Inter- and Intra-Agglomerate Fracture in Nanocrystalline Nickel

Zhiwei Shan,[1] J. A. Knapp,[2] D. M. Follstaedt,[2] E. A. Stach,[3] J. M. K Wiezorek,[1] and S. X. Mao[1,*]

[1]*Department of Mechanical Engineering and Materials Science, University of Pittsburgh, Pittsburgh, Pennsylvania 15261, USA*
[2]*Physical, Chemical and Nano Sciences Center, Sandia National Laboratories, Albuquerque, New Mexico 87185-1056, USA*
[3]*School of Materials Engineering, Purdue University, West Lafayette, Indiana 47907-2044, USA*

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In situ tensile straining transmission electron microscopy tests have been carried out on nanocrystalline Ni. Grain agglomerates (GAs) were found to form very frequently and rapidly ahead of an advancing crack with sizes much larger than the initial average grain size. High-resolution electron microscopy indicated that the GAs most probably consist of nanograins separated by low-angle grain boundaries. Furthermore, both inter- and intra-GA fractures were observed. The observations suggest that these newly formed GAs may play an important role in the formation of the dimpled fracture surfaces of nanocrystalline materials.

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In nanocrystalline metals, tensile stress-strain curves at room temperature show very high strengths accompanied by limited uniform deformation [1,2]. This behavior is very similar to that observed during brittle fracture. Consequently, it may be expected that fracture occurs intergranularly and that the three-dimensional nature of the grains would be revealed on the fracture surface. However, experimental observations of fracture surfaces of nanocrystalline metals typically exhibit dimple features with sizes considerably larger than the grain size [3–12]. Fracture surfaces of this type are most frequently characteristic of ductile fracture.

Several explanations have been proposed to account for this apparent paradox of ductilelike dimpled fracture surfaces in nanocrystalline metals. Studying nanocrystalline Ni, Kumar *et al.* [6] proposed that the dimpled fracture surfaces may have resulted from the evolution of those grain boundaries (GBs) and/or triple junction voids which form when intragranular slip (dislocation motion) is coupled with unaccommodated GB sliding. This mechanism reasonably accounts for the experimental observations in nanocrystalline Ni with an average grain size of about 30 nm, where dislocation-mediated plasticity has been proven to be the dominant deformation mode [6]. However, it cannot explain the dimple features observed on the fracture surface of nanocrystalline materials with a much smaller grain size (e.g., less than 10 nm [11]). It is generally expected that GB mediated plasticity (GB sliding and/or grain rotation) will begin to replace dislocation-mediated plasticity as the dominant deformation mechanism for such small grain size [13–15]. Iwasaki *et al.* [11] recently reported deformation and fracture characteristics of an electrodeposited nanocrystalline Ni-W alloy with an average grain size of 8.1 nm. The fracture surface also showed dimple features with sizes 2.5 to 25 times larger than the average grain size. The authors [11] proposed that the dimpled fracture surface is a result of grains sliding in clusters and that the dominant deformation mechanism in nanocrystalline Ni-W is GB sliding. However, the authors did not mention how or why grains might slide as clusters, nor directly demonstrate this mechanism in operation. Molecular dynamics (MD) computer simulations have also been used to study the fracture surfaces of nanocrystalline material. Hasnaoui *et al.* [9] demonstrated that due to the presence of GBs that are resistant to sliding, local shear planes are concentrated around their neighboring planes, creating a cluster of grains embedded in a sliding environment. Thus, an inherent plasticity length emerges that is on the order of several grain sizes and corresponds to the dimensions of the dimple features documented on experimental fracture surfaces.

If we take all of these findings [6,9,11] into consideration, a common characteristic can be identified: GB sliding plays an important role in the formation of dimpled features on the fracture surfaces of nanocrystalline materials, although no direct experimental confirmation of the role of this mechanism has been reported in these studies. Therefore, confirming the prevalence of GB-related deformation seems to be a key point for discovering the underlying physical mechanism that dominates the formation of the dimpled fracture surfaces in nanocrystalline metals. With its inherently dynamic character and atomic-scale resolution, *in situ* TEM observations during tensile straining may be expected to provide additional insights into the nature of the formation of dimple features on the fracture surfaces of the nanocrystalline materials.

