Strong Strain Hardening in Nanocrystalline Nickel

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Low strain hardening has hitherto been considered an intrinsic behavior for most nanocrystalline (NC) metals, due to their perceived inability to accumulate dislocations. In this Letter, we show strong strain hardening in NC nickel with a grain size of ~20 nm under large plastic strains. Contrary to common belief, we have observed significant dislocation accumulation in the grain interior. This is enabled primarily by Lomer-Cottrell locks, which pin the lock-forming dislocations and obstruct dislocation motion. These observations may help with developing strong and ductile NC metals and alloys.

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Is low strain hardening an intrinsic behavior of nanocrystalline (NC, <100 nm) metals? For most people in the materials community the answer is "yes" because it has been supported by the majority of experimental results so far [1–4]. Low strain hardening leads to low tensile ductility, which has become a major issue for structural applications of NC materials. For simplicity, we hereafter refer to NC metals as those with "largely clean" grain interior, which contains no dominating twins, second phase particles or other structures. Note that improved strain hardening has been reported recently in *nanostructured* metals [5–8]. However, defined as metals with structural features less than 100 nm, they are not nanocrystalline because their grain sizes are usually larger than 100 nm. Molecular dynamics (MD) simulations have shown that in NC metals dislocations may be emitted from and disappear at grain boundaries without accumulation [9–11], providing support to the widely accepted belief that they have intrinsically diminutive strain hardening.

On the other hand, there are pieces of indirect evidence that limited dislocation accumulation might be possible in NC grains [12–15]. For example, dislocations have been observed in grains as small as 20 nm [14–17]. It is also generally observed that NC metals exhibit early necking under tensile stress [1,2,18]. These observations raise the second question: Has the traditional tensile testing deprived NC metals of any opportunity to show strain hardening, which might develop at larger strains? This possibility is supported by the strong strain hardening in NC Cu consolidated *in situ* during ball milling [14,15], which naturally raises the third question: Is the strain hardening at large strains, if it exists, caused by dislocation accumulation?

To answer these questions, we cryogenically rolled electrodeposited NC Ni with an initial grain size of ~20 nm in a confined manner to produce very large strains. Figure 1 shows a sharp strength increase of ~1.0 GPa with rolling strain, reaching a maximum value of 2.37 GPa. This strength increase is caused by significant strain hardening during cold rolling. In other words, the strength-rolling strain relationship shown in Fig. 1 is somewhat similar to a stress-strain curve obtained in mechanical testing. A closer examination of Fig. 1 reveals three strain hardening regimes. In Regime I, the strain hardening is very high, as indicated by the sharp strength increase with the imposed rolling strain. This is followed by Regime II, where the strain hardening slows down until a strength peak is reached. Then the material enters into Regime III, where the strength decreases with rolling strain until a plateau is reached.

The result in Fig. 1 reveals that NC metals can have strong strain hardening if they are deformed to large strains. This answers the aforementioned first and second

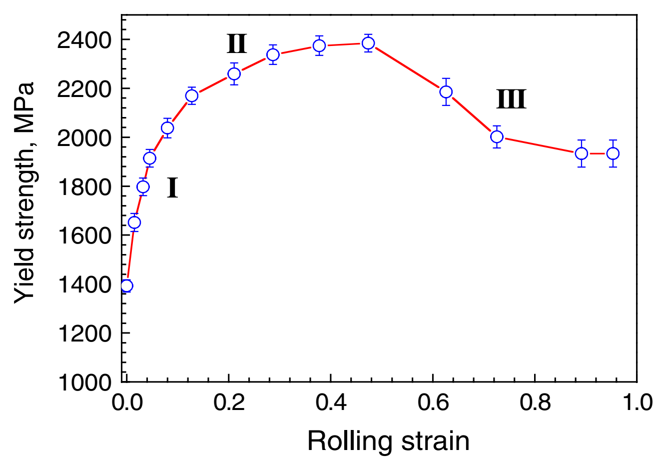

FIG. 1 (color online). Yield strength (1/3 of Vickers microhardness) vs rolling strain. The NC Ni film with an initial thickness of 0.15 mm was cold rolled at liquid nitrogen temperature between two stainless steel sheets at a strain rate of $\sim 2 \times 10^{-2}\ s^{-1}$. The rolling strains were calculated as ln(initial thickness/final thickness). Ten Vickers hardness data points were measured for each rolling strain, using a 10 g load, samples more than 8 times thicker than the indent depth, and a standard sample support with an average microhardness of 900 Hv.

