Computational Materials Science 85 (2014) 8–15

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

# Hydrostatic pressure effects on deformation mechanisms of nanocrystalline fcc metals

Fuping Yuan *, Xiaolei Wu

*State Key Laboratory of Nonlinear Mechanics, Institute of Mechanics, Chinese Academy of Science, Beijing 100190, People's Republic of China*

ARTICLE INFO

*Article history:*
Received 23 October 2013
Received in revised form 10 December 2013
Accepted 20 December 2013
Available online 11 January 2014

*Keywords:*
Molecular dynamics
Nanocrystalline metals
Hydrostatic pressure

ABSTRACT

A series of large-scale molecular dynamics (MD) simulations have been performed to investigate hydrostatic pressure effects, and the interplay between pressure and grain size, on the flow stress and the related atomic-level deformation mechanisms in nanocrystalline (NC) Cu. The strength of NC Cu increases with increasing hydrostatic pressures for all grain sizes studies in the present paper (3–15 nm). The critical grain size for maximum strength first shifts towards lower values with increasing hydrostatic pressure (0–5 GPa), and then shifts towards higher values as the hydrostatic pressure becomes even higher (5–80 GPa). Below the critical hydrostatic pressure, the dislocation behaviors increase with increasing hydrostatic pressure for all grain sizes and the dependency of effective modulus as a function of hydrostatic pressure is almost the same for all grain sizes, which should lead to the position shifting of maximum strength towards lower grain sizes. Above the critical hydrostatic pressure, the dislocation behaviors start to decrease with increasing hydrostatic pressure for small grain sizes, and continue to increase with increasing hydrostatic pressure for large grain sizes. The slopes of effective modulus as a function of hydrostatic pressure increase slightly with increasing grain size above the critical hydrostatic pressure. The position shifting of maximum strength towards larger grain sizes at large hydrostatic pressure should be attributed to these two observations. Moreover, GB thickening is observed to increase monotonically with increasing pressure for all grain sizes, and the NC Cu with 3 nm grain size has the trend to become amorphous state under hydrostatic pressure of 80 GPa, which gives a new way to produce crystalline-to-amorphous transition. The findings in the present study should provide insights to the potential applications of NC metals under extreme environments.



## 1. Introduction

Nanocrystalline (NC) metals (grain size less than 100 nm) have attracted considerable interests due to many unique mechanical properties, such as increased strength/hardness, improved toughness and enhanced diffusivity compared to coarse grained counterparts [1,2]. The strength/hardness has been found to increase with decreasing grain size down to a critical value (10–20 nm), following the well known Hall–Petch (H–P) relation. The increased strength/hardness has been attributed to the increased area fraction of grain boundaries (GBs), which act as strong barriers to dislocation gliding. However, both experiments and simulations [3–14] have also shown that the strength/hardness decreases with further grain refinement below the critical value (10–20 nm), suggesting that dislocation activities give way to GB-associated plasticity such as GB sliding, GB diffusion and grain rotation. Moreover, twin boundary spacing (TBS) has been found to affect the strength of nanotwinned (NT) Cu in a similar way [15–22]. The strength of NT Cu has been found to first increase with decreasing TBS, reaching a maximal strength at a critical TBS, then decrease with further reduced TBS. However, the softening trend below the critical TBS for NT Cu has been attributed to a dislocation-nucleation-controlled softening mechanism with twin-boundary migration [18], not necessarily related to GB-mediated process.

It is now commonly accepted that interplay between dislocation activities and GB process controls the intrinsic deformation behavior and strength of NC metals. Harder materials could be created if softening effects, such as GB process, could be suppressed under extreme environment. However, the precise trade-offs between these two deformation mechanisms are still unclear, especially the effects of pressure on these two mechanisms are still vague [21,23–27]. Bringa et al. [23] have studied pressure effect on the shock compression of NC Cu. An ultra-high strength behind the shock front was observed due to the high pressure and the suppression of GB sliding under shock loading. As pressure increased, a shift in the maximum strength to lower grain sizes was observed due to the suppression of GB associated plasticity. However, beyond a critical pressure, higher temperatures due to adiabatic heating resulted in a drop in strength. In our previous study [21],

* Corresponding author. Tel.: +86 10 82544409; fax: +86 10 82543977.
*E-mail address:* fpyuan@lnm.imech.ac.cn (F. Yuan).

