A study of mechanical properties of pure and nitrogen-doped ultrananocrystalline diamond films under various loading conditions

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**Abstract**

To better understand the mechanical responses of ultrananocrystalline diamond (UNCD) under various loading conditions, a numerical study is performed to investigate the size, loading rate and temperature effects on the material properties of pure and nitrogen-doped UNCD films. Since the UNCD growth mechanism is not completely understood yet, a simple procedure by combining kinetic Monte Carlo and molecular dynamics (MD) methods is developed to form a polycrystalline UNCD block with an artificial grain boundary (GB). By randomly inserting different numbers of nitrogen (N) atoms into the GB of the resulting polycrystalline UNCD films, N-doped UNCD films can be formed. The responses of the simulated pure and N-doped UNCD films with various grain sizes are then investigated by applying displacement-controlled tensile loading under different rates and temperatures in the MD simulations. The simulation results presented in this paper provide a better understanding of the combined size, rate and thermal effects on the material responses of pure and N-doped UNCD films.

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1. Introduction

Nanoelectromechanical/microelectromechanical systems (NEMS/MEMS) devices are playing an increasingly important role in modern engineering applications, which may involve material responses at different spatial and temporal scales under various temperatures. Since the material properties are essentially size-, rate- and temperature-dependent, a thorough study of these effects on the material responses is crucial not only in designing and fabricating NEMS/MEMS devices but also in bridging different spatial and temporal scales under various temperatures within a unified framework for multiscale multi-physics simulations, which could guide future experimental work and design of new device architectures that can better exploit the properties of new materials.

Owing to their outstanding mechanical, tribological, electronic transport, chemical and biocompatibility properties, the ultrananocrystalline diamond (UNCD) films grown by a microwave plasma chemical vapor deposition (CVD) method under hydrogen-poor conditions have become the subject of intense research interest in recent years, as shown by representative papers (Auciello et al., 2004; Birrell et al., 2002, 2003; Espinosa et al., 2003a,b; Gruen, 1999; Gruen et al., 1994, 1996; Sternberg et al., 2003; Zapol et al., 2001; among others). UNCD films are superior in many ways to traditional nanocrystalline diamond (NCD) films and microcrystalline diamond (MCD) films because they are hard, smooth, dense and pinhole free, have very small or negligible residual stress depending on growth conditions, and exhibit the diamond sp\(^3\) bonding in the grains...
and a mixture of sp³ and sp² bonding in the grain boundaries. All these special features give UNCD the unique combination of properties. UNCD can be conformally grown on a wide variety of materials and high-aspect-ratio structures (Auciglio et al., 2004), which is critical for NEMS/MEMS device applications. Since the deposited UNCD films are extremely smooth, UNCD could be the excellent candidate of future wear-resistant and protective coating for mechanical seal applications (Sumant et al., 2005). In fact, UNCD coated mechanical pump seals have been recently introduced in the market, as can be found from Advanced Diamond Technologies website. UNCD’s high mechanical strength, exceptional chemical inertness, and outstanding thermal stability make UNCD well suited for moving mechanical assembly devices (Krauss et al., 2001). Recent research by Bhattacharyya et al. (2001) has demonstrated that the conductivity of UNCD increases by as much as five orders of magnitude (to $10^4 \Omega^{-1}$ cm⁻¹) when nitrogen (N) is added to the plasma during growth. Moreover, the N-doped UNCD films have been considered for a variety of applications including MEMS/NEMS such as electrochemical electrodes, field emission, heterostructures, and high-temperature stable ohmic contacts (Williams et al., 2005).

The characterization by Raman spectroscopy, transmission electron microscopy (Zhou et al., 1998), electron-energy-loss spectroscopy (Birrell et al., 2002) and near-edge X-ray absorption fine-structure (Gruen et al., 1996; Birrell et al., 2003) has suggested that UNCD generally consists of phase-pure diamond grains with mixed sp³/sp² carbon bonds at the grain boundaries (GBs). Hence, it is the specific crystallite size and nanostructure of the GBs in UNCD films that distinguish them from natural diamond, MCD and NCD films in terms of physical properties. Further investigation by Birrell et al. (2003) on the bonding structure of UNCD as a function of N-doping has shown that although the grains themselves remain pure diamond, the overall grain boundary volume in UNCD is increased after N-doping. The physical properties of UNCD are thus modified by N-doping.

