Grain size effect on the hardness of nanocrystal measured by the nanosize indenter

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The hardness measured by the nanosize indenter under atomic indentation is examined for the cases of nanocrystalline nickel by means of molecular dynamics (MD) simulations. The grain size effect observed is different from the one by uniform deformation or deep indentation. The results show that hardness can only show inverse Hall–Petch (H–P) effect, no H–P effect is observed with the grain size up to 40 nm. Grain boundary (GB) absorption of the localized strain is the main deformation mechanism when the indenter size and the depth both come to nano size. The area of plastic zone generated beneath the tip is strongly dependent on the GB density, sample with small grain size results in larger plastic area, which leads to the softer response of hardness.

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1. Introduction

Nanocrystalline metals (grain size less than 100 nm) have been the subject of 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 and verified to increase with decreasing grain size down to a critical value (10–20 nm) by several classical experiments, 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 motions. However, this relation has been questioned by several investigations which indicate the decrease of hardness below a critical grain size [3–5], both experiments and simulations [6–8] have also shown that the strength/hardness decreases with further grain refinement below the critical value (10–20 nm), suggesting a shift in the dominated deformation mechanisms from dislocation-mediated plasticity to grain-boundary-associated plasticity such as grain-boundary sliding, grain-boundary diffusion and grain rotation.

MD simulations [9,8] have concluded that the strongest grain size for nanocrystal metal, for instance copper, is about 10 nm. However, it is not easy to conclude from the experimental side since the experimental data [5,10] for grain size below 100 nm were largely scattered because of difficulties in preparing high-quality samples, as well as problems of measurement of the average grain size. Koch et al. [10] reviewed the literature which gives the inverse H–P effect at the finest grain sizes, they concluded that only a few experiments [11] which have reported the inverse H–P effect are free from obvious or possible artifacts. The mechanism behind is that the conventional dislocation pile-up theory is not applicable to nanocrystal material with the finest grain size. And the role of grain boundary activities, such as grain boundary sliding and diffusion, has yet been clearly identified from recent TEM technologies, thus it is reasonable to expect different plastic behavior, i.e. the inverse H–P effect, at the finest grain sizes from experiments [12,13].

This transition of deformation mechanisms has been well studied. Schütz et al. [6] studied the yield strength of bulk nanocrystal copper by using molecular dynamic (MD) simulations; their results showed that the strength exhibited a maximum at the grain size of 10–15 nm. The inverse H–P effect in their study was because of a shift in the microscopic deformation mechanism from dislocation-mediated plasticity in the coarse-grained material to grain boundary sliding in the nanocrystalline region. Cao et al. [14] studied size effect on the hardness of nanocrystalline copper by using experiment; their results showed the dislocation mediated mechanism dominated plastic yielding when the grain size was above 16.4 nm. Joen et al. [15] carried out MD simulations to clarify the effect of grain size on the deformation behavior of nanocrystalline body-centered cubic Fe; the major deformation...
mechanism was found to change from dislocation glide in a sample with a 19.7 nm grain size to atomic sliding within GBs in a sample with a finer grain size of 3.7 nm. They concluded that this change in deformation mechanism appears to be the direct cause of the breakdown in the conventional H-P relation. Vo et al. [16] studied the yielding of polycrystalline metal with grain sizes falling below 10–15 nm; they illustrated at small scale grain-boundary relaxation suppressed grain-boundary sliding and forced the material to be deformed by allowing dislocation glide. In all previous studies, either uniform deformation (axial tensile tests) or deep indentation (more than hundred nanometers) were undertaken to investigate the size dependent plastic properties (such as yielding strength and hardness). However, in the modern applications propelled by the discoveries of scanning tunneling and atomic force microscopies, the interface contacts or penetrations are usually emphasized in nanometer levels, and much lower contact forces in the nano-Newton regime are principally addressed by the physics and chemistry communities. Moreover, ultra shallow indentation or scratch techniques are often carried out to examine various nanotribology issues in application of nano-machining process. In this regions, it is well known that continuum solution such as strain gradient theory [17] appears insufficient to explain the indentation size effect (ISE) at depths less than hundred nanometers [18]. Thus, understanding the influence of microstructure on nanohardness during ultra shallow contacts is of vital significance for synthesizing nano devices with controllable new features. What is more, the existence of H-P or inverse H-P effect on hardness at such a small scale contact is not yet well understood, and has not been investigated.

