JOM
DOI: 10.1007/s11837-012-0436-8
© 2012 TMS

In Situ TEM Investigation of the Mechanical Behavior of Micronanoscaled Metal Pillars

ZHIWEI SHAN[1,2]

1.—Center for Advancing Materials Performance from the Nanoscale (CAMP-Nano) & Hysitron Applied Research Center in China (HARCC), State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an 710049, People's Republic of China. 2.—e-mail: zwshan@mail.xjtu.edu.cn

In this article, our most recent progress on applying a unique quantitative transmission electron microscope deformation technique on micronanoscaled metal pillars will be reviewed. We found that single-crystal pillars fabricated through focused ion beam always contain high density of defects. However, if the sample size is small enough, then both face-centered-cubic metals and body-centered-cubic metal pillars can experience "mechanical annealing," i.e., a phenomena referring to the reduction of dislocation density in the deforming volume, when dislocation generation is outweighed by dislocation annihilation through the free surface. We also found that when the sample size was reduced below 1 μm or so, stress saturation and deformation mechanism transition occurred in a hexagonal-close-packed Ti alloy. Unlike crystalline materials, metallic glasses do not allow the presence and movement of dislocations or deformation twinning. However, we demonstrated the metallic glasses also follow the well-established tenet for crystalline materials: i.e., smaller is stronger and can reach its theoretical elastic limit under appropriate testing conditions. In addition, for the tested size regime, we found that high-energy electron beam has no obvious effect on the mechanical properties of materials with metallic bond. However, for materials with covalent bond and ionic bond, significant electron beam effects have been confirmed.

INTRODUCTION

Micronanoscale refers to the size regime ranged from 10 nm to 10,000 nm. In recent years, to study the structure and properties of micronanoscaled materials is becoming a burgeoning and frontier scientific research field.[1–5] The giant driving force behind this is that the society has a need for miniaturizing the functional devices. As mentioned by Nix et al.,[6]

> Nano-mechanical devices are certain to play an important role in future technologies. Already sensors and actuators based on MEMS technologies are common and new devices based on NEMS are just around the corner. These developments are part of a decade-long trend to build useful properties of materials at these small length scales.

In this article, I will first review our recent progress on revealing the novel properties of micronanoscaled metals, including face-centered-cubic (fcc) single-crystal Ni,[4] body-centered-cubic (bcc) single-crystal Mo alloy,[7,8] hexagonal-close-packed (HCP) α-Ti alloy,[9] and metallic glasses.[10,11] Next, I will proceed to answer a frequently asked question, i.e., whether the high-energy electron beam affects the mechanical properties of materials tested inside a transmission electron microscope (TEM).[12] Finally, I will conclude this paper by raising a number of questions inspired from our previous research works.

FCC SINGLE-CRYSTAL NI: MECHANICAL ANNEALING

Ever since Uchic et al.[1] published their elegant work in 2004, there have been revived interests on studying the sample dimensions effect on materials' strength.[2,13,14] The general trend found so far, i.e., smaller is stronger, is consistent with that found in the studies of whiskers carried out more than 50 years ago.[15–17] However, the underlying physical

Published online: 13 September 2012

mechanism remains a subject for considerable scientific debates. For example, for samples prepared through focused ion beam (FIB), is there any ion implantation? Are there preexisting dislocations in the tested pillars? If yes, then how will these affect the mechanical behavior of the tested samples? In addition, it is well known that almost all the metals have an oxidation layer on its surface. How will this oxidation layer affect the dislocation dynamics? In order to solve these puzzles, we chose to study the FIBed single-crystal Ni pillars using a quantitative, *in situ* TEM compression technique.[18]