0927-0256/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.commatsci.2013.12.047

an ultra-high strength behind the shock front has also been found in NT Cu due to increased dislocation behaviors. Under shock loading conditions, the uniaxial loading is carried by a shock wave traveling faster than the sound velocity, pressure builds up along with inhomogeneous deformation and temperature rise by adiabatic heating. In order to investigate the pressure effect solely, excluding the temperature and shock effects, uniaxial compression experiments under high hydrostatic pressure by the panoramic-type diamond anvil cell have been adopted [24,25,28]. Such deformation experiments at high pressure on polycrystalline nickel suggest that dislocation activity is still operative in 3 nm crystals [24]. The observations of pressure-promoted texturing indicate dislocation activity can be extended down to a few-nm-length scale under high external hydrostatic pressures [24]. In situ observation of plastic accommodation by dislocations and/or GB processes in NC metals is difficult due to technical limitations, and the extremely high hydrostatic pressures are also difficult to achieve by the set-up of diamond anvil cell. However, molecular dynamics (MD) simulations have proven to be particularly useful for investigating the plastic deformation mechanism of NC metals with carefully designed model system, in which the extremely high hydrostatic pressures can be easily build up by a Nose–Hoover barostat and the transient responses of the system can be examined [6,7,29,30]. The MD simulations should enable uncovering various deformation and microstructural processes in well-designed model systems, something that has proven difficult to achieve in experiments. In this regard, the focus of this paper is to understand the hydrostatic pressure effects and the interplay between pressure and grain size on determining the strength and the related atomic-level deformation mechanisms in NC Cu using MD simulations.

## 2. Simulation techniques

The MD simulations were carried out using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) code and a Cu EAM potential developed by Mishin et al. [31]. This potential has been extensively calibrated by calculating FCC lattice properties, point and extended defects, various structural energies, and transformation paths according to the corresponding experimental or ab *initio* values. These parameters for pure Cu metal are compared and shown in Table 1, where $a_0$ is lattice constant, $B$ is bulk modulus, $c_{11}$, $c_{12}$ and $c_{44}$ are the corresponding elastic constants, $\gamma_{SF}$ is intrinsic stacking fault (ISF) energy, $\gamma_s$ is the surface energy for the corresponding planes, and $\gamma_T$ is TB energy.

The initial three-dimensional polycrystalline Cu samples containing 27 grains with random orientations were created using the Voronoi polyhedral construction, in which most GBs are high-angle GBs. Seven grain sizes ($d$ = 3.0, 5.0, 6.5, 8.0, 9.5, 11.0, 15.0 nm, determined from the mean length of the cube for the grain) were considered in order to investigate the grain size effect on the deformation behaviors of polycrystalline Cu. The sample with grain size of 15 nm has dimensions of $45 \times 45 \times 45$ nm$^3$, and contains approximately 7,800,000 atoms. The same Voronoi grain structure and the same crystallographic orientations of all grains were retained for all grain sizes. The typical relaxed NC Cu with grain size of 9.5 nm is shown in Fig. 1(a). Periodic boundary conditions were imposed along all three directions. Before loading, the as-created samples were first subjected to energy minimization by the conjugate gradient method, then gradually heated up to the desired temperature in a step-wise fashion, and finally relaxed in the Nose/Hoover isobaric–isothermal ensemble (NPT) under both the pressure 0 bar and the desired temperature (1 K) for 100 ps. The relaxed NC samples, initially at $P$ = 0 GPa, were compressed up to the desired hydrostatic pressure $P$ and relaxed at that pressure in the Nose/Hoover NPT ensemble until the volumes reached the equilibrium (Fig. 1(a)), and then were compressed to 15% at strain rate of $5 \times 10^8$/s along the $x$ direction while keeping $\sigma_{yy} = \sigma_{zz} = P$ (Fig. 1(b)). Seven hydrostatic pressures ($P$ = 0, 2, 5, 10, 20, 40, 80 GPa) were considered in order to investigate the pressure effect on the deformation behaviors of NC Cu.