The fracture strength of UNCD was measured by Espinosa et al. (2003a) using tensile testing of freestanding submicron films, and the data followed a Weibull distribution. Paci et al. (2005a,b, 2006) performed several theoretical investigations on the mechanical properties of both pure and N-doped UNCD by using the MSINDO semiempirical self-consistent field molecular orbital program and density functional theory (DFT) calculations with Spanish initiative for electronic simulations with thousands of atoms (SIESTA). The theoretical estimations of the fracture strengths of both pure and N-doped UNCD in these studies are 30–40 times larger than those experimental values measured at micro-scale by Espinosa et al. (2003a). The large difference between the theoretical and experimental values has been mainly attributed to the existence of defects in the experimental samples by Paci et al. Shen and Chen (2007a) studied the grain size and loading rate effects on the mechanical responses of pure and N-doped UNCD by using molecular dynamics (MD) simulations. The simulated UNCD strength decreases as the specimen size or the number density of doped N atoms within the GB increases. It seems that the effect of specimen size may also contribute to the difference between the UNCD fracture strengths obtained by Paci et al. (2005a,b, 2006) and Espinosa et al. (2003a).

Since the UNCD-based MEMS devices might be required to work under extreme loading conditions, it is essential to thoroughly understand the mechanical responses of pure and N-doped UNCD films of different sizes under various loading rates and temperatures. As can be found from the open literature, however, little research has been conducted to investigate the combined effects of size, N-doping, loading rate and temperature on the mechanical properties of UNCD. With the use of a simple simulation procedure proposed in the previous work (Shen and Chen, 2006, 2007a) the mechanical responses of pure and N-doped polycrystalline UNCD blocks of various sizes are investigated under different uniaxial tensile loading rates and temperatures in this study. It appears from the preliminary results that the proposed procedure might provide an effective means to bridge different spatial and temporal scales in a unified multiscale modeling framework at different temperatures for UNCD.

The remaining sections of the paper are arranged as follows. The formation of the N-doped UNCD film from two pieces of single crystal diamond film is briefly described in Section 2, which is followed by the MD simulation procedure of the resulting UNCD film under tensile loading at different loading rates and temperatures. The simulation results are then discussed in Section 3. Based on the previous study of the effects of size, rate and temperature on the material properties of single crystal diamond, the fracture strength of UNCD as a function of loading rate, size and temperature is roughly estimated in Section 4. The conclusions and future work are given in Section 5.

2. Simulation procedure

2.1. Formation of UNCD specimens

The fundamental growth mechanism of UNCD films is not completely understood yet. It was initially believed that the growth mechanism for UNCD films from hydrogen poor plasmas should be much different from those in conventional MCD growth regimes, with C₂ playing a critical role in the nucleation and growth process (Gruen et al., 1994; Zhou et al., 1998; Sternberg et al., 2003). Recently it has been proposed by Rabeau et al. (2004) that C₂ does not appear to contribute as the growth species in the formation of NCD, and by May et al. (2006) that the UNCD growth mechanism is similar to that of MCD. So far, however, the UNCD film growth mechanism is still unclear since the actual experimental data for verifying the above-mentioned theories are not yet available. Due to the lack of thorough understanding of the UNCD growth mechanism and the complexity involved in the GB growth simulation, a simple procedure has been developed to create a UNCD block with an artificial GB (Shen and Chen, 2006, 2007a).
Although nitrogen atoms preferentially enter the GB rather than the diamond lattice with the grains remaining pure diamond (Birrell et al., 2003; Corrigan et al., 2002), the high-resolution transmission electron microscopy results suggest that both grain size and GB width increase as the amount of nitrogen added during the CVD process increases (Birrell et al., 2002). The width of GBs could increase from 0.2 to 2 nm as the nitrogen content in the plasma increases from 0% to 20%.

In the previous work (Shen and Chen, 2007a), two pieces of single crystal diamond film were employed for formation of the GB between two grains of UNCD by using the kinetic Monte Carlo (KMC) method with their growth surfaces being formed based on the randomness nature of the KMC method. The two diamond crystallites are then put together with the two growth surfaces touching each other under certain level of uniaxial compression. As a result, a polycrystalline UNCD block could be formed.