It was found that submicrosized fcc single-crystal nickel pillars fabricated through FIB always contain high density of defects (Fig. 1a). However, quite unexpectedly, the dislocation density was observed to decrease dramatically during the following compression tests and, in some cases, even resulted in a dislocation-free crystal (Fig. 1b). Neither the surface oxidation layer nor the assumed ion-affected layer can stop the above process. The phenomenon, which we termed as "mechanical annealing," is the first direct observation of the dislocation starvation mechanism[5] and sheds new light on understanding the unusual mechanical properties associated with micronanoscaled metals. The underlying physical mechanism can be attributed to the interaction among image force, external applied stress, and sample size. The magnitude of the image force is inverse proportional to the distance between the dislocations and free surface.[19] Therefore, the preexisting dislocations, especially those that are close to the free surface are not stable. Once these dislocations are activated by external applied stress, they will be accelerated by the image force to escape from the free surface. Due to the limited sample size, those dislocations only allowed to travel very short distance during their lifespan and, therefore, have little or no chance to interact with other dislocations and form new Frank-Read like sources before they annihilate at the free surface. Consequently, the dislocation density in the submicrosized pillars will be reduced dramatically in response to the external applied stress. For given deformation conditions, the smaller the sample, the more significant of mechanical annealing phenomena. Following our observation in Ni,[4] similar phenomena were also observed in other fcc metals, like Al[20] and Cu.[21]

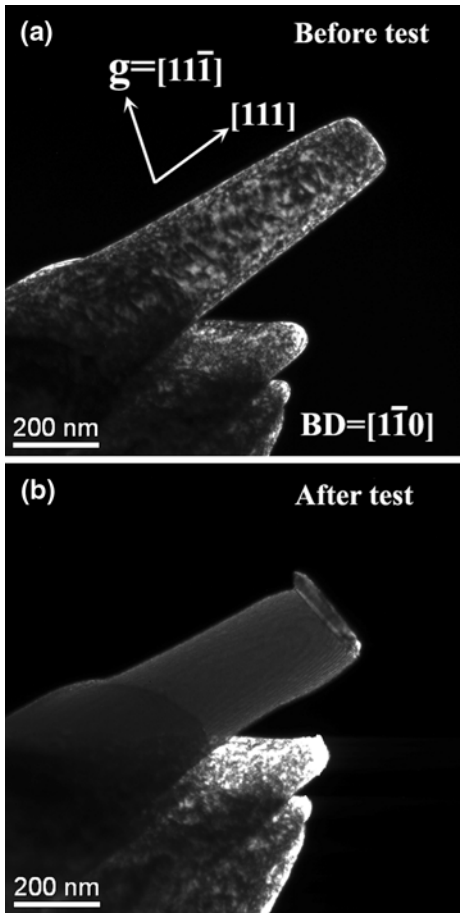

Fig. 1. Mechanical annealing of a single-crystal Ni pillar. (a) The Ni pillar fabricated through FIB contained very high density of dislocations. (b) After compression test, the Ni pillar became a near-perfect crystal without any detectable defects, as was further confirmed by multiple dark-field TEM observations (see Ref. [4]).

BCC Single-Crystal Mo: Size Effect Itself Has a Size Effect

Although mechanical annealing has been widely observed in fcc metals, many in the community believe that such phenomena cannot exist in bcc metals for the following reasons. First, computer simulation[22] found that under the combined effects from the image force and dislocation core structure, a dislocation nucleated from the surface of a bcc pillar will generate one or more dislocations in the opposite direction before it exits from the surface. This self-multiplication mechanism is very different from that for fcc metals. Second, investigations[23–25] indicated that bcc metals exhibit relatively weak sample size dependence at room temperature. Third, postmortem TEM observation found that deformed, nanoscaled, single crystal Mo still have obvious dislocation-like contrast.[26] Literature research found that if we can fabricate small enough samples, according to the tenet of "smaller is stronger," we may be able to apply enough high stress so that the velocity of screw dislocation can be close to that of edge dislocation in bcc metals. Consequently, the mechanical behavior of bcc metals may become similar to that of fcc metals under ultrahigh stress. Keeping this in mind, by conquering a series of difficulties in sample preparation, we were able to prepare single-crystal Mo pillars with their size reaching an unprecedented small scale. Using *in situ* compression of nanopillars inside a transmission electron microscope, we demonstrate that with the pillar diameter decreasing to hundreds of nanometers, significant mechanical