Our previous studies [19,20] show that the GB plays a very critical role in nanoscale material, present work concentrates on further understanding the GB effect (or grain size effect) on nanoscale hardness and the corresponding intrinsic deformation mechanism. The results are quite distinct from the H-P effect found in those of axial deformation of bulk materials [6,21], and the mechanism behind the soft response while refining the grain size under the atomic scale indentation is discussed.

2. Simulation methods

In the present study, MD simulations were used to investigate the indentation process of nanocrystalline nickel with grain size \( d \) varying from 5 nm to 40 nm using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [22] code. The embedded atom method (EAM) potential [23] for Ni is adopted. From previous work [4,24,25], the strongest size of bulk polycrystalline nickel is found at the crossover from inverse H-P regime to classical H-P region, and the value of the transition point is approximate 11 nm. We choose grain size from 5 nm to 40 nm in order to check if this transition point is still valid in shallow nanoindentation cases. The polycrystalline block has the dimension sizes of \( x \sim 160 \, \text{nm}, \, y \sim 800 \, \text{nm}, \) and \( z \sim 1.5 \, \text{nm}, \) respectively. The \( x \) and \( z \) dimensions are periodic, while top side of \( y \) direction is treated as the surface for indentation, and the other side of \( y \) direction has the fixed boundary condition.

All samples contain regular hexagonally shaped columnar grains with identical size. These grains are rotated by an angle of \( \Phi \) with respect to each other about the \([110]\) texture axis which defines the \( z \) direction. For simplicity, the grain orientations chosen for this study are \( \Phi = 0^\circ, 30^\circ, 60^\circ, 90^\circ \) respectively, thus all GBs in the simulation cell are asymmetric high-angle (110) tilt boundaries. Before each indentation case, the sample is first subjected to energy minimization by the conjugate gradient method, and then gradually heated up to the desired temperature in a step-wise fashion. In order to reduce thermal effect, the whole system is kept at a temperature of 10 K via an external Nose–Hoover thermostat during the indentation. Indentation is conducted in displacement control by positioning a cylindrical indenter, simulated by a repulsive potential as Eq. (1), into the surface of the atomistic sample.

\[
F = -A(r - R)^2
\]

where \( A \) is the specified force constant, \( r \) is the distance from the atom to the center axis of the cylinder, and \( R \) is the radius of the indenter. In the atomic force microscope, a sharp tip with a radius typically between 10 and 100 nm is used [26], thus in the present study, three different values of \( R \) are studied, i.e. \( R = 10 \, \text{nm}, 20 \, \text{nm} \) and \( 40 \, \text{nm} \). To keep the computational time into a reasonable value, the indentation is chosen at a constant penetration speed of 50 m/s, which is a typical value in usual nanoindentation and scratch simulations.

A typical configuration of the indentation process is shown in Fig. 1. For each combination of indenter radius \( R \) and crystal size \( d \), we chose 10 sites evenly distributed along \( l \) distance above the 4 grain unit on the surface, and one nanoindentation test is carried out at each site and the results are averaged on ten tests to mimic the sparse distribution of crystal orientations in realistic material system. It should be noted that the indentation depths were lower than 10% of the sample’s length in the \( y \) direction, therefore there was less influence of the fixed bottom boundary on the measured hardness.

Fig. 2. Hardness as a function of indentation depth for various grain sizes with \( R = 10 \, \text{nm} \).
3. Results and discussion

The hardness curves are realized over ten cases with different grain size \(d\) as shown in Fig. 2 in case of \(R = 10\) nm; it is clearly shown that the hardness variations deviate from the elastic responses at the indentation depth approximately 0.5 nm, and at the plastic stage, larger grain size sample shows the higher hardness. The hardness between indentation depths from 4.5 nm to 5.5 nm is averaged to characterize the grain size effect as shown in Fig. 3, and the error bars represent standard deviation obtained from tests by using different size of indenter \((R = 10\) nm, 20 nm, 40 nm). In general, the hardness increases from approximately 13.8 GPa to 20 GPa as the grain size increases from 5 nm to 40 nm. The hardness of single crystal is also obtained by averaging hardness on single crystals with four different orientations, and the result is presented as comparison in Fig. 3; it shows that the single crystal has the highest hardness.

From different experiments in the past decade, it is shown that the hardness of metals usually increases with decreasing indentation depth, and the extra high hardness at shallow depths is interpreted by existence of a large increasing of geometrically necessary dislocation, thus the effect of work hardening is most pronounced [17,27]. However, at the atomic depth less than hundred nanometers, the continuum solution is incapable of explaining the indentation depth effect. Experiment [28] and simulation [29] have shown that the hardness at hundred nanometers depth can reach as high as 2–5 GPa, and further experiment [18] indicated that the hardness at few nanometers depth can be even as much as 20 GPa. Our results also agree with results [30] from indentation test on nano nickel coating, which gave hardness a value of around 20 GPa in a depth of few nanometers.

