Reverse Hall-Petch effect in ultra nanocrystalline diamond

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We present atomistic simulations for the mechanical response of ultra nanocrystalline diamond, a polycrystalline form of diamond with grain diameters of the order of a few nm. We consider fully three-dimensional model structures, having several grains of random sizes and orientations, and employ state-of-the-art Monte Carlo simulations. We calculate structural properties, elastic constants and the hardness of the material; our results compare well with experimental observations for this material. Moreover, we verify that this material becomes softer at small grain sizes, in analogy to the observed reversal of the Hall-Petch effect in various nanocrystalline metals. The effect is attributed to the large concentration of grain boundary atoms at smaller grain sizes. Our analysis yields scaling relations for the elastic constants as a function of the average grain size.

Keywords: nanocrystalline materials; carbon; hardness

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I. INTRODUCTION

Most solids are polycrystalline, having grains in the micrometer to millimeter range. As the percentage of atoms residing on grain boundaries is negligible, the polycrystallinity only marginally affects the properties of the material. In particular, mechanical properties of such solids usually depend on bulk properties of the ideal material and the concentration of various defects, such as cracks, dislocations, vacancies and interstitials; usually the grain size is of minor importance. There are, however, properties where grain size plays a key role, hardness being one of them. The Hall-Petch law states that the hardness \( H \) of polycrystalline metals increases with decreasing average grain size \( d \), being a linear function of \( d^{-n} \), where \( n > 0 \). The effect is attributed to the impedance of dislocation motion due to grain boundaries (Bata and Pereloma 2004).

Modern nanotechnology makes it possible to synthesize nanocrystalline solids, i.e. polycrystalline solids with average grain sizes of a few nm. Such materials offer new possibilities for technological applications, mainly due to their unique mechanical properties (Meyers et al. 2006). The Hall-Petch law dictates that a nanocrystalline solid should have huge hardness, usually much higher than its usual polycrystalline phase. While this is true in most cases, Cu was found to become softer with decreasing grain size in the range between 3 and 7 nm (Schiøtz et al. 1998). This was called the “reverse Hall-Petch effect”. Later, it was found that many materials possess a “strongest size” (Yip 1998), which turned out to be around 15 nm for Cu (Schiøtz and Jacobsen 2003). A similar effect has been observed recently for BN (Dubrovinskaia 2007).

The existence of a “strongest size” suggests that the mechanism of undertaking mechanical load should be different in the nano-world. In this region, the presence of dislocations no longer governs the mechanical response on the material: as dislocations are extended defects, they cannot reside in the limited space of nano-grains. Any external mechanical load will be primarily undertaken by sliding along grain boundaries (Schiøtz et al. 1998, van Swygenhoven et al. 1999, Yamakov et al. 2004). This, in turn, is a direct consequence of the enormous concentration of grain boundary atoms in a nanocrystalline material. Imagine for example a cube of side \( d \), containing \( N \times N \times N \) atoms. The fraction of surface atoms is roughly proportional to \( 6N^2/N^3 = 6/N \approx 1 \text{ nm}/d \), ranging from 1 per million when \( d \) is of the order of mm, to 30% when \( d \) is around 3 nm.

Contrary to a large number of studies for metals, very few studies have addressed the mechanical properties of semiconductors and insulators as a function of their grain size, although several pioneer workers have examined the mechanical response of nanocrystalline ceramics (Demkowicz et al. 2007; Szlufarska et al. 2005). Covalent solids are characterized by their open structures and the strong directionality of their bonds. Such bonds should not allow easy sliding along grain boundaries. At the same time, bonds on grain boundaries will be con-

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siderably weaker than those in the bulk of grains, due to the loss of the ideal local bonding geometry (Keblinski et al. 1999). Recent studies in BN (Dubrovinskaia et al. 2007), together with the well-established results for various metals, suggest that the effect might be universal. To check whether this is the case, we study diamond, which comprises the ideal test suite for this purpose. C atoms form perhaps the most directional bonds known, as indicated by the supreme hardness and shear modulus of diamond. In addition to being strong, C-C might in some cases break and form a more stable structure, as threefold \( sp^2 \) C atoms are more stable than fourfold \( sp^3 \) ones, the latter being responsible for mechanical failure in carbon-based materials (Fyta et al. 2006; Remediakis et al. 2007).

Ultra nanocrystalline diamond (UNCD) is a polycrystalline carbon-based material, with grain diameters mostly between 2 and 5 nm (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). Despite the strong directional C-C bonds, resulting in inhomogeneity at the atomic scale, the material can be considered as isotropic at larger scales, as no particular orientation for the grain boundaries in UNCD seems to be favoured in the experiment (Gruen 1999) or simulations (Zapol et al. 2001, Kopidakis et al. 2007).