questions. To address the third question, we carefully characterized the microstructure using high-resolution transmission electron microscopy (HREM) and measured the dislocation density as a function of imposed rolling strain using both HREM and x-ray diffraction (XRD) analysis. Figure 2 shows a representative HREM image of the cryorolled NC Ni, which reveals high density of dislocations in the grain interior. Figure 3 shows that dislocation density first increased and then decreased with increasing rolling strain. Note that the scatter of dislocation density measured by HREM is caused by the local nature, i.e., individual NC grains, of HREM measurement. XRD analysis measures the global average density of dislocations. The values of dislocation density measured by XRD analysis (red solid squares) are comparable with those measured by HREM (blue unfilled circles). The observed increase in dislocation density is in sharp contrast to the belief that dislocations cannot be stored in such nanometer-sized grains during plastic straining [10].

Comparing Fig. 1 and Fig. 3, one might see a correlated trend in the strain hardening or softening and the dislocation density. Based on this observation, we hypothesize that dislocation accumulation is the main cause for strain hardening. This raises another question: What caused dislocations to accumulate? Examination of Fig. 2 reveals that dislocations are pinned and accumulated in the grain interior. Since the grain interior is relatively "clean," without second phase particles or other structural features to block these dislocations, the only possible crystalline defects to pin the dislocations would be sessile dislocation structures, which, as discussed below, are primarily Lomer-Cottrell (L-C) locks [19,20].

We have experimentally observed high density of L-C locks in NC Ni subjected to large rolling strains. Figure 4(a) shows three closely-spaced L-C locks in a 35 nm grain in NC Ni near a triple junction. They were formed by an extended Lomer dislocation [19], and its structure consists of two stacking faults meeting each other at a 70.5° angle and connected by a stair-rod dislocation [see Fig. 4(b)] [19–21]. Detailed description on the core lattice structure of the L-C lock can be found in [22]. It should be noted that this is the first time that L-C locks are observed experimentally in NC materials, although they have been previously revealed by MD simulations in NC Al [21]. They can be formed by the reaction of two leading partials from two dissociated 60° lattice dislocations on two intercrossing slip planes [19]. As shown in Fig. 2, high density of dislocations on two intercrossing (111) planes exist in NC Ni, which provides high probability for the formation of L-C locks. These dislocations have been observed to originate from grain boundaries [21] or from the cross-slip of dislocations [23]. The formation of L-C locks also needs the participation of stacking faults. NC materials are known to produce wider stacking faults than their coarse-grained counterparts, especially near the grain boundaries [24,25], and therefore should be more favorable to producing L-C locks. Since the cross-slip of perfect dislocations occurs more readily near grain boundaries, where stress concentrations exist [23], there should be higher density of L-C locks, and consequently higher dislocation accumulation near grain boundaries. This is exactly what we have observed in our HREM investigation.

It is our hypothesis that the L-C locks played the most critical role in the strain hardening observed in NC Ni. This hypothesis is supported by both experimental evidence [19,22,26,27] and MD simulation results [28–30]. First, experimental studies on the latent hardening of Al and Cu revealed that L-C locks are most effective in producing hardening among all dislocation barriers formed by dislocation intersections [18,25,26]. This observation is believed to be typical of fcc metals with medium-to-high

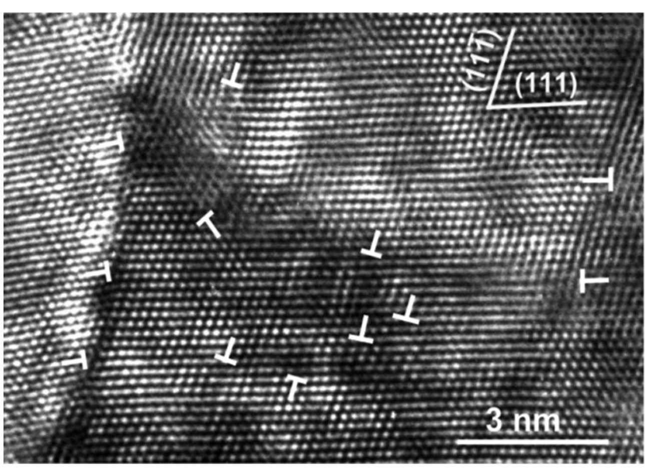

FIG. 2. HREM image showing high density of dislocations in a NC grain of cold-rolled NC Ni.