It can be seen that at the atomic depth indentation, the hardness on the single crystal is higher than all the hardness values measured from nanocrystal samples, which is controversial to classical H-P size effect observed at bulk material. In previous studies, Ma et al. [31] suggested that indentation at inner grain or grain boundary showed a more compliant response and single crystal gave the stiffest hardness. And it was also observed by Swygenhoven et al. [32] through nanoindentation on gold samples that single crystal is harder than nanocrystal, and 5 nm crystal shows the softer behavior than 10 nm crystal. Moreover, hardness curves also revealed a inverse H-P effect with layer thicknesses in the nanoscale range for multilayer metal [33]. Jang et al. [34] studied indentation on the substrate with and without a grain boundary, and lower hardness was observed in the case with a grain boundary, which is attributed to the interaction of dislocations with the grain boundary. The attractive interaction between dislocations and interfaces was observed for incoherent interfaces [35]. All the previous results agree with present study as shown in Fig. 3. However, the strongest size of bulk polycrystalline nickel is found at the crossover from inverse H-P regime to classical H-P region; the value of the transition point is approximately 11 nm [4,24,25]. And also from Shan’s work [36], the “strongest size” for polycrystalline nickel is in the region from 11 nm to 22 nm. The hardness in Fig. 3 does not show a similar trend, no softening is observed with the increasing grain size above the transition size \(d_t\). The conventional H-P effect is derived from dislocation pile-up theory; it is observed at bulk deformation or deep indentation cases since large amount of dislocations are generated and propagated in those procedures. However, in cases of atomic indentation, the mechanism must be different since there are far less dislocations involved in the deformation.

In order to check the detailed local deformation mechanism, a local equivalent strain \(\varepsilon_v\) is calculated by using atomic local strain components:

\[
\varepsilon_v = \sqrt{3\varepsilon_{ij}\varepsilon_{ij}}
\]  

Fig. 4. Equivalent strain \(\varepsilon_v\) distribution for grain size \(d=5\) nm: (a) \(R=10\) nm and (b) \(R=40\) nm.
where $J_2(\varepsilon)$ is the second deviatoric strain invariant. The atomic local strain tensor $\varepsilon$ is computed as a best fit of the local affine transformation, and is obtained by running a least-square fitting procedure using all the local neighbor atom’s information [37].

The detailed distributions of strain $\varepsilon_v$ are plotted in Figs. 4 and 5 for $d = 5$ nm and 40 nm respectively. It can be seen generally that the distribution of strain is more uniform in small grain size case ($d = 5$ nm), and is more localized in large grain size ($d = 40$ nm) case. The detailed observations are as follows:

1. In smaller grain case ($d = 5$ nm) as shown in Fig. 4, more GBs are involved in absorption of the indentation deformation, and large amount of slip planes are activated, which allows the
Fig. 6. Deformation shielding effect of GB by blocking dislocation extension, equivalent strain $\varepsilon_e$ distributions of indentation at the site with same crystal orientation 60° in single crystal (a) and in polycrystal (b), and with same crystal orientation 0° in single crystal (c) and in polycrystal (d).

Emission of partial dislocations from one side of GB to the other side.

(2) In the larger grain case ($d = 40\text{ nm}$) as shown in Fig. 5, most of the slip systems are localized in the present crystal, and few slip systems belonging to adjacent grains are activated. It should be noted that Fig. 5(a), (b), (d) and (e) correspond to indentations on GBs and the rest correspond to indentations on interior grain. In all cases, most of the deformations are localized in few slip planes, only one or two grain boundaries are associated with the absorption of indentation deformation, and serve as dislocation sinks or nucleation sources.

(3) A key result common for both cases is that significant strain in excess of 50% (colored red) was found on GBs, such strain indicates the localized sliding of crystalline interfaces. And the number of the sliding interfaces is bigger in small grain case.