II. COMPUTATIONAL METHOD

We use fully three-dimensional atomistic models for UNCD, having grains of different random size and orientations separated by random grain boundaries. The simulations were performed using a continuous-space Monte Carlo method. We employ the many-body potential of Tersoff (Tersoff 1988), which provides a very good description of the structure and energetics for a wide range of carbon-based materials (Kelires 1994; Kelires 2000). This method, although considerably demanding computationally, allows for great statistical accuracy, as it is possible to have samples at full thermodynamic equilibrium. Such accuracy is necessary in order to capture all hybridizations of C.

We model UNCD by a periodic repetition of cubic supercells that consist of eight different regions (grains). The number of grains in the unit cell guarantees the absence of artificial interactions between a grain and its periodic images. The grains have random shapes and sizes, and are filled with atoms in a randomly oriented diamond structure. The method we use is identical to the method used by Schiøtz et al. (Schiøtz et al. 1998; Schiøtz and Jacobsen 2003). To achieve a fully equilibrated structure for each grain size, we perform four steps: first, the structure is compressed and equilibrated at constant volume at 300 K, in order to eliminate large void regions near some grain boundaries, that are an artifact of the randomly generated structure. In the second step, we anneal the system at 800 K allowing volume relaxation and quench down to 300 K. Third, we anneal once more, at 1200 K this time, in order to ensure full equilibration. Fourth, we fully relax the structure at 300 K allowing for changes in both volume and shape of the unit cell.

| \( d \) | \( N \) | \( N_3 \) | \( \rho \) | \( E_c \) | \( B \) | \( E \) | \( G \) | \( H \) |
|------|------|------|------|------|------|------|------|------|
| 2.4  | 18,528 | 26   | 3.22 | -7.06 | 323  | 808  | 373  | 89.8 |
| 3.4  | 53,494 | 12   | 3.30 | -7.10 | 363  | 939  | 439  | 90.9 |
| 4.4  | 116,941| 9    | 3.40 | -7.15 | 384  | 987  | 461  | 91.6 |
| \( \infty \) | \( \infty \) | 0    | 3.51 | -7.33 | 443  | 1066 | 485  | 94.2 |

FIG. 1 Relaxed model structure for Ultra-Nanocrystalline Diamond, with an average grain size of 4.4 nm. Atoms are coloured according to their number of neighbours (\( z \)) and average angle between their bonds (\( \theta \)). Atoms in the diamond structure (\( z=4, \cos \theta=-1/3 \)) are coloured gray; all other atoms are coloured blue.
III. STRUCTURE AND ELASTIC MODULI

The relaxed structure for a typical sample is shown in Fig. 1. The grain boundaries are a few atomic diameters across, in accordance with experiments showing widths of 0.2-0.5 nm (Gruen 1999). Atoms at grain boundaries are either three-fold coordinated or form bonds at different lengths or angles from those observed in diamond. The structural and elastic properties for characteristic samples are summarized in Table I. The fraction of the three-fold atoms in the samples is about 1/10 for grain sizes between 3.5 and 4.5 nm; in experiment, it was observed that the fraction of atoms residing at grain boundaries is close to 10% for similar crystallite sizes (Gruen 1999). The density of UNCD increases with increasing grain size, as both the percentage of \( sp^2 \) atoms and the concentration of voids is decreased. The cohesive energy decreases with increasing grain size, suggesting that most grain boundary atoms should be considered as defective ones.

The bulk modulus of UNCD decreases with decreasing grain size, despite the increase in the fraction of energetically favorable \( sp^2 \) atoms. Although they have lower energy, \( sp^2 \) C atoms are actually easier to deform compared to \( sp^3 \) ones. This can be demonstrated by employing the concept of local bulk moduli (Kelires 2000). A similar analysis of our samples yields the average local bulk modulus of \( sp^2 \) atoms to be around 250 GPa, while the average bulk modulus of \( sp^3 \) atoms is around 420 GPa. This agrees very well with experimental observations for UNCD where the grain boundaries have been found to have much lower local bulk moduli than the bulk of grains (Pantea et al. 2006).

IV. HARDNESS

Decrease of all elastic moduli with decreasing average grain size suggests that the hardness of the material should also drop with decreasing grain size, as the hardness of many materials is proportional to the Young’s or shear modulus (Brazhkin et al. 2002); in particular, the hardness of all known carbon-based materials has been found to be between 10% and 16% of the Young’s modulus (Robertson 2002). Elastic moduli are reliable probes of hardness for nanocrystalline solids, as the later cannot contain extended defects, such as cracks or dislocations, that have characteristic lengths exceeding the size of the grains.