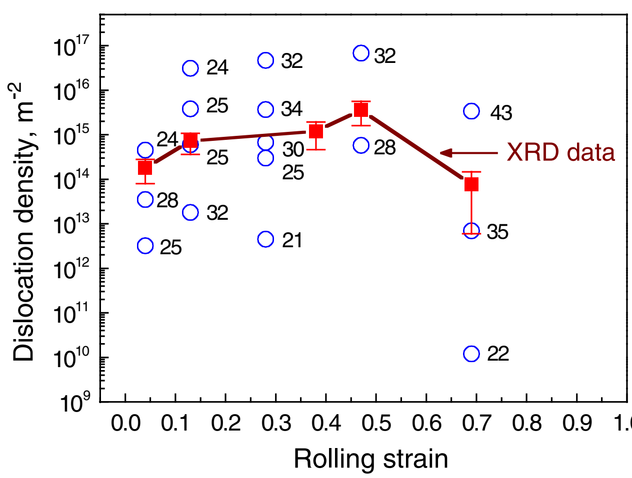

FIG. 3 (color online). Dislocation density as a function of rolling strain in NC Ni, measured from HREM images of individual grain (blue unfilled circles) and XRD analysis of a large sample (red solid squares). Numbers beside unfilled blue circles indicate the corresponding grain size (nm).

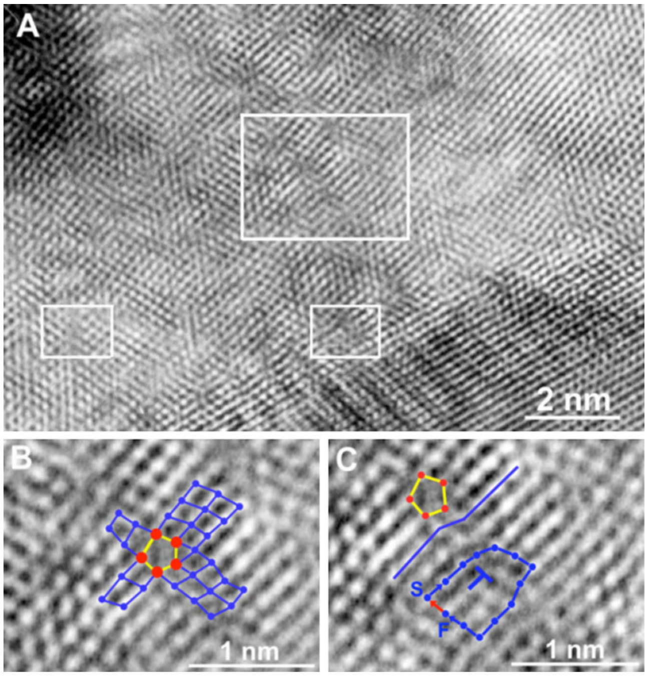

FIG. 4 (color online). (a) HREM lattice image near a triple junction in cryorolled NC Ni. The three white rectangular frames mark three Lomer-Cottrell (L-C) locks. (b) Enlarged image of the area in the upper frame, which shows the core (a stair-rod dislocation) of the L-C lock (marked by the pentagon with five red dots at its corners). It also shows the two extra half planes (stacking faults) as delineated in [22] as part of the L-C structure. (c) Burgers circuit enclosing a Shockley partial near the L-C lock.

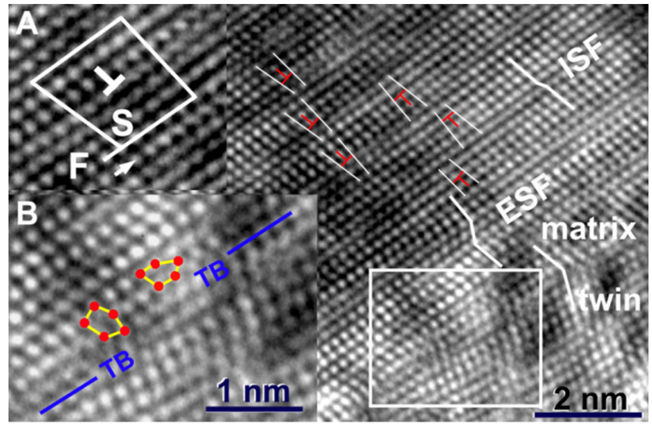

FIG. 5 (color online). HREM micrograph showing various crystalline defects near a twin boundary (TB), including 60° perfect dislocations (marked with "T"), intrinsic stacking fault (ISF) and extrinsic SF (ESF). Inset (a). Burgers circuit, starting at S and ending at F, encloses the core of a perfect dislocation ("T"). Inset (b). Two sessile stair-rod dislocations are marked with two pentagons near the twin boundary.

stacking fault energies. Ni has high stacking fault energy. Second, we have observed high density of L-C locks in cryorolled NC Ni (see Fig. 4). This is critical in producing very high strain hardening. Other sessile dislocation structures that may contribute to strain hardening include dislocation jogs [31] and multiple junctions [32]. However, it was reported that experimentally observed latent hardening does not correlate with jog formation [27]. The probability of forming multiple junctions is much lower than that of forming L-C locks because a multiple junction requires three or more dislocations to meet by chance and then react. This makes multiple junctions unlikely to contribute significantly to the observed strain hardening in NC Ni.