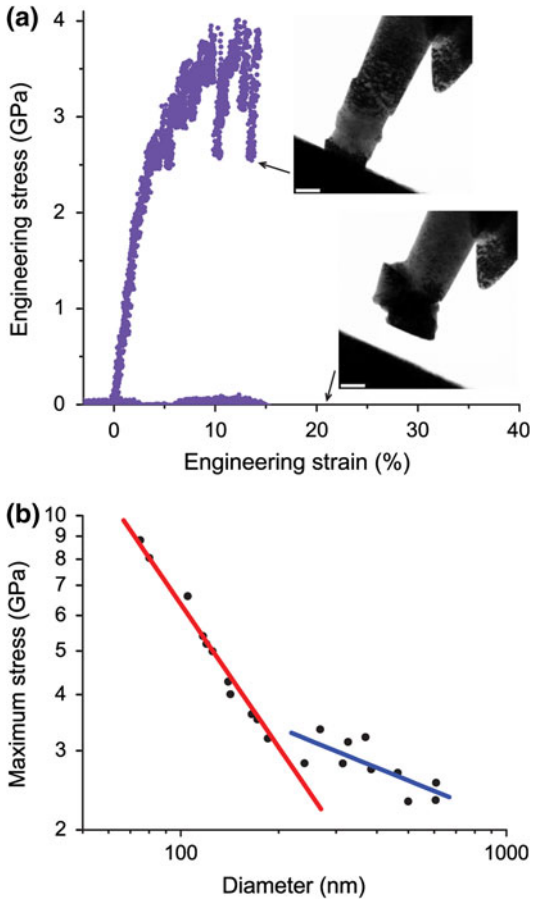

Fig. 2. Size effect itself has size effect for bcc single-crystal Mo. (a) The typical engineering stress versus engineering strain curve for a FIB single-crystal Mo pillar with diameter of 142 nm. The insets are two bright-field TEM images taken before and after the dramatic strain burst. The scale bar in each image represents 100 nm. (b) Maximum flow stress plotted as a double-log function of pillar diameter *D* (black dots), showing two different strengthening exponent α values, 1.0 and 0.29 for red and blue lines, respectively (Courtesy of Ling Huang from CAMP-Nano) (Color figure online).

annealing does occur in bcc Mo (Fig. 2a). In addition, there exists a critical size ($\sim$ 200 nm for Mo at room temperature) below which the strengthening exponent in Hall-Petch-like regression increases dramatically to that similar to fcc metals (Fig. 2b). Thus, a new regime for size effects in bcc is discovered that converges to that of fcc, revealing deep connection in the dislocation dynamics of the two systems. We attribute the observed phenomena to the diminishing importance of lattice friction at high stresses, when the size-enhanced flow stress exceeds a single screw dislocation's lattice friction.

HCP Ti Alloy: Deformation Mechanism Transition and Stress Saturation

Strong size effect is also observed in HCP structured Ti alloy.[9] The initial motivation of this work is inspired by Meyers et al.[27] For polycrystalline materials, it has been found that the apparent strength and grain size follows a Hall-Petch-like relationship.[28] However, the Hall-Petch slope for deformation-twinning-mediated plasticity (DTMP) is much larger than that for ordinary-dislocation-mediated plasticity (ODMP). For example, this difference for titanium is about three times.[27] In recent years, it has been demonstrated that single-crystal metals deformed through ODMP also follow a Hall-Petch type behavior.[29] But it is still unknown if sample dimension has a strong effect on single-crystal metals deformed through DTMP. If yes, then the Hall-Petch-like relationship for DTMP must break down at a much larger sample size than that for ODMP because of the large Hall-Petch slope difference. In this work, we chose <0001> oriented single-crystal α-Ti alloy pillars as our object of study. This is because deformation twinning is known to be the main plasticity carrier for as-oriented bulk materials. By using a combination of microcompression and *in situ* nanocompression experiments, we found a critical sample size ($\sim$1 μm). For samples larger than this critical size, large strain burst is always observed following certain elastic and plastic deformation (Fig. 3a). Correspondingly, obvious shear steps are the main characteristics of the deformed samples (Fig. 3d). Electron backscatter diffraction analysis of these deformed pillars suggested that deformation twinning did occur during the deformation, as was confirmed by cross-sectional TEM observation. At the same time, the strength and the sample size clearly follow a Hall-Petch-type relationship with the strengthening exponent equal to 1 instead of 0.5 (Fig. 3c). However, when the sample size was reduced below this critical size, plastic deformation is observed to concentrate on the top part of the pillar, resulting in a "mushroom" geometry (Fig. 3e). Correspondingly, the plastic flow became quite continuous without any major strain burst (Fig. 3b). *In situ* TEM observation found no sign for deformation twinning any more (Fig. 3f). Most interestingly, at this size regime, the maximum flow stress is observed to saturate at close to the ideal strength of Ti (Fig. 3c). The "stimulated slip" model we proposed explained well of the observed phenomena.[9] Because the critical size, i.e., $\sim$1 μm, is easily accessible, our findings do have promising future for industry applications.[30]

