bands were formed, the magnitude of stress-drops will be much more substantial than what we observed here. In other words, the rapid nucleation and propagation of shear bands will lead to reduction of stresses to a very low level (probably near zero stress), which was not observed in this study.

Figure 4 provides a hypothetical explanation to illustrate the formation of nanocrystals during successive indentation cycles. During the first two indentation cycles (Figure 4(a)), low stress and shallow indentation induced a layer of nanocrystals under the indenter. The formation of nanocrystals in the amorphous matrix has been shown to increase the strength of amorphous alloys.[23] Such a hardened matrix makes it difficult to form new nanocrystals during successive loading events. The excess free volume has been depleted from the surrounding nanocrystals, making it difficult to form new nanocrystals in the adjacent region. Consequently, it is more difficult to trigger nanocrystallization under stress. At higher stress, the indenter penetrates deeper into the amorphous alloy, hence probes more virgin areas that are available for nanocrystallization as shown in Figure 4(b)–(c). A stress level of 0.5–0.6 GPa may be sufficient to overcome the nucleation energy barrier for nanocrystallization. The formation of nanocrystals preceding shear bands makes it difficult to deform surrounding regions. Consequently, greater stress is required to nucleate more nanocrystals.

In conclusion, via *in situ* nanoindentation of the amorphous  $\text{Cu}_{44}\text{Zr}_{44}\text{Al}_{12}$  alloy, we revealed that the formation of nanocrystals occurred at an ultra-low stress level of 0.25 GPa in the elastic deformation regime, accompanied by load-drops without evidence of shear

bands. During successive loading, repetitive nanocrystal nucleation events were observed at increasing stress, up to  $\sim 0.54$  GPa, implying the occurrence of a ‘hardening’ effect in the amorphous alloy. Of course it is premature and inappropriate to assume that nanocrystallization always occurs prior to the formation of shear bands in all metallic glasses. Extensive *in situ* nanoindentation studies across a broad range of metallic glasses system will help to construct a comprehensive view on the relationship between nanocrystallization, shear band formation and eventually plasticity in metallic glasses. This study provides important evidence and a forward step to advance our understanding on deformation-induced nanocrystallization of an important class of Cu–Zr-based amorphous alloys.

**Supplementary online material.** A more detailed information on experiments is available at <http://dx.doi.org/10.1080/21663831.2014.911778>.

**Acknowledgements** Discussion with Prof. Frans Spaepen (Harvard University) is highly appreciated. Financial supports by NSF-CMMI (grant no. 1161978 for XZ), Office of Naval Research (under Dr Lawrence Kabacoff with contract number: N00014-08-0510 for HW), the National Key Basic Research Program of China (2012CB825700), National Natural Science Foundation of China (grants no 10979002, 51371157, 11179026 and 51071141), Natural Science Foundation of Zhejiang Province (grants Z1110196 and Y4110192), Zhejiang University-Helmholtz cooperation fund, and the Fundamental Research Funds for the Central Universities are acknowledged. Access to the microscopes at the Microscopy and Imaging Center at Texas A&M University is also acknowledged.