Most of GBs have finite dislocation absorption ability, which could accommodate few pairs of dislocations. After saturated by enough dislocations, GBs either are taken place as shear planes for rigid translation, or considered as barrier for formation of dislocation pileup [38]. In atomic shallow indentation, the finite penetration depth ensures that the number of dislocation (partial or full) generated is much less compared to deep indentation or severe bulk deformation, thus the dislocation pileup can hardly be formed, which could be one of the reasons why Fig. 3 does not show the H-P effect above the transition size $d_c$. In order to understand the higher hardness in single crystal than polycrystal, the strain distributions for both cases are plotted in Fig. 6. From Fig. 6, different deformation behaviors are observed for single crystal and nano polycrystal, the absorption effect of GB can clearly be seen. The dislocations propagate away from the indenter in single crystal cases as shown in Fig. 6(a) and (c), while dislocation extensions are shielded by the grain boundary as shown in Fig. 6(b) and (d). It is interesting to find that the small deformation propagation can be completely blocked by the local GB structure as in Fig. 6(b). However the larger deformation propagation can only be partly absorbed as in Fig. 6(d), and dislocation transmission or local GB shear can be activated near GB. This is also observed by Van Swygenhoven et al. [39] in nanoindentation with cases where the indenter size is smaller than the grain size; they concluded that grain boundaries not only acted as a sink for dislocations, but also reflect or emit dislocations.

The percentage of accumulated strain $\varepsilon_a$ at GBs during indentation as a function of grain size $d$ is plotted in Fig. 7. It is shown that GB contribution to the indentation strain decreases as the grain size increases; this can be also verified by comparison of the strain distribution in Figs. 4 and 5, in which more GBs are involved in the deformation in small grain size case. However, on the other hand, the grain interior slip is still the main deformation pattern; it sustains more than 68% strain in small grain size $d = 5\text{ nm}$, and its value increases to more than 90% in larger grain size $d = 40\text{ nm}$. The more grain interior is involved, the higher hardness will be; this is consistent with hardness plot as shown in Fig. 3.
Our observation indicates that higher GB density underneath the indenter leads to reduction of hardness; it contradicts with observation trend [40,41], in which the yield strength is linearly proportional to GB density. The differences result from the basic assumption of GB properties. In the previous models [40,41], the GB is treated as impenetrable boundary, and the hardening mechanisms behind it are dislocation pileup at GB. In our model, the GB serves mostly as a sink for dislocation absorption, and the softening effect is due to the increased GB absorption capacity of deformation with increasing GB density. It is reasonable to neglect GB absorption capacity in continuum theory [40,41] since much larger amount of dislocations are generated. However, in the atomic scale indentation or scratch, the absorption part should not be neglected, since the total number of dislocation nucleated is not that high.

The plastic area caused by GB absorption or GB sliding is also grain size dependent. Fig. 8 shows the plastic area as a function of grain size; the area is determined by accumulating region where...
$\varepsilon_p > 10\%$, the area of plastic zone decreases with the increasing grain size. Also as shown in Fig. 8, it is reasonable to find out that the larger tip causes larger plastic zone area. In case of $R = 20$ nm, the detailed plastic zones beneath the tip are shown in Fig. 9. It can be clearly seen that the area of plastic zone decreases with increasing of grain size; the region is more uniform in small $d$ as a result of mediated effect of higher density of GBs. It can be concluded that the area of plastic zone beneath tip is size dependent; smaller grain size generates larger plastic area, resulting in softer responses in terms of hardness or yield strength.

4. Conclusions

In summary, atomic depth indentation on nanocrystalline nickel with grain size from 5 nm to 40 nm using indenters with various sizes have revealed that only inverse H-P effect appears. Following can be concluded.

1. The inverse H-P effect could be explained by the strain contributions from GBs and grain interior. The larger grain size results in large portion of strain in grain interior, producing higher hardness under ultra shallow indentation. The H-P relation does not hold even the crystal size is above the conventional transition size. Our observation indicates the GB absorption and GB sliding comes to play an important role in the ultra shallow contact, few generated dislocations can be easily absorbed by GBs.

2. The area of plastic zone generated beneath the tip is size dependent; larger GB density induces larger plastic area from GB mediation, and thus causes softer response.

There are several models describing the inverse H-P effect. Chokshi et al. [42] firstly suggested grain boundary diffusional creep (Coble creep) as the dominant deformation mode. This mechanism was further studied by Masumura et al. [13], who indicated that a critical grain size exists at which value the H-P mechanism switches to the Coble creep mechanism. Sun et al. [43] suggested that the atomic bond order might be another factor affecting the H-P transition; they concluded that the inverse H-P effect originated from the competition between the bond order loss and the associated bond strength gain near facet defects, such as the surface, grain boundary. All these models indicated that the facet defects, which in our case are GBs, were the origin of inverse H-P effect at nanoscale.

It should be noted that for severe deformation such as traditional axial tension, compression or deep indentation, the pileup mechanism begins to play a critical role since dislocation absorption at GBs takes very less contribution in the total plastic deformation, thus it is not strange to see H-P relation takes effect in all the indentation experiment with larger tip and deeper depth.

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