Metallic Glass: Smaller is Stronger and Approaching Ideal Elastic Limit

Unlike crystalline metals, metallic glass does not have long-range coherency in their structure and therefore does not allow the presence and movement of dislocations or deformation twinning, which are two main plastic carriers for crystalline metals.[11] As a consequence, bulk metallic glasses exhibit ultra-high-yield stress compared with their crystalline counterpart before failure in a brittle manner. In addition, the yield strain of bulk metallic glasses

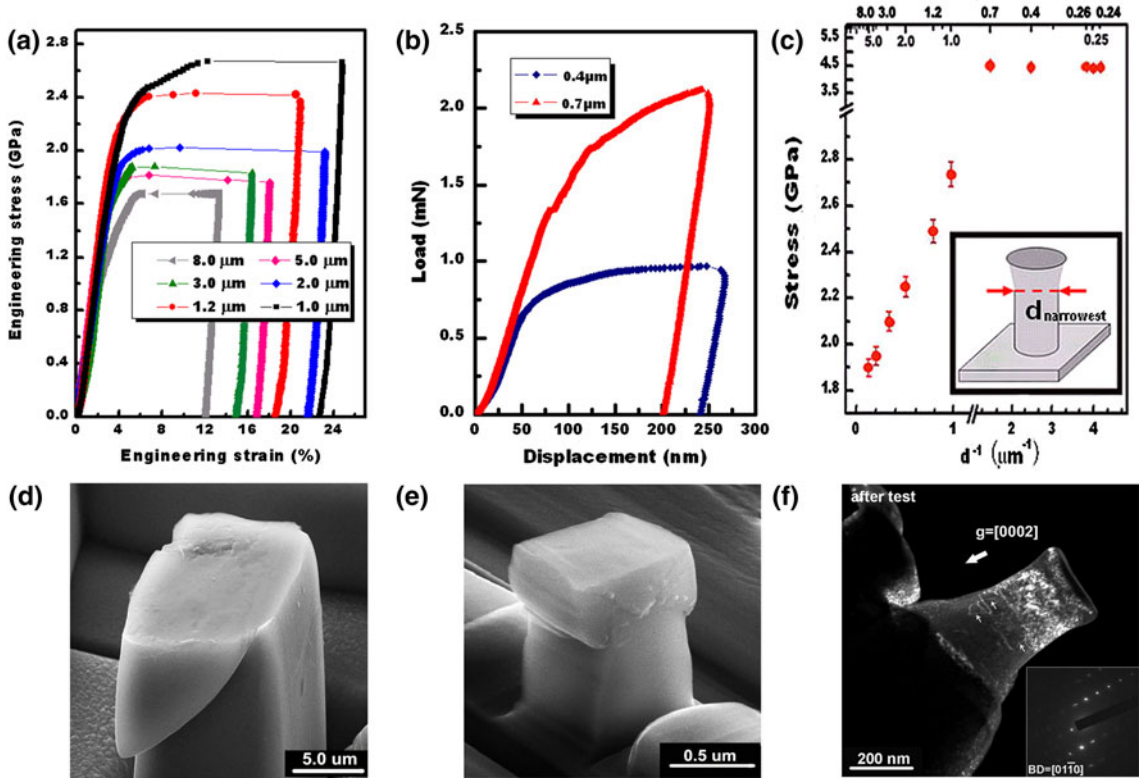

Fig. 3. Strong size effect on deformation twinning in a α-Ti alloy. (a) Stress-strain curves for pillars with their diameters larger than 1.0 μm. (b) Load displacement for pillars with their diameters less than 1.0 μm. (c) Stress-diameter data for all the tested pillars. (d) SEM image of a deformed 8-μm pillar. Note the shear-off geometry. (e) SEM image of a deformed 0.7-μm pillar. Note the mushroom geometry. (f) TEM image of a deformed 250-nm pillar. Only dislocations were observed (see Ref. [9]).

almost universally reaches ~2%. This clearly stands out from that of bulk metals (0.2%). However, according to theoretical calculation, these already high apparent yield strain are still much lower than the ideal limit.[31] Presumably, this is because of the inevitable presence of defects in the as-prepared bulk metallic glasses, such as surface notches, casting pores/flaws, and so on. These defects can serve as effective stress concentrators, which will lead premature failure of metallic glasses. It has been well established in crystalline metals that the presence of extrinsic flaws can be minimized if the samples were reduced to micronanoscale. Therefore, in order to reach the elastic limit of a given metallic glass, we may adopt the similar strategy, i.e., reducing the sample size to micronanoscale.