The average grain size of the Ni samples used in this study is about 10 nm [16,17]. Thin films were formed rocksalt by pulsed laser deposition, with the salt being dissolved away to produce freestanding films that exhibited no voids. Because of the tensile specimen design [16–18], the discernable deformation and the fracture process were usually concentrated in a long, narrow bandlike area ahead of the crack tip. Under bright field TEM (BFTEM) imaging conditions, rapid changes in contrast of many different grains are observed to occur continuously in the bandlike

area where the local strain rate is usually high upon loading. This type of BFTEM contrast change has been reported previously [19,20] and has usually been identified as dislocation activity, although it may also result from other strain induced deformation mechanisms, such as GB mediated plasticity.

Figure 1 shows dark field (DF) TEM images extracted from videotape, which depict the dynamic evolution of the deformation and fracture process of nanocrystalline Ni upon loading. Figure 1(a) shows an area before deformation occurred. The right-hand-side inset in Fig. 1(a) is a DFTEM image taken from an area that had been thinned using low temperature ion thinning for improved imaging. This micrograph confirms the narrow grain size distribution of the as-deposited nanocrystalline Ni with an average grain size of about 10 nm. Upon loading, many bright contrast features form very frequently and rapidly at many locations in the narrow, long bandlike area ahead of the crack tip, apparently independent of one another, under the influence of the applied stress as shown in Fig. 1(b). These features have been identified as agglomerates formed through the orientation changes of groups of neighboring smaller grains and the details of their formation are discussed in Refs. [16,21,22], where timed sequences showing local grain reorientation to form agglomerates were well recorded. Grain growth in nanocrystalline Cu during indentation is similarly thought to occur by grain rotation [23]. Clearly, the size of these bright contrast features [up to about 80 nm in Fig. 1(b)] is much larger than the average grain size. Further loading causes the crack to propagate through this bandlike thinner area, where the grain agglomerates are concentrated [Fig. 1(c)]. Careful examination of the video sequence between Figs. 1(b) and 1(c) found that, instead of remaining constant after formation, the sizes and shapes of the grain agglomerates changed in a rather irregular manner during the deformation and fracture process. This implies that GB-related plasticity mechanisms were active among the groups of smaller grains that constitute the larger grain agglomerates in response to the additional loading pulses. Figure 1(d) shows the final crack propagation path. The large bright contrast features at the edges of the propagating crack indicate that some grain agglomerates behave in a collective manner during the fracture process and the crack advances around them rather than through them (i.e., in an interagglomerate mode of crack propagation and fracture).

However, deformation and fracture across the grain agglomerates are also observed. Figure 2 shows DFTEM images extracted from video tape, which demonstrate the dynamic fracture process occurring in an intra-agglomerate manner. At the beginning of this sequence, the image of the agglomerate indicated by the white arrow had a dimension of about 60 by 90 nm [Fig. 2(a)]. However, only 0.13 s later, the agglomerate was observed to split into two parts [Fig. 2(b)]. It is worth noting that the total size of the two split parts in Fig. 2(b) appears smaller than the original agglomerate [Fig. 2(a)] due to a gray zone between them. This suggests that grains in the middle of the original agglomerate have rotated out of contrast, and that grain-boundary processes are active in producing the fracture. Note also that the contrast of several neighboring agglomerates is essentially unchanged between Figs. 2(a) and 2(b), indicating that the image changes are local and are not due to reorientation of the Ni film within the observation area. At $t = 0.23$ s, a crack has propagated through the agglomerate and the two residual parts (tracked continuously in the video) located at the opposite edges of the crack can be seen clearly, as indicated by the white arrows in Fig. 2(c).

