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Structure and mechanical properties of ultra-nanocrystalline diamond and nanocrystalline Cu from atomistic simulations



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ABSTRACT

Several nanocrystalline metals demonstrate the so-called “reverse Hall–Petch effect” and become softer as their average grain size, d , decreases. Using atomistic simulations, we found that ultra-nanocrystalline diamond (UNCD) shows the same behaviour. We also examined a typical metal (Cu) and found that softening at small grain sizes is not limited to hardness or yield stress, but is also evident in the cohesive energy and elastic constants of the material. The effect is attributed to the larger concentration of grain boundary atoms at smaller d . Our model, which separately considers contributions to the cohesive energy, and consequently to elastic constants, from atoms in the grains and from atoms at the grain boundaries, fits simulation results extremely well for both materials. We calculate structural properties, elastic constants and estimate the hardness to find that the two materials have several qualitative similarities, such as linear scaling of the fraction of non-crystalline atoms with respect to $1/d$ and similar scaling laws for cohesive energy and elastic constants. At the same time, several quantitative differences, such as broader peaks in the pair correlation function for UNCD, lead to different magnitude for the scaling coefficients. Our results compare well with experimental observations. Moreover, our theoretical analysis yields universal scaling relations for properties of nanocrystalline materials as a function of the average grain size.

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1. Introduction

Understanding phenomena at the nanoscale is crucial for developing materials with tailored properties. Modern nanotechnology makes it possible to process polycrystalline solids with grains in the nanometre range. These nanocrystalline materials often behave differently from their common polycrystalline counterparts and it is important to predict and control their behaviour. Mechanical properties of polycrystalline metals exhibit a particularly interesting dependence on the average grain size, d (Meyers et al., 2006). The hardness and yield stress of these materials increases with decreasing grain size as d^{-n} , where $n \approx 1/2$, according to the well known empirical Hall–Petch

relation (Hall, 1951). This improvement in mechanical properties is attributed to the impeding of dislocation motion by grain boundaries (Zhao et al., 2003; Bata and Pere-loma, 2004). On the other hand, nanocrystalline metals become softer when the average grain size is reduced to a few nanometres (Choksi et al., 1989; Schiøtz et al., 1998; Conrad and Narayan, 2000; Schiøtz, 2004; Galanis et al., 2010). This “reverse Hall–Petch” effect implies the existence of a “strongest size”, which is around 15 nm for Cu (Yip, 1998; Schiøtz and Jacobsen, 2003; Argon and Yip, 2006).

Reverse Hall–Petch effect, i.e., softening of nanocrystalline metals, has important ramifications in materials design for practical applications. Recent studies of non-metallic granular materials, such as nanocrystalline ceramics (Kebllinski et al., 1998a; Kebllinski et al., 1998b; Kebllinski et al., 1999; Demkowicz et al., 2007; Szlufarska et al., 2005) and ultra-nanocrystalline diamond (UNCD)

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(Remediakis et al., 2008; Remediakis et al., 2009), indicate that this softening may be a general effect and that the mechanism of undertaking mechanical load is different in the nanoscale. Atomistic simulations of tensile-strength tests on nanocrystalline copper (nc-Cu) showed that there is a crossover from dislocation-dominated plasticity to grain boundary sliding (Schjøtz et al., 1998; van Swygenhoven et al., 1999; Yamakov et al., 2004; Shimokawa et al., 2005; Koblinski et al., 1998a). As grain size is reduced, deformation mechanisms change from dislocation nucleation and mobility to sliding on grain boundaries, i.e., from a process involving bulk defects to an interface related one. Then, a reasonable assumption is that mechanical properties of nanocrystalline materials with grain size smaller than a certain, material dependent, critical value should generally depend on inter-granular effects rather than intra-granular processes. Furthermore, elastic moduli should be reliable probes of plastic properties for nanocrystalline solids, which do not contain extended defects such as cracks or dislocations that have characteristic lengths exceeding the size of the grains.