The material we chose is $Cu_{49}Zr_{51}$ metallic glass prepared using melt spinning. The samples were FIBed from the parent body into a dog-bone shape (inset in Fig. 4). The most creative design of the testing samples is the fiduciary markers made in the gauge part by electron-beam-induced carbon deposition in the FIB chamber. This enables us to measure the strain precisely and accurately. Previously, the strain measurement has been one of the most challenging problems for micronanoscaled mechanical tests. For the size range we have tested (200–300 nm in diameter), *in situ* and quantitative TEM tensile tests revealed that the total recoverable elastic strain (~4.4%) is indeed very close to the predicted theoretical limit (4.5%) (Fig. 4). At the same time, the measured fracture strength is about twice of that observed in bulk metallic glass samples.[10] Further reducing the sample size will result the ductile deformation characterized by necking. The size dependence on strength and ductility, i.e., smaller is stronger and more ductile, are consistent with our observations for Al-based[11] and Cu-based metallic glasses[32] as well as those from other groups.[33]

Effects of High-Energy Electron Beam

For mechanical tests carried out inside TEM, one frequently asked question is: Does the high-energy electron beam (e-beam) affect the measured mechanical properties? For materials with metallic bond, no obvious e-beam effect has been observed so far. However, for materials with covalent bond and ionic bond, significant e-beam effects have been confirmed. One typical example is our study on amorphous SiO_2 spheres.[12] We found that during the compression test at room temperature, the flow stress can be decreased by four times if we changed the beam status from "blocked" to "on" (Fig. 5). Here "blocked" means that the e-beam is shielded from

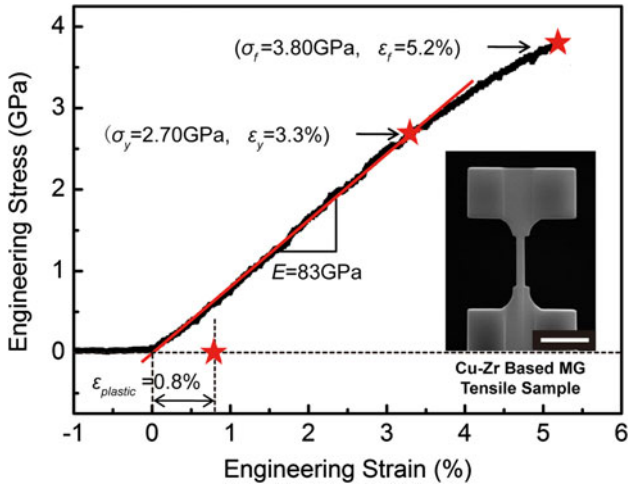

Fig. 4. Engineering stress-strain curve of a Cu-Zr metallic glass sample with effective diameter of 220 nm. The average strain rate was about 2×10^{-3} s^{-1}. Mechanical properties extracted from the stress-strain curve include Young's modulus (E), proportional elastic limit of strength (σ_y) and strain (ε_y), fracture strength (σ_f) and total elongation to failure (ε_f), as well as the plastic strain ($\varepsilon_{plastic}$) in the gauge length. The inset is an SEM image of the tensile sample. The scale bar is 1 μm (Courtesy of Lin Tian from CAMP-Nano).