Thermodynamic considerations imply that deformation-induced changes in the GB structure would favor the genesis of low-angle grain boundaries (LAGB) from high-angle grain boundaries (HAGB), allowing for a re-

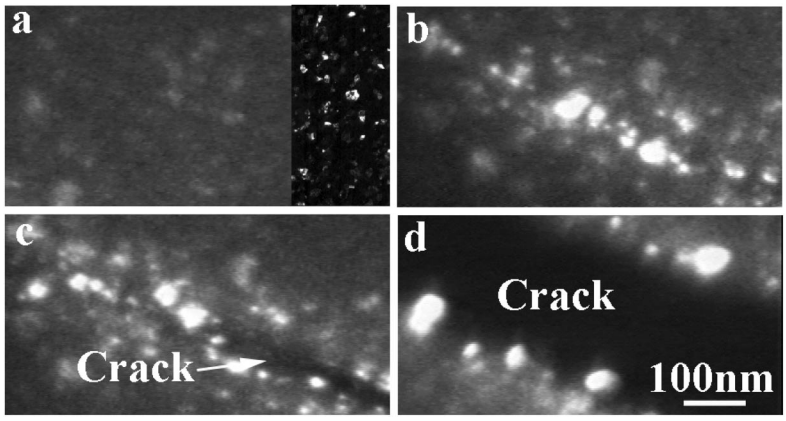

FIG. 1. DFTEM observation of the deformation and fracture process of as-deposited nanocrystalline Ni. (a) DF image of the sample prior to deformation. The inset at the right-hand side of (a) is taken from a prethinned area. (b) Upon loading, many grain agglomerates were observed to form very rapidly and frequently prior to fracture. (c) Further loading leads to the crack propagating among the agglomerates. (d) The final crack path of the fractured nanocrystalline Ni.

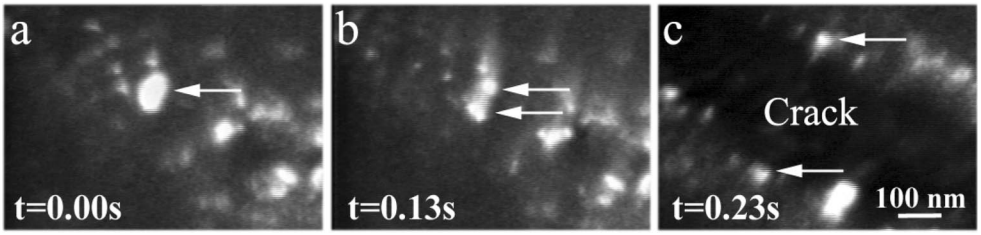

FIG. 2. DFTEM observation of intra-agglomerate fracture depicted by individual still frames extracted from a dynamic video-sequence. (a) $t = 0$ s, a agglomerate with dimension of about 60 nm by 90 nm is indicated by the white arrow. (b) The agglomerate split at $t = 0.13$ s. (c) At $t = 0.23$ s, the crack propagated across the agglomerate; the residual parts located at the crack edges are indicted by the white arrows.

duction in free energy of the system. In order to verify the GB structure of the grains constituting the agglomerates, HREM images were taken along the crack edge where, as shown in Figs. 1 and 2, inter- and/or intra-agglomerate fractures are expected to occur. An example is shown in Fig. 3. In comparison with the as-deposited state (HREM shows most of the grains are divided by HAGB) [16], it was surprising to identify more than 8 grains in such a small area and to find that all of the grains appear to be delineated by LAGB. This evidence strongly supports the genesis of LAGB from HAGB during the deformation-induced formation of the larger grain agglomerates. Because of the small diffraction angles for fast electrons used in the TEM, lattice fringe images are produced only for those crystal planes in a nearly edge-on orientation, i.e., those with normals approximately perpendicular to the incident beam direction. After calibrating the magnification, it was found that most of the lattice fringes in the HREM images are consistent with (002) planes of the fcc Ni lattice. This appears unusual since (111) planes are expected to be more readily imaged than (002) planes because of their larger interplanar distance. However, improved crystalline alignments of (002) lattice planes are also observed during tensile straining of thicker electro-deposited films (~ 200 μm) by x-ray diffraction [24]. This is consistent with our TEM observation in Fig. 3 with $\sim$100 nm films of the unusually high incidence of (002) type planes in an edge-on orientation in the group of nanocrystalline grains constituting an agglomerate.