The L-C locks derive their effectiveness in strain hardening from their capability to accumulate dislocations. First, when two dislocations meet to produce an L-C lock, the length of the lock is usually short, and each end of the lock pins two dislocation segments [19]. In other words, four dislocation segments are pinned by each L-C lock. Second, L-C locks are effective barriers in accumulating other dislocations [19]. For example, careful examination of Fig. 4(c) reveals a Shockley partial near an L-C lock. Furthermore, the L-C locks are very stable, i.e., very resistant to dissociation [19], although they could be destroyed under extremely high stresses [33]. These superior properties of L-C locks, together with their high density, make them very effective in producing strain hardening.

Twin-dislocation interactions should also have contributed to the observed strong strain hardening in NC Ni. Figure 5 shows several types of defects near the twin boundary (TB), including high density of 60° perfect dislocations (marked with "T"), an intrinsic stacking fault (ISF) and an extrinsic stacking fault (ESF). Inset (a) shows the Burger circuit of a 60° perfect dislocation (marked by a "T"). Figure 5 also shows a framed rectangular area that contains two stair-rod dislocations near the TB, as delineated by the pentagons in inset (b). The stair-rod dislocation is identical to that in an L-C lock. However, it was formed by the cross-slip of a partial at the twin boundary, as revealed by MD simulations [34]. In other words, these two stair-rod dislocations do not represent the cores of L-C locks. These defects on and near twin boundaries attest to the effectiveness of twin boundaries in accumulating crystalline defects, which consequently cause strain hardening. Deformation twinning is also a contributing mechanism of plastic deformation in NC Ni [35]. Statistically, our HREM investigation revealed that 28% of the NC Ni grains contain twins after cold rolling to a strain of 46%. Therefore, the twin-dislocation interactions should have some limited contribution to the strain hardening.

Nonuniform grain size distribution has been theorized to cause strain hardening [5]. However, we tested our electrodeposited NC Ni in tension mode and did not observe significant strain hardening [17], indicating that it is not primarily responsible for the observed strong strain hardening shown in Fig. 1. Texture evolution could also have affected the strain hardening behavior of NC Ni. Our x-ray analysis shows that the texture does not change much at

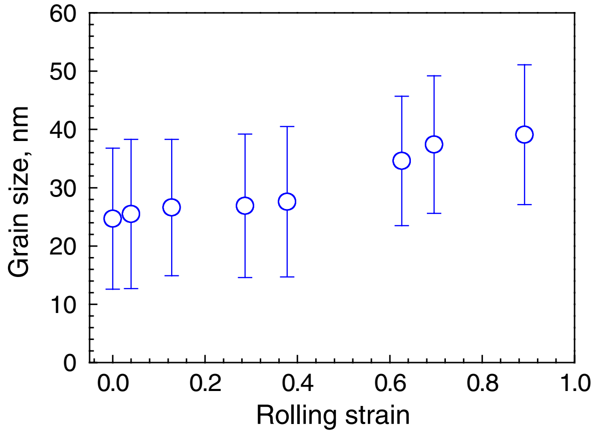

FIG. 6 (color online). XRD data show grain growth with rolling strain.

rolling strains larger than 0.1. However, Fig. 1 shows that strain hardening continues to significantly increase at rolling strains higher than 0.1. Thus texture evolution could not have been responsible for the observed strong strain hardening in the NC Ni. Figure 6 shows that the grain size increased slowly at first with imposed rolling strain and then faster at strains higher than 0.4. Careful inspection of Figs. 1, 3, and 6 shows that the strength decrease in Regime III (Fig. 1) is well correlated with the dislocations density decrease (Fig. 3) and the grain growth (Fig. 6).

In conclusion, we have observed strong strain hardening in NC Ni ($\sim$20 nm) upon cryogenic rolling in a confined fashion. The strain hardening is primarily caused by dislocation accumulation in the grain interior. Large plastic deformation produced high density of Lomer-Cottrell locks, which are primarily responsible for the dislocation accumulation. These observations dispel the conventional myth that NC metals intrinsically have low ductility because dislocations cannot accumulate inside the grains. The findings in this Letter shed new insight into the mechanical behavior of nanocrystalline metals, which may help to guide processing and designing NC metals and alloys for both high strength and high ductility.

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