**Table 1**
Comparison of parameters from experimental results and Mishin's potential for Cu.

| | Exp. | EAM | | Exp. | EAM |
|---|---|---|---|---|---|
| $a_0$ (Å) | 3.615 | 3.615 | $\gamma_{SF}$ (mJ/m$^2$) | 45 | 44.4 |
| $B$ ($10^{11}$ Pa) | 1.383 | 1.383 | $\gamma_s$ (111) (mJ/m$^2$) | 1790 | 1239 |
| $c_{11}$ ($10^{11}$ Pa) | 1.700 | 1.699 | $\gamma_s$ (110) (mJ/m$^2$) | 1790 | 1475 |
| $c_{12}$ ($10^{11}$ Pa) | 1.225 | 1.226 | $\gamma_s$ (100) (mJ/m$^2$) | 1790 | 1345 |
| $c_{44}$ ($10^{11}$ Pa) | 0.758 | 0.762 | $\gamma_T$ (mJ/m$^2$) | 24 | 22.2 |

The structural analysis was carried out at different times during the deformation. For this purpose, the pair correlation function and the common neighbor analysis (CNA) [32] were employed. The CNA is a tool used in atomistic simulations which allows us to determine the local ordering in a given structure. In CNA, nearest neighbors can be determined if the distance between them is less or equal to the cutoff distance, which is in general defined as the first minimum in the pair distribution function and is also lattice constant dependent (density dependent). The CNA not only considers the number of neighbors at a given distance but also their location with respect to other common neighboring atoms. With CNA one can distinguish atoms in FCC, HCP and BCC regions by calculating the statistics of diagrams formed from the nearest neighbors of each atom and comparing it with those previously known from standard crystals.

## 3. Results and discussions

As indicated earlier, the NC samples were first compressed at desired hydrostatic pressure $P$ and relaxed at that pressure until the volumes reached the equilibrium. Under hydrostatic compression, the materials generally shrink in volume and the density of materials increases with increasing hydrostatic pressure. The relation between the hydrostatic pressure and the volume/density of a solid at a given temperature is generally called equation of state. Fig. 2(a) shows the relationship between the normalized density and the hydrostatic pressure at a given temperature of 1 K for NC Cu with various grain sizes. The densities for NC Cu at various hydrostatic pressures were normalized by the density of single crystal at 0 pressure and 1 K. It is interesting to note that the compressibility with increasing pressures is similar for all grain sizes. The fitting curve for the normalized density as a function of hydrostatic pressure can be obtained by least squares method and expressed as: $\rho_{norm} = 0.99477 + 0.00626P - 2.65361 \times 10^{-5}P^2$. Fig. 2(b) and (c) shows the simulated microstructural configurations for NC Cu with a grain size of 3 nm under zero hydrostatic compression and under hydrostatic compression at 80 GPa, respectively. Fig. 2(d) and (e) shows the simulated microstructural configurations for NC Cu with a grain size of 15 nm under zero hydrostatic compression and under hydrostatic compression at 80 GPa, respectively. GB thickening is observed for NC Cu with all grain sizes under hydrostatic compression and the thickness of GBs increase with increasing hydrostatic pressure. Moreover, no dislocation behaviors are observed under hydrostatic compression for NC Cu with all grain sizes, which is consistent with the classical plastic theory.

After hydrostatic compression, the NC samples were compressed to 15% at strain rate of $5 \times 10^8$/s along the $x$ direction while keeping $\sigma_{yy} = \sigma_{zz} = P$. According to either Von Mises criteria or Tresca criteria, the equivalent stress under this stress state can be calculated by: $\sigma_{equivalent} = \sigma_{xx} - P$. The simulated stress–strain