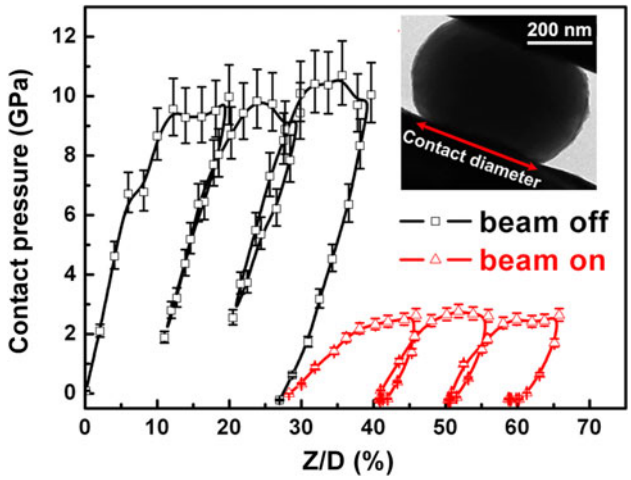

Fig. 5. E-beam effect on the mechanical behavior of an amorphous silica particle. The contact pressure (defined as force divided by the instantaneous contact area) decreased about four times when electron beam was switched from off (black curve) to on (red curve). The inset is a still frame extracted from the recorded movie during the compression test (Courtesy of Chengcai Wang from CAMP-Nano) (Color figure online).

the sample and "on" means that the e-beam is illuminating the sample. This is the first time that the effect of electron beam on materials' mechanical properties has been evaluated quantitatively. Our findings, on the one hand, suggest that one should be cautious in using TEM to characterize the mechanical or other properties of materials with covalent bond and ionic bond; on the other hand, they indicate that e-beam may be useful for processing and tailoring amorphous silica and other conventional-brittle materials for their applications in nanotechnology.

CONCLUSIONS

Besides the miniaturization trend of functinal devices, e.g., computer and cell phone, the past 30 years also witnessed the remarkable progress for nanoscience and nanotechnology. Consequently, study of the properties of materials at the micronanoscale has been a thriving research field worldwide. In the past, many great ideas with promising potential for industry applications have been proposed. However, in order to convert these ideas into reliable devices and products, it is paramount to build up the knowledge system of micronanoscaled materials in a quantitative manner. This will be a decade-long mission that needs the efforts from all those who have involved. The following are the questions inspired from our previous research as well as those from other research groups.

For single-crystal metals, "smaller is stronger" has been proven to be a general trend. However, the strength of metals cannot be unlimited. Therefore, one natural question is: Where is the limit of "smaller is stronger" that can be measured experimentally? How can this be realized?

The existence of dislocations and its evolution have been thought as the underlying reason for the size effect of metals. However, we found that single-crystal Al pillars still exhibit strong size effect on strength even after thorough "mechanical annealing."[20] What is the underlying physical mechanism for this?

We have reported that if the pillar size is less than 1 μm, then dislocation will replace deformation twinning as the sole plasticity carrier in a α-Ti alloy at room temperature. For polycrystalline materials, it has been reported that twinning probability will change from high to low and then high along with the decrease the grain size. The question now is: If we further reduce the size of α-Ti alloy, will deformation twinning begin to set in again and finally become a prominent deformation mechanism?

Bulk metal materials, e.g., Au, exhibit excellent ductility and malleability. However, after its size is reduced to micronanoscale, the plasticity of Au becomes intermittent and even accompanies the structural collapse.[34] The phenomena cannot be explained by general dislocation behavior. Then what is the real reason for this? Is there any temperature rise accompanying the structural collapse? If yes, then what is its effect on the following deformation process?

Even though it has been confirmed that a high-energy e-beam can have significant effect on the mechanical properties of materials with covalent and ionic bond, its underlying physical mechanism remains a subject for considerable scientific debate. In addition, what is the critical voltage and/or beam intensity below which e-beam will no longer have an effect on the mechanical properties of materials?

ACKNOWLEDGEMENTS

This work was supported by the Grants from NSFC (50925104 and 11132006) and 973 Programs of China (2010CB631003). We also appreciate the support from the 111 Project of China (B06025).