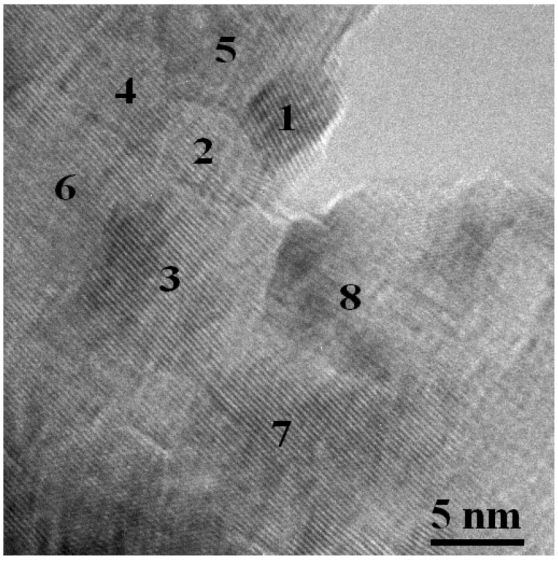

FIG. 3. Typical HREM image taken along the edge of a propagating crack. All the grains identified show only slight changes in the relative orientation of lattice fringes associated with same type planes and are therefore separated by low-angle grain boundaries.

The observations presented above and earlier ones [20,21] clearly reveal that the grain agglomerates, which formed very rapidly and independently in areas experiencing large plastic deformation prior to the fracture, result from grain rotation. Following the formation of these grain agglomerates, cracks are observed to propagate in an inter- or intra-agglomerate manner. HREM indicates that these grain agglomerates are very likely comprised of numerous small grains that are separated by LAGB. The mechanistic process envisioned by us from these observations can be described as follows: The nanocrystalline material with its dense network of grain boundaries is in a metastable state. This metastable state can be destabilized by an applied external stress. Individual grains with especially favorable characteristics (size, shape, orientation, etc.) rearrange first by grain rotation or even dislocation activities [16]. These grains can then serve as seeds and eventually trigger an avalanche of interactions in the neighboring grains, followed by further reorientation and/or coalescence to produce agglomerates with LAGB and aligned lattice planes.

Our observations of the formation of grain agglomerates, as well as their deformation and fracture characteristics, allow us to speculate on their role in the fracture process and final surface structure. Firstly, the grains that are adjacent to the outer boundaries of the grain agglomerates presumably have a stable structure; i.e., they are not easily deformed. If this were not the case they would likely become incorporated into the agglomerate, favored by an accompanying decrease in the free energy of the system. Rapid diffusion along grain boundaries in nanocrystalline materials [25–27] during the formation of the grain agglomerates will inevitably lead to the transportation of point defects, such as vacancies, to the agglomerate

boundaries in order to conserve volume. This renders the boundaries of the agglomerates favorable sites for the nucleation, growth and propagation of voids and cracks. As a consequence, the grain agglomerates, which are much larger than the average grain size, may tend to stay together as a unit during the deformation and fracture process [as shown in Fig. 1(d)]. If the cracks propagate along the boundaries that surround the agglomerates, the fracture surfaces would be expected to exhibit dimple features on the order of the agglomerate size. The first-order correlation between observed dimple sizes during fracture [6,9] and the size of the grain agglomerates suggests that this may be the case.

Secondly, the genesis of the LAGB from HAGB inside the grain agglomerates indicates that the smaller grains in some grain agglomerates could share at least some of their available slip systems. This would facilitate dislocation-mediated plasticity within the agglomerates via dislocation transfer across the LAGB's at stress levels that are lower than would be expected for randomly oriented nanocrystalline grains with the same grain size, for instance. Dislocations have been found within Ni nanograins in deformed areas and their dynamic processes investigated while under applied strain [17]. Therefore, the formation of these softer grain agglomerates must inevitably lead to plastic instabilities during deformation. Consequently, the associated plastic deformation of such agglomerates can be expected to yield a fracture surface with features that appear ductile in nature. Such ductile features also have sizes larger than the initial grain size.