In this paper, we employ atomistic simulations coupled to an empirical model in order to compare a prototypical covalent solid (diamond) and a metal (Cu) in their pure nanocrystalline forms, UNCD and nc-Cu. We present simulation results for both materials on the same footing, employing the same theoretical model for analyzing the dependence of cohesive energy and mechanical properties on the average grain size, and highlighting the similarities and differences between them. Although the two materials have very different chemical bonding and structure at the atomic level, their physical properties are found to follow the same scaling laws with grain size. We explain this behaviour by the increased fraction of grain boundary atoms at smaller d . More specifically, we develop a model for the cohesive energy and the related elastic constants where the contributions of crystalline atoms inside the grains and of non-crystalline atoms in the grain boundaries, which form weaker bonds, are considered separately. For both UNCD and nc-Cu, we find that nanocrystalline solids are weaker than the ideal single-crystal in many aspects, including cohesive energy and elastic constants, and that the agreement between our theoretical predictions and simulation results is excellent. Therefore, softening at small grain sizes appears to be universal and not limited to hardness or yield strength of metals as described in the context of the reverse Hall–Petch effect.

2. Simulation method

UNCD, and its mechanical properties, has been simulated extensively by employing either clusters (Paci et al., 2005) or infinite rods (Shen and Chen, 2006; Angadi et al., 2006). Following the methodology of Schjøtz et al. (1998) for nc-Cu, we generated fully three-dimensional, computer-generated atomistic models of UNCD and nc-Cu, having grains of different sizes separated by random grain boundaries. Samples are created using the Voronoi construction method. Following experimen-

tal observations of Chawla and Chandra (2009), we study samples with grains of comparable sizes. For each value of the average grain size, we consider several different structures and use the average values for the cohesive energy and mechanical properties. The choice of the empirical potential is important; for example, different potentials give different responses in Si under large pressures (Godet et al., 2004). For UNCD, we use the potential of Tersoff (1988). For nc-Cu, we use the Effective-Medium Theory (EMT) potential of Jacobsen et al. (1987, 1996) as implemented in the open-source ASAP code. Samples are annealed and equilibrated at near zero temperature, using NPT dynamics. The supercells contain up to 250000 atoms. For more details on the simulation method, see Remediakis et al. (2008) and Galanis et al. (2010). The choice of different simulation methods, namely Monte Carlo for C and Molecular Dynamics for Cu, originates from the different chemistry of these materials. The method of choice for these simulations would have been Molecular Dynamics, as it is faster and can run more efficiently in a parallel computer. For C, however, where a multitude of local minima exists due to the ability of C atoms to form two, three or four bonds with very close energies, a global minimum method such as simulated-annealing is preferable. For this reason, we used fine-tuned Monte Carlo. For Cu, on the other hand, there was no need to use the time-consuming Monte Carlo method. We have verified that the two methods give the same results for many model systems.

3. Structural properties

Fig. 1 represents two fully relaxed structures used in the simulations. Atoms that are away from grain boundaries are very close to their ideal crystal structure, which is the diamond lattice for C and the face-centred cubic (fcc) lattice for Cu. Atoms between grains are in some disordered amorphous phase. Fig. 2 shows data on the pair distribution function (PDF) of the two materials. The first peak in the PDF corresponds to the bulk nearest-neighbour distance which is 1.54 Å for C and 2.55 Å for Cu. All characteristic peaks corresponding to the bulk crystalline phase are observed. Due to the presence of atoms in non-crystalline phases, the peaks have finite widths; moreover, peaks corresponding to higher-order neighbours disappear at small grain sizes, where the percentage of atoms in crystalline phases drops and the random grain orientation is evident.

A fundamental difference between UNCD and nc-Cu can be seen when comparing the two panels of Fig. 2. UNCD exhibits higher disorder compared to nc-Cu. This is a result of the strong directional bonds of C, compared to the metallic bonding in Cu. C atoms that are not in the ideal tetrahedral coordination of diamond might occur in a variety of structures due to the ability of C atoms to change their hybridization. On the contrary, Cu atoms, even if they are not in their ideal close-packed geometry, maintain very similar distances from their neighbours. Thus the PDF for nc-Cu is closer to that of bulk Cu.