REFERENCES

1. M.D. Uchic, D.M. Dimiduk, J.N. Florando, and W.D. Nix, *Science* 305, 986 (2004).
2. M.D. Uchic, P.A. Shade, and D.M. Dimiduk, *Annual Review of Materials Research*, vol. 39 (Palo Alto, CA: Annual Reviews, 2009), pp. 361–386.
3. S.H. Oh, M. Legros, D. Kiener, and G. Dehm, *Nat. Mater.* 8, 95 (2009).
4. Z.W. Shan, R.K. Mishra, S.A.S. Asif, O.L. Warren, and A.M. Minor, *Nat. Mater.* 7, 115 (2008).
5. J.R. Greer, W.C. Oliver, and W.D. Nix, *Acta Mater.* 53, 1821 (2005).
6. W.D. Nix, J.R. Greer, G. Feng, and E.T. Lilleodden, *Thin Solid Films* 515, 3152 (2007).
7. L. Huang, Q.J. Li, Z.W. Shan, J. Li, J. Sun, and E. Ma, *Nat. Commun.* 2, 579 (2011).
8. C. Chisholm, H. Bei, M.B. Lowry, J. Oh, S.A.A. Asif, O.L. Warren, Z.W. Shan, E.P. George, and A.M. Minor, *Acta Mater.* 60, 2258 (2012).
9. Q. Yu, Z.W. Shan, J. Li, X.X. Huang, L. Xiao, J. Sun, and E. Ma, *Nature* 463, 335 (2010).
10. L. Tian, Y.Q. Cheng, Z.W. Shan, J. Li, C.C. Wang, X.D. Han, J. Sun, and E. Ma, *Nat. Commun.* 3, 609 (2012).
11. Z.W. Shan, J. Li, Y.Q. Cheng, A.M. Minor, S.A.S. Asif, O.L. Warren, and E. Ma, *Phys. Rev. B* 77, 155419 (2008).
12. K. Zheng, C.C. Wang, Y.Q. Cheng, Y.H. Yue, X.D. Han, Z. Zhang, Z.W. Shan, S.X. Mao, M.M. Ye, Y.D. Yin, and E. Ma, *Nat. Commun.* 1, 144 (2010).
13. O. Kraft, P.A. Gruber, R. Moenig, and D. Weygand, *Annual Review of Materials Research,* vol. 40, ed. D.R.R.M.Z.F. Clarke (Palo Alto, CA: Annual Reviews, 2010), pp. 293–317.
14. D.S. Gianola and C. Eberl, *JOM* 61, 24 (2009).
15. S.S. Brenner, *J. Appl. Phys.* 27, 1484 (1956).
16. S.S. Brenner, *J. Appl. Phys.* 28, 1023 (1957).
17. S.S. Brenner, *Science* 128, 568 (1958).
18. A.M. Minor, S.A.S. Asif, Z.W. Shan, E.A. Stach, E. Cyrankowski, T.J. Wyrobek, and O.L. Warren, *Nat. Mater.* 5, 697 (2006).
19. J. Weertman and J.R. Weertman, *Elementary Dislocation Theory* (New York, NY: Oxford University Press, 1992), pp. 11, 213.
20. Z.J. Wang, Q.J. Li, Z.W. Shan, J. Li, J. Sun, and E. Ma, *Appl. Phys. Lett.* 100, 122405 (2012).
21. D. Kiener and A.M. Minor, *Acta Mater.* 59, 1328 (2011).
22. C.R. Weinberger and W. Cai, *Proc. Natl. Acad. Sci. USA* 105, 14304 (2008).
23. J.R. Greer, C.R. Weinberger, and W. Cai, *Mater. Sci. Eng. A* 493, 21 (2008).
24. J.Y. Kim and J.R. Greer, *Appl. Phys. Lett.* 93, 10916 (2008).
25. S. Brinckmann, J.Y. Kim, and J.R. Greer, *Phys. Rev. Lett.* 100, 155502 (2008).
26. J.R. Greer, C.R. Weinberger, and W. Cai, *Mater. Sci. Eng. A* 493, 21 (2008).
27. M.A. Meyers, O. Vohringer, and V.A. Lubarda, *Acta Mater.* 49, 4025 (2001).
28. J.A. Knapp and D.M. Follstaedt, *J. Mater. Res.* 19, 218 (2004).
29. M.D. Uchic, P.A. Shade, and D.M. Dimiduk, *JOM* 61 (3), 36 (2009).
30. O. Kraft, *Nat. Mater.* 9, 295 (2010).
31. Y.Q. Cheng and E. Ma, *Acta Mater.* 59, 1800 (2011).
32. C.C. Wang, J. Ding, Y.Q. Cheng, J.C. Wan, L. Tian, J. Sun, Z.W. Shan, J. Li, and E. Ma, *Acta Mater.* 60, 5370 (2012).
33. D.C. Jang and J.R. Greer, *Nat. Mater.* 9, 215 (2010).
34. Z.J. Wang, Z.W. Shan, J. Li, J. Sun, and E. Ma, *Acta Mater.* 60, 1368 (2012).