In summary, DFTEM investigations of a freestanding nanocrystalline Ni film during *in situ* tensile straining have shown that grain agglomerates formed very frequently and rapidly in many locations, apparently independently of one another. Cracks are observed to nucleate and propagate in a combined inter- and intra-agglomerate manner. Post mortem HREM observations show evidence for the genesis of LAGB from the initial HAGB in forming the agglomerates. Guided by the *in situ* TEM tensile experiments as well as other reported experiments, we propose that the dimple formation in nanocrystalline materials during tensile loading to failure results from the formation of the grain agglomerations.

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*Corresponding author.
smao@engr.pitt.edu

[1] J. R. Weertman, *Mechanical Behavior of Nanocrystalline Metals in Nanostructured Materials: Processing, Properties, and Potential Applications* (William Andrew, Norwich, CT, 2002).
[2] C. C. Koch, D. G. Morris, K. Lu, and A. Inoue, MRS Bull. **24**, 54 (1999).
[3] F. Ebrahimi, Q. Zhai, and D. Kong, Scr. Mater. **39**, 315 (1998).
[4] F. Ebrahimi, G. R. Bourne, M. S. Kelly, and T. E. Matthews, Nanostruct. Mater. **11**, 343 (1999).
[5] F. Dalla Torre, H. Van Swygenhoven, and M. Victoria, Acta Mater. **50**, 3957 (2002).
[6] K. S. Kumar, S. Suresh, M. F. Chisholm, J. A. Horton, and P. Wang, Acta Mater. **51**, 387 (2003).
[7] T. Mukai, S. Suresh, K. Kita, H. Sasaki, N. Kobayashi, K. Higashi, and A. Inoue, Acta Mater. **51**, 4197 (2003).
[8] R. Schwaiger, B. Moser, M. Dao, N. Chollacoop, and S. Suresh, Acta Mater. **51**, 5159 (2003).
[9] A. Hasnaoui, H. Van Swygenhoven, and P. M. Derlet, Science **300**, 1550 (2003).
[10] K. S. Kumar, H. Van Swygenhoven, and S. Suresh, Acta Mater. **51**, 5743 (2003).
[11] H. Iwasaki, K. Higashi, and T. G. Nieh, Scr. Mater. **50**, 395 (2004).
[12] H. Li and F. Ebrahimi, Adv. Mater., **17**, 1969 (2005).
[13] J. Schiotz, F. D. Di Tolla, and K. W. Jacobsen, Nature (London) **391**, 561 (1998).
[14] H. Van Swygenhoven, Science **296**, 66 (2002).
[15] S. Yip, Nature (London) **391**, 532 (1998).
[16] Z. W. Shan, E. A. Stach, J. M. K. Wiezorek, J. A. Knapp, D. M. Follstaedt, and S. X. Mao, Science **305**, 654 (2004).
[17] Z. W. Shan, E. A. Stach, J. M. K. Wiezorek, J. A. Knapp, D. M. Follstaedt, and S. X. Mao, Phys. Rev. Lett. **98**, 095502 (2007).
[18] Z. W. Shan and S. X. Mao, Adv. Eng. Mater. **7**, 603 (2005).
[19] C. J. Youngdahl, J. R. Weertman, R. C. Hugo, and H. H. Kung, Scr. Mater. **44**, 1475 (2001).
[20] R. C. Hugo, H. Kung, J. R. Weertman, R. Mitra, J. A. Knapp, and D. M. Follstaedt, Acta Mater. **51**, 1937 (2003).
[21] Z. W. Shan, E. A. Stach, J. M. K. Wiezorek, J. A. Knapp, D. M. Follstaedt, and S. X. Mao, Science **308**, 356 (2005).
[22] M. W. Chen and X. Q. Yan, Science **308**, 356 (2005).
[23] P. L. Gai, K. Zhang, and J. Weertman, Scr. Mater. **56**, 25 (2007).
[24] Z. Budrovic, H. Van Swygenhoven, P. M. Derlet, S. Van Petegem, and B. Schmitt, Science **304**, 273 (2004).
[25] C. Suryanarayana, Bull. Mater. Sci. **17**, 307 (1994).
[26] R. A. Masumura, P. M. Hazzledine, and C. S. Pande, Acta Mater. **46**, 4527 (1998).
[27] B. Cai, Q. P. Kong, L. Lu, and K. Lu, Scr. Mater. **41**, 755 (1999).