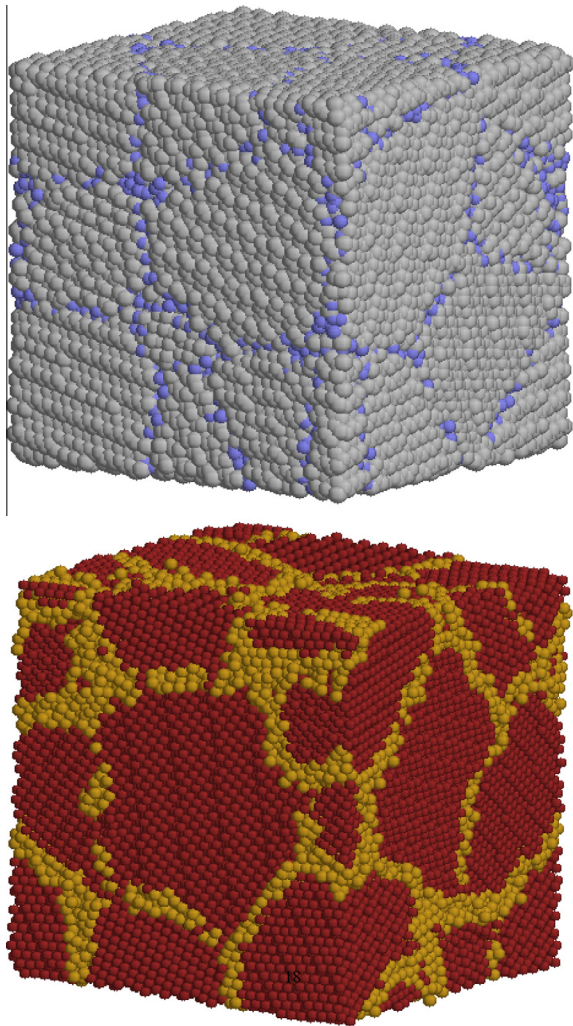


Fig. 1. Two typical fully relaxed simulation cells for ultra-nanocrystalline diamond (UNCD) and nanocrystalline Cu (nc-Cu). C atoms in the diamond lattice are coloured grey; other C atoms are coloured blue. Cu atoms in the fcc lattice are coloured red; other atoms are coloured yellow. Both samples contain 8 grains each, with average grain size $d = 3.9$ nm for UNCD and $d = 4.9$ nm for nc-Cu. UNCD sample contains 81561 atoms; nc-Cu sample contains 78085 atoms. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

4. Reverse Hall–Petch effect in ultra-nanocrystalline diamond

Ultra-nanocrystalline diamond (UNCD) is a polycrystalline carbon-based material, having grains a few nanometres big (Gruen, 1999). It is a low-cost material with a potential for a wide range of applications due to its unique mechanical and electronic properties (Krauss et al., 2001; Espinosa et al., 2006); in addition, its properties can be tailored by modifying the dopant concentration or the preparation conditions (Philip et al., 2003; Shen et al., 2006; Rovere et al., 2006). UNCD samples are found to have very high elastic moduli, only slightly lower than those of diamond, placing thus UNCD into the family of super-hard materials (Kaner et al., 2005). Despite the strong

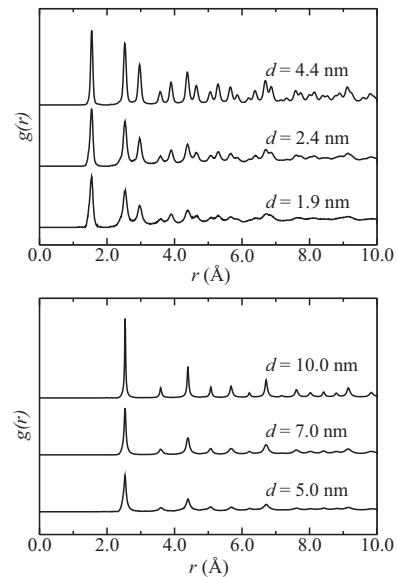


Fig. 2. Pair distribution function (PDF) for ultra-nanocrystalline diamond (UNCD, top) and nanocrystalline Cu (nc-Cu, bottom). Three characteristic samples with different grain sizes are shown for each case.

directional C–C bonds resulting in inhomogeneity at the atomic scale, the grain boundary energies have a weak dependence on the orientation (Zapol et al., 2001), as do the energies of the interfaces between amorphous C and diamond (Kopidakis et al., 2007).