To get a quantitative description of hardness, we use the theory of Gao et al., who correlate the Vickers hardness of covalent crystals with the electron density per bond and the energy gap of the material (Gao et al. 2003). 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.

V. SCALING LAWS FOR THE PROPERTIES OF UNCD

To understand the mechanism behind softening of UNCD, as well as other materials, at low grain sizes, we consider the different types of atoms and local bonding geometries that exist in a nanocrystalline material. The main dramatic change that takes place in a poly-
crystalline material as its grain size enters the nm regime is the increase in the fraction of atoms residing near grain boundaries. Atoms at grain faces, edges or vertexes, as well as atoms near other discontinuities, will naturally form bonds that are weaker than those formed by atoms in the bulk. Such weaker bonds will then bend or stretch with greater ease, compared to the bonds in the crystalline region. This explains the softening of polycrystalline solids when the grain size is at the nanometer range. For much larger grain sizes, the number of grain-boundary atoms will be negligible compared to the number of bulk atoms; in this regime, the behavior of the material under mechanical load will be mostly determined by bulk defects, such as dislocations.

To make this picture quantitative, let us divide the atoms in the polycrystalline material into three categories:

1. Atoms deep inside the grains, forming bonds that are similar to those in the single-crystal material. The number of such atoms is proportional to $d^3$, where $d$ is the average grain size.

2. Atoms near the grain boundary; these behave similarly to surface or interface atoms. The number of such atoms is proportional to $d^2$.

3. Atoms near grain boundary edges; these are similar to kink surface atoms, or atoms near dislocation cores. The number of such atoms is proportional to $d$.

Of course, there will be other types of atoms, such as vertex atoms or atoms near topologic defects, but their number will be much smaller than the numbers of atoms falling in one of the aforementioned categories. The cohesive energy of the solid will be the sum of the energies of the three different atom types, multiplied by their respective numbers, and divided by the total number of atoms, which is proportional to $d^3$. Therefore, the cohesive energy should be described by a function of the form

$$E_c = E_0 + a/d + b/d^2,$$

where $a$ and $b$ are constants, and $E_0$ is the cohesive energy of the single crystal.

Indeed, such a function fits our data perfectly, the rms error being less than 0.5%. Moreover, $E_0$ is found to be -7.31 eV, very close to the calculated cohesive free energy of diamond at 300 K, which is -7.33 eV. As B is proportional to the second derivative of the total energy with respect to the system volume, it can also be decomposed into contributions from bulk, interface and vertex atoms. As shown in Fig. 2, a quadratic function of $1/d$ fits the results of the simulation very nicely. The constant value, 467 GPa, corresponding to the ideal monocristalline solid, is only 5% off the calculated value for diamond (see Table I). Such a decomposition of the total bulk modulus to a sum of atomic-level moduli has been used previously, in order to investigate the rigidity of amorphous carbon (Kelires 2000).

A similar scaling law should also hold for the mass density of UNCD as a function of grain size, assuming that the volume per atom is different for atoms in grain boundaries and atoms in the bulk of grains. Fitting our data to a quadratic form of $1/d$ gives $\rho = 3.6 - 1.2/d + 0.4/d^2$. Again, the agreement of the constant value with the calculation for ideal diamond (Table I) is very good (3%).

Hardness is related to the electron density according to Gao et al.; the local electron density is proportional to the local mass density, as all C atoms have the same number of electrons. Therefore, hardness should also be decomposed into contributions from different kinds of atoms. As shown in Fig. 3, the 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 at 300 K, calculated using the same method (see Table I).

The Young’s and shear modulus of UNCD will not necessarily follow the same scaling law. As both moduli are related to bond bending, the nature of the inter-atomic bonds is perhaps equally important to their number. We tried to fit our simulation data to a quadratic form of $1/d$. Although the fit does not look disappointing, the rms error in the fits were significantly higher than those for the fits of $E_c$, $B$, $\rho$ or $H$; moreover, the constant values deviate from the properties of diamond by more than 20%. However, even such a poor agreement between model and simulation provides extra evidence that our model has some solid basis.