## References

- [1] Klement W, Willens R, Duwez P. Non-crystalline structure in solidified gold–silicon alloys. *Nature*. 1960;187:869–870.
- [2] Cheng Y-T, Johnson WL. Disordered materials: a survey of amorphous solids. *Science*. 1987;235:997–1002.
- [3] He Y, Poon SJ, Shiflet GJ. Synthesis and properties of metallic glasses that contain aluminum. *Science*. 1988;241:1640–1642.
- [4] Ma E. Alloys created between immiscible elements. *Prog Mater Sci*. 2005;50:413–509.
- [5] Wang WH. The elastic properties, elastic models and elastic perspectives of metallic glasses. *Prog Mater Sci*. 2012;57:487–656.
- [6] Chen M. Mechanical behavior of metallic glasses: microscopic understanding of strength and ductility. *Annu Rev Mater Sci*. 2008;38:445–469.
- [7] Schuh CA, Hufnagel TC, Ramamurty U. Mechanical behavior of amorphous alloys. *Acta Mater*. 2007;55:4067–4109.
- [8] Wang WH, Dong C, Shek CH. Bulk metallic glasses. *Mater Sci Eng R Rep*. 2004;44:45–89.
- [9] Jiang QK, Liu P, Ma Y, Cao QP, Wang XD, Zhang DX, Han XD, Zhang Z, Jiang JZ. Super elastic strain limit in metallic glass films. *Sci Rep*. 2012;2:852.
- [10] Bei H, Lu ZP, George EP. Theoretical strength and the onset of plasticity in bulk metallic glasses investigated by nanoindentation with a spherical indenter. *Phys Rev Lett*. 2004;93:125504.
- [11] Pang SJ, Zhang T, Asami K, Inoue A. Synthesis of Fe–Cr–Mo–C–B–P bulk metallic glasses with high corrosion resistance. *Acta Mater*. 2002;50:489–497.
- [12] Greer AL, Rutherford KL, Hutchings IM. Wear resistance of amorphous alloys and related materials. *Int Mater Rev*. 2002;47:87–112.
- [13] Yavari AR, Lewandowski JJ, Eckert J. Mechanical properties of bulk metallic glasses. *MRS Bulletin*. 2007;32:635–638.
- [14] Greer AL, Ma E. Bulk metallic glasses: at the cutting edge of metals research. *MRS Bulletin*. 2007;32:611–619.
- [15] Spaepen F. A microscopic mechanism for steady state inhomogeneous flow in metallic glasses. *Acta Metall*. 1977;25:407–415.
- [16] Argon AS. Plastic deformation in metallic glasses. *Acta Metall*. 1979;27:47–58.
- [17] Falk ML. Molecular-dynamics study of ductile and brittle fracture in model noncrystalline solids. *Phys Rev B*. 1999;60:7062–7070.
- [18] Lund AC, Schuh CA. Yield surface of a simulated metallic glass. *Acta Mater*. 2003;51:5399–5411.
- [19] Langer JS, Pechenik L. Dynamics of shear-transformation zones in amorphous plasticity: energetic constraints in a minimal theory. *Phys Rev E*. 2003;68:061507.
- [20] Schroers J, Johnson WL. Ductile bulk metallic glass. *Phys Rev Lett*. 2004;93:255506.
- [21] Chen LY, Fu ZD, Zhang GQ, Hao XP, Jiang QK, Wang XD, Cao QP, Franz H, Liu YG, Xie HS, Zhang SL, Wang BY, Zeng YW, Jiang JZ. New class of plastic bulk metallic glass. *Phys Rev Lett*. 2008;100:075501.
- [22] Cao QP, Liu JW, Yang KJ, Xu F, Yao ZQ, Minkow A, Fecht HJ, Ivanisenko J, Chen LY, Wang XD, Qu SX, Jiang JZ. Effect of pre-existing shear bands on the tensile mechanical properties of a bulk metallic glass. *Acta Mater*. 2010;58:1276–1292.
- [23] Fan C, Li C, Inoue A, Haas V. Deformation behavior of Zr-based bulk nanocrystalline amorphous alloys. *Phys Rev B*. 2000;61:R3761–R3763.
- [24] Chen M, Inoue A, Zhang W, Sakurai T. Extraordinary plasticity of ductile bulk metallic glasses. *Phys Rev Lett*. 2006;96:245502.
- [25] Das J, Tang MB, Kim KB, Theissmann R, Baier F, Wang WH, Eckert J. “Work-Hardenable” ductile bulk metallic glass. *Phys Rev Lett*. 2005;94:205501.
- [26] Liu YH, Wang G, Wang RJ, Zhao DQ, Pan MX, Wang WH. Super plastic bulk metallic glasses at room temperature. *Science*. 2007;315:1385–1388.
- [27] Torre FHD, Dubach A, Siegrist ME, Löffler JF. Negative strain rate sensitivity in bulk metallic glass and its similarities with the dynamic strain aging effect during deformation. *Appl Phys Lett*. 2006;89:091918.
- [28] Yoo B-G, Choi I-C, Kim Y-J, Suh J-Y, Ramamurty U, Jang J-I. Further evidence for room temperature, indentation-induced nanocrystallization in a bulk metallic glass. *Mater Sci Eng A*. 2012;545:225–228.
- [29] Chen H, He Y, Shiflet GJ, Poon SJ. Deformation-induced nanocrystal formation in shear bands of amorphous alloys. *Nature*. 1994;367:541–543.
- [30] Kim J-J, Choi Y, Suresh S, Argon AS. Nanocrystallization during nanoindentation of a bulk amorphous metal alloy at room temperature. *Science*. 2002;295:654–657.
- [31] Jiang WH, Atzmon M. The effect of compression and tension on shear-band structure and nanocrystallization in