There is no unique way to predict material hardness from atomistic simulations. For metals, hardness is usually determined by large-scale defects, such as cracks or dislocations. Such defects have characteristic lengths well above the nm scale (Bobrovnichii et al., 2007). On the other hand, for covalent or ionic solids, where dislocation motion is hindered by huge activation energies, hardness is primarily determined by bond breaking at the atomistic level (Fyta et al., 2006). For this reason, the hardness of many materials, and in particular C-based nanocomposites, is proportional to the Young's or shear modulus (Brazhkin et al., 2002; Robertson, 2002).

To get a quantitative description of hardness, we use the theory of Gao et al. (2003), who correlate the Vickers hardness of covalent crystals with the electron density per bond and the energy gap of the material. The hardness of a complex material is the geometrical mean of the values of hardness for each subsystem. Here, we consider each individual pair of neighbouring C atoms as a subsystem. The density of valence electrons in a particular bond can be obtained from the bond length and the coordination numbers of the two atoms that participate in this bond. The calculated hardness of UNCD is shown in Fig. 3, demonstrating the existence of the “reverse Hall–Petch” effect for this material.

5. Properties of nanocrystalline materials as a function of grain size

In this Section, we present a model for the cohesive energy and other properties of nanocrystalline materials as a

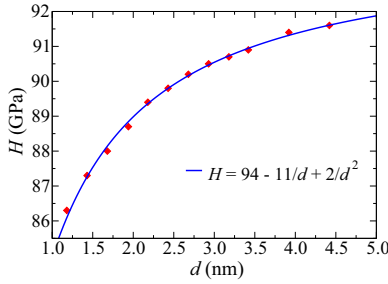


Fig. 3. Estimated hardness of UNCD as a function of the average grain size.

function of grain size. We begin by defining all the parameters of the model, with emphasis on the relationships between them and other properties of the material.

5.1. Parameters

The main parameters that enter the model are:

Average grain size, d . $d = V^{1/3}$, where V is the average grain volume, defined as total volume over total number of grains.

Atom size, r . $r = V_{at}^{1/3}$, where V_{at} is the volume per atom in the ideal crystal structure. For Cu, $r = 0.361 \text{ nm}/4^{1/3} = 0.227 \text{ nm}$; for C, $r = 0.357 \text{ nm}/8^{1/3} = 0.179 \text{ nm}$.

Number of atoms per grain, N . $N = V/V_{at} = d^3/r^3$. Fitting our results for N to a cubic power of d yields $r = 0.227 \text{ nm}$ for Cu, in excellent agreement with experiment.

Grain shape constants, S and L . Dimensional analysis dictates that no matter what is the shape of the grain, the total length of its edges, D has to be proportional to the grain size, d . Similarly, the total area, A , will be proportional to the grain size squared, d^2 . Denoting the proportionality constants by S and L , we have that $A = Sd^2$ and $D = Ld$. For tetrahedral grains, $L = 12.2$ and $S = 7.21$; for icosahedral, $L = 23.1$ and $S = 5.14$. Other platonic solids (cube, octahedron, dodecahedron) have values in between these two. A Voronoi partition of the space, as the one used to generate our samples, would yield grains with average values $L = 17.5$ and $S = 5.82$ (Kumar et al., 1992). We use these values in the following.

Average number of atoms per grain on edges and surfaces of grains, N_e and N_s . The number of edge atoms, N_e , will be given by the ratio of the total length of the grain edges over the atom size. Therefore $N_e = D/r$, or

$$N_e = L \frac{d}{r}. \quad (1)$$

The volume of the grain boundary region equals the grain boundary area ($A = Sd^2$) times the grain boundary thickness, $N_{gb}r$ (see below). To obtain the number of grain boundary atoms, we divide this volume by the atomic volume, r^3 . As this grain boundary volume is shared between two surfaces, we divide the result by two. Also, edge atoms need to be subtracted from this formula. Therefore

$$N_s = \frac{N_{gb}S}{2} \frac{d^2}{r^2} - N_e. \quad (2)$$

Thickness of grain boundaries, N_{gb} . It is the average thickness of the grain boundary region in units of the atom size, r . From Eqs. (1) and (2), we find that the fraction of atoms that are not in the bulk of grains are

$$\frac{N_e + N_s}{N} = \frac{N_{gb}S}{2} \frac{r}{d}. \quad (3)$$

These will be the atoms that are in non-ideal crystalline environment. We identify these atoms by performing common-neighbour analysis for Cu and by calculating the average bond angle and coordination number for C. We plot the fraction of non-crystalline atoms as a function of the inverse grain size r/d in Fig. 4. The slope gives us $N_{gb} = 2.1$ for Cu and $N_{gb} = 1.8$ for C.