VI. CONCLUSIONS

Using ultra-nanocrystalline diamond (UNCD) as a prototype for a polycrystalline covalent solid with grains at the nanometer region, we have observed softening of the material as the grain size decreases, in analogy with the reverse Hall-Petch effect observed in nanocrystalline metals. The effect is attributed to the increasing fraction of grain-boundary atoms as the grain size decreasing. A simple quadratic form in $1/d$, where $d$ is the average grain size, suffices to provide excellent fit of our results for cohesive energy, mass density, bulk modulus and estimated hardness, while it yields the correct values for bulk diamond. The measured Young’s modulus of UNCD is reproduced well by the simulations. Our results provide further evidence that softening at low grain sizes might be a universal property for nanocrystalline solids.

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References

[1] Bata V, Pereloma EV (2004) An alternative physical explanation of the Hall-Petch relation. Acta Mater 52:657-665
[2] Brazhkin VV, Lyapin AG, Hemley RJ (2002) Harder than diamond: dreams and reality. Philos Mag A 82:231-253
[3] Demkowicz MJ, Argonz AS, Farkas D, Frary M (2007) Simulation of plasticity in nanocrystalline silicon. Philos Mag 87:4253-4271
[4] Dubrovinskaia N, Solozhenko VL, Miyajima N, Dmitriev V, Palosz B, Wang Y, Zerda TW, Liu H, Ding Y, Stephens PW, Botez CE (2006) Nano-Diamond compressibility at pressures up to 85 GPa, 2006 NSTI Nanotechnology Conference and Trade Show, pp 823-826.
[5] Fyta MG, Remediakis IN, Kelires PC, Papaconstantopoulos DA (2006) Insights into the fracture mechanisms and strength of amorphous and nanocomposite carbon. Appl Phys Lett 90:101912
[6] Gruen DM (1999) Nanocrystalline diamond films. Annu Rev Mater Sci 29:211-259
[7] Kaner RB, Gilman JJ, Tolbert SH (2005) Materials science - Designing superhard materials. Science 308:1268-1269
[8] Keblinski P, Phillpot SR, Wolf D, Gleiter H (1999) On the nature of grain boundaries in nanocrystalline diamond. Nanostruct Mater 12:339-344
[9] Kelires PC (1994) Elastic Properties Of Amorphous-Carbon Networks. Phys Rev Lett 73:2460-2463
[10] Kelires PC (2000) Intrinsic stress and local rigidity in tetrahedral amorphous carbon. Phys Rev B 62:15686-15694
[11] Kopidakis G, Remediakis IN, Fyta MG, Kelires PC (2007) Atomic and electronic structure of crystalline-amorphous carbon interfaces. Diam Relat Mater 16:1875-1881
[12] Krauss AR, Auciello O, Gruen DM, Jayatissa A, Sumant A, Tucek J, Mancini DC, Moldovan N, Erdemir A, Ersay D, Gardos MN, Busmann HG, Meyer EM, Ding MQ (2001) Ultrananocrystalline diamond thin films for MEMS and moving mechanical assembly devices. Diam Relat Mater 10:1952-1961
[13] Meyers MA, Mishra A, Benson DJ (2006) Mechanical properties of nanocrystalline materials. Progr Mater Sci 51:427-556
[14] Pantea C, Zhang J, Qian J, Zhao Y, Migliori A, Grzanka E, Palosz B, Wang Y, Zerda TW, Liu H, Ding Y, Stephens PW, Botez CE (2006) Nano-Diamond compressibility at pressures up to 85 GPa, 2006 NSTI Nanotechnology Conference and Trade Show, pp 823-826.
[15] Remediakis IN, Fyta MG, Mathioudakis C, Kopidakis G, Kelires PC (2007) Structure, elastic properties and strength of amorphous and nanocomposite carbon. Diam Relat Mater 16:1835-1840.
[16] Robertson J (2002) Diamond-like amorphous carbon. Mat Sci Eng R 37:129-281
[17] Schiotz J, Dittolla FD, Jacobsen KW (1998) Softening of nanocrystalline metals at very small grain sizes. Nature 391:561-563.
[18] Schiotz J, Jacobsen KW (2003) A maximum in the strength of nanocrystalline copper. Science 301:1357-1359
[19] Schiotz J, Jacobsen KW (1999) Competing plastic deformation mechanisms in nanophase metals. Phys Rev B 60:22-25
[20] Yamakov V, Wolf D, Phillpot SR, Mukherjee AK, Gleiter H (2004) Deformation-mechanism map for nanocrystalline metals by molecular-dynamics simulation. Nat Mater 3:43-47
[21] Yip S (1998) Nanocrystals - The strongest size. Nature 391:532-533
[22] Zapol P, Sternberg M, Curtis LA, Frauenheim T, Gruen DM (2002) Tight-binding molecular-dynamics simulation of impurities in ultrananocrystalline diamond grain boundaries. Phys Rev B 65:045403