- amorphous Al90Fe5Gd5: a high-resolution transmission electron microscopy study. *Acta Mater.* 2003;51:4095–4105.
- [32] Chen LY, Li BZ, Wang XD, Jiang F, Ren Y, Liaw PK, Jiang JZ. Atomic-scale mechanisms of tension–compression asymmetry in a metallic glass. *Acta Mater.* 2013;61:1843–1850.
- [33] Li N, Wang J, Huang JY, Misra A, Zhang X. In situ TEM observations of room temperature dislocation climb at interfaces in nanolayered Al/Nb composites. *Scripta Mater.* 2010;63:363–366.
- [34] Minor AM, Syed Asif SA, Shan Z, Stach EA, Cyrankowski E, Wyrobek TJ, Warren OL. A new view of the onset of plasticity during the nanoindentation of aluminium. *Nature Mater.* 2006;5:697–702.
- [35] Lee JH, Holland TB, Mukherjee AK, Zhang X, Wang H. Direct observation of Lomer-Cottrell Locks during strain hardening in nanocrystalline nickel by in situ TEM. *Sci Rep.* 2013;3:1061.
- [36] Liu Y, Karaman I, Wang H, Zhang X. Two types of martensitic phase transformations in magnetic shape memory alloys by in-situ nanoindentation studies. *Adv Mater.* Epub 2014 Mar 31.
- [37] Lee JH, Kim I, Hulbert DM, Jiang D, Mukherjee AK, Zhang X, Wang H. Grain and grain boundary activities observed in alumina–zirconia–magnesia spinel nanocomposites by in situ nanoindentation using transmission electron microscopy. *Acta Mater.* 2010;58:4891–4899.
- [38] Guo H, Yan PF, Wang YB, Tan J, Zhang ZF, Sui ML, Ma E. Tensile ductility and necking of metallic glass. *Nature Mater.* 2007;6:735–739.
- [39] Wang YB, Qu DD, Wang XH, Cao Y, Liao XZ, Kawasaki M, Ringer SP, Shan ZW, Langdon TG, Shen J. Introducing a strain-hardening capability to improve the ductility of bulk metallic glasses via severe plastic deformation. *Acta Mater.* 2012;60:253–260.
- [40] Shan ZW, Li J, Cheng YQ, Minor AM, Syed Asif SA, Warren OL, Ma E. Plastic flow and failure resistance of metallic glass: Insight from in situ compression of nanopillars. *Phys Rev B.* 2008;77:155419.
- [41] Pauly S, Gorantla S, Wang G, Kühn U, Eckert J. Transformation-mediated ductility in CuZr-based bulk metallic glasses. *Nature Mater.* 2010;9:473–477.
- [42] Herbert EG, Pharr GM, Oliver WC, Lucas BN, Hay JL. On the measurement of stress–strain curves by spherical indentation. *Thin Solid Films.* 2001;398–399:331–335.
- [43] Churyumov AY, Bazlov AI, Zadorozhnyy VY, Solonin AN, Caron A, Louzguine-Luzgin DV. Phase transformations in Zr-based bulk metallic glass cyclically loaded before plastic yielding. *Mater Sci Eng A.* 2012;550:358–362.
- [44] Johnson WL, Samwer K. A universal criterion for plastic yielding of metallic glasses with a  $(T/T_g)^{2/3}$  temperature dependence. *Phys Rev Lett.* 2005;95:195501.
- [45] Fernández R, Carrasco W, Zúñiga A. Structure and crystallization of amorphous Cu–Zr–Al powders. *J Non-Cryst Solids.* 2010;356:1665–1669.
- [46] Lee S-W, Huh M-Y, Fleury E, Lee J-C. Crystallization-induced plasticity of Cu–Zr containing bulk amorphous alloys. *Acta Mater.* 2006;54:349–355.
- [47] Jin M, Minor AM, Stach EA, Morris Jr JW. Direct observation of deformation-induced grain growth during the nanoindentation of ultrafine-grained Al at room temperature. *Acta Mater.* 2004;52:5381–5387.
- [48] Shan Z, Stach EA, Wiezorek JMK, Knapp JA, Forstaedt DM, Mao SX. Grain boundary-mediated plasticity in nanocrystalline nickel. *Science.* 2004;305:654–657.
- [49] Packard CE, Witmer LM, Schuh CA. Hardening of a metallic glass during cyclic loading in the elastic range. *Appl Phys Lett.* 2008;92:171911.
- [50] Launey ME, Busch R, Kruzic JJ. Influence of structural relaxation on the fatigue behavior of a  $Zr_{41.25}Ti_{13.75}Ni_{10}Cu_{12.5}Be_{22.5}$  bulk amorphous alloy. *Scripta Mater.* 2006;54:483–487.
- [51] Launey ME, Busch R, Kruzic JJ. Effects of free volume changes and residual stresses on the fatigue and fracture behavior of a Zr–Ti–Ni–Cu–Be bulk metallic glass. *Acta Mater.* 2008;56:500–510.
- [52] Oh SH, Legros M, Kiener D, Dehm G. In situ observation of dislocation nucleation and escape in a submicrometre aluminum single crystal. *Nature Mater.* 2009;8:95–100.