Average number of atoms per grain in the bulk of grains, N_b . It is the total number of atoms minus the numbers of edge and surface atoms:

$$N_b = N - N_s - N_e = \frac{d^3}{r^3} - \frac{N_{gb}S}{2} \frac{d^2}{r^2}. \quad (4)$$

5.2. Grain-size-dependent cohesive energy

We can now find the scaling of the cohesive energy with the grain size. The following discussion applies also to several other properties of the material as well. The cohesive energy of the solid, E_c , can be expressed as

$$E_c = \frac{N_b E_b + N_s E_s + N_e E_e}{N}, \quad (5)$$

where E_b , E_s , and E_e , are the average energies of bulk-, surface-, and edge atoms, respectively. Substituting Eqs. (1)–(4), we derive a simple quadratic form of r/d :

$$\frac{E_c}{E_b} = 1 + \frac{\alpha r}{d} + \frac{\beta r^2}{d^2}, \quad (6)$$

where α and β are material-dependent constants:

$$\alpha = \frac{N_{gb}}{2} \frac{E_s - E_b}{E_b} S \quad \text{and} \quad \beta = \frac{N_{gb}}{2} \frac{E_e - E_s}{E_b} L. \quad (7)$$

From its definition, Eq. (7), α should be negative while β could be positive or negative depending on the particular material. In the top panel of Fig. 5 we present data from the simulations together with their fit according to Eq. (6). The proposed scaling formula provides an excellent fit to the data. The fitting functions are $y = 0.988 - 0.164/x - 1.687/x^2$ for C and $y = 1.000 - 0.256/x + 0.992/x^2$ for

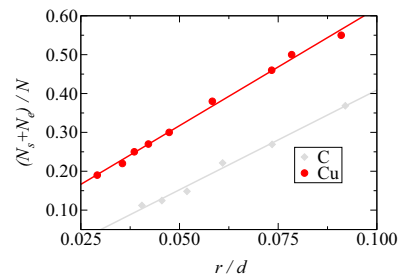


Fig. 4. Fraction of atoms that are not in ideal crystalline environment as a function of inverse scaled grain size, r/d .

Cu, where $y = E_c/E_b$ and $x = d/r$. The first term of the fit is found in both cases to be very close to 1, as it should. Moreover, using the values of N_{gb} calculated above, we find that $\frac{E_s - E_b}{E_b}$ equals -0.03 for C and -0.04 for Cu. Taking into account that $E_c = 7.33$ eV for C and $E_c = 3.51$ eV for Cu, we find that E_s equals 7.10 eV for C and 3.36 eV for Cu.

These numbers are very close to the cohesive energies of amorphous C and amorphous Cu, respectively. For Cu, we find that the energy difference between bulk and grain boundary atoms to be 0.13 eV per atom. Brown and Adams (1995), using an Embedded-Atom-Method (EAM) potential, have found the difference in enthalpy between amorphous and crystalline Cu to be about 0.1 eV (Fig. 5 of Brown and Adams, 1995). Our EMT simulations for amorphous Cu confirm that result, too. For amorphous C, calculations using the same methodology yield cohesive energies around 7 eV for tetrahedral amorphous C (Kelires, 1992), in agreement to our findings.

5.3. Grain-size-dependent bulk modulus

The bulk modulus is expected to have a grain-size dependence similar to the cohesive energy, since it is proportional to the second derivative of the binding energy with respect to volume. Experiments have already measured grain-size dependent elastic moduli for various materials (Palosz et al., 2006; Chen et al., 2009). The grain-size dependence of elastic moduli has been analyzed with the rule of mixture for composite materials (Shen et al., 1995; Latapie et al., 2003; Zhao et al., 2006). For our analysis to be valid, there should exist an extensive thermodynamic property related to the bulk modulus. Such a property was introduced by Kelires (2000) and is called local bulk modulus. The local bulk moduli are local

quantities that can be added to give the total bulk modulus of the system.

We thus fit our simulation data to a function similar to Eq. (6):

$$\frac{B}{B_b} = 1 + \frac{\gamma r}{d} + \frac{\delta r^2}{d^2}. \tag{8}$$

As shown in the lower panel of Fig. 5, the proposed scaling formula provides an excellent fit to the data. The fitting functions are $y = 1.054 - 5.390/x + 14.45/x^2$ for C and $y = 0.985 - 0.847/x + 3.5483/x^2$ for Cu, where $y = B/B_b$ and $x = d/r$. The first term of the fit is found in both cases to be very close to 1, and the second is negative, as they should be.

In analogy to Eq. (7), we take that $\gamma = \frac{N_{gb}}{2} (B_s - B_b)S/B_b$, where B_s is the bulk modulus of hypothetical structures consisting of atoms that are in the same state as the grain boundary atoms of the material. We find that $\frac{B_s - B_b}{B_b}$ equals -0.14 for Cu. Taking into account that $B = 135$ GPa for Cu, we find that $B_s = 116$ GPa for Cu. This number should be compared to the bulk modulus of amorphous Cu. Our simulations for amorphous Cu yield bulk modulus of the order of 120 GPa, in good agreement with the result of the fit.

5.4. Grain-size-dependent hardness

Hardness is related to the electron density according to Gao et al. (2003); the local electron density is proportional to the local mass density. Therefore, hardness could also be decomposed into contributions from different kinds of atoms. Unfortunately this method is not appropriate for metals, where perhaps only direct simulations of indentation (Szulfarska et al., 2005) can yield realistic values for hardness. As shown in Fig. 3, hardness of UNCD can be fitted to a quadratic form of $1/d$. Moreover, the constant term, showing the limit of hardness as d goes to infinity, coincides with the hardness of diamond calculated using the same method.

6. Conclusions

Computer simulations can provide accurate quantitative description for complex materials, such as nanocrystalline solids. By coupling our atomistic simulations to a model for the grain-size dependence of properties, we are able to predict the behaviour of the material at conditions inaccessible to both simulation and experiment, such as hardness measurements for nanocrystalline diamond at large grain sizes. We find that a nanocrystalline material is always weaker than a single-crystalline one. This softness is not only present in the yield stress or hardness, but also in the cohesive energy and elastic constants. We attribute this decrease to the increase of the fraction of grain boundary atoms as grain size decreases. We derive simple scaling laws for material properties, such as the bulk modulus, as a function of the grain size by decomposing the energy into contributions from crystalline atoms in the bulk of grains and from atoms at the grain boundaries. Despite their obvious differences, nanocrystalline diamond and copper exhibit same qualitative features regarding scaling with respect

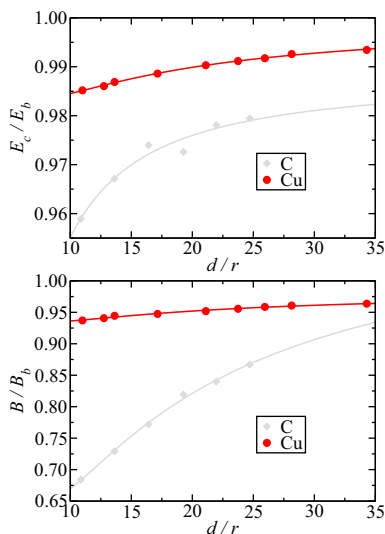


Fig. 5. Cohesive energy (upper panel) and bulk modulus (lower panel) of UNCD and nc-Cu as a function of the average grain size. Circles denote results from the simulations; solid line is a fit to the data according to Eqs. (6) and (8).

to the average grain size, d : for both materials, the fraction of non-crystalline atoms is a linear function of $1/d$, whereas the cohesive energy, density, and bulk modulus are quadratic functions of $1/d$. The unique chemistry of C, allowing it to form two, three or four bonds, as well as the unique strength of these bonds results in broader peaks in $g(r)$, and different scaling coefficients compared to those found for Cu. Our theoretical predictions fit very well our results from atomistic simulations of different nanocrystalline materials, suggesting that softening at very small grain might be a universal nanoscale effect.

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