To create an N-doped UNCD block here, a pure polycrystalline UNCD block is first formed with a representative GB width, based on the experimental data. The number of C atoms within the chosen GB region will be counted and a defined number of N atoms are then randomly inserted into the chosen GB region to reach the expected N atom number density. Fig. 1 shows the configuration of the initially assembled N-doped UNCD block under uniaxial loading with $W_{GB}$ being the chosen width of GB. The so assembled UNCD block consists of two parts as shown in Fig. 1. One part, the central unwrapped portion, is referred to as the active zone in which the atoms move according to the interactions among the neighboring atoms; the other part, two end portions wrapped in boxes, is referred to as the boundary zone where the atoms are assigned a prescribed velocity with the same magnitude but in the opposite direction at each end to simulate a displacement-controlled tensile loading in the $z$-direction. The dimensions of the active zone in the $x$-, $y$- and $z$-directions are $D$, $W$ and $L$, respectively, while the thickness of each boundary zone is $t \geq 1.25a_0$ with $a_0$ being the lattice constant of diamond.

PBC is applied in both the $x$- and $y$-directions. The method employed to integrate the equations of motion is the 6-value Gear predictor–corrector algorithm with corrector coefficients for a second-order equation. For the purpose of simplicity, a velocity scaling technique (Allen and Tildesley, 1990) is applied when maintaining a constant temperature is required during the simulation.

MD studies require appropriate interatomic potentials that accurately reproduce the properties and behavior of the materials being simulated. In this study, the Tersoff potential (Tersoff, 1989) is used to model the interactions among carbon atoms and an empirical potential model using the Tersoff functional form is employed to describe the interactions among carbon and nitrogen atoms. The readers are referred to the reference (Shen and Chen, 2007a) for the detailed discussion on modeling the C–N interaction.

In the beginning of MD simulation, the system temperature is gradually increased from 273 to 1773 K. By applying a constant velocity along the $z$-direction to the atoms in the boundary zone with a strain rate of $2 \times 10^9$ s$^{-1}$, these two diamond blocks are compressed towards each other until reaching a strain $e_o$. Atomic bonds between two diamond surfaces are quickly formed during this pre-compression process at the elevated temperature. After the system reaches its equilibrium state, the temperature is gradually reduced to a specific temperature. As can be seen from Fig. 1, initially there would be no or very few atomic bonds between the two surfaces in contact. With the optimization in the MD self-assembly process, these two diamond crystallites will be firmly connected through an artificial GB. The resulting polycrystalline UNCD block will then be subjected to a displacement-controlled uniaxial tensile loading to investigate its mechanical response under various conditions. Note that the width and nanostructure of GB formed using the MD self-assembly process in this study might be different from those experimentally measured due to the lack of a thorough understanding of the UNCD growth mechanism.

![Fig. 1. Configuration of an initially assembled N-doped UNCD block under uniaxial loading (larger green dots represent nitrogen atoms). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this paper.)](image-url)
2.2. Stress and strain calculations

Stress calculation in the MD simulations has been the focus of many investigations over the past decades (Cheung and Yip, 1991; Irving and Kirkwood, 1950; Zhou, 2003; among others). In this study, the formulations employed to calculate atomic-level stresses are motivated by the previous work (Horstemeyer et al., 2001; Shen and Chen, 2004; Zhou, 2003). At each atom, the local stress tensor is defined to be

$$\mathbf{\sigma}_i = -\frac{1}{\Omega_i} \sum_{j \neq i}^{N_n} f_{ij} \otimes \mathbf{r}_{ij}$$

(1)

where \(i\) refers to the atom considered and \(j\) refers to the neighboring atom, \(\mathbf{r}_{ij}\) is the position vector between atoms \(i\) and \(j\), \(N_n\) is the number of neighboring atoms surrounding atom \(i\), \(\Omega_i\) is the control volume of atom \(i\), and \(f_{ij}\) is the force vector on atom \(i\) due to atom \(j\). The global continuum stress tensor is then defined as a volume average, namely,

$$\mathbf{\sigma} = \frac{1}{N'} \sum_{i}^{N'} \mathbf{\sigma}_i$$

(2)

in which \(N'\) represents the total number of atoms in a representative volume of a continuum. To deal with large uniaxial deformations, true strain, a nonlinear strain measure that is dependent upon the current length of the specimen, is used in this study, namely,

$$\varepsilon = \ln \left( \frac{L}{L_0} \right)$$

(3)

with \(L_0\) and \(L\) being the original and deformed lengths of the specimen, respectively.

3. Simulation results

3.1. Pure UNCD under tension

Three polycrystalline UNCD blocks with different initial active zone sizes, as listed in Table 1, are formed using the procedure outlined in Section 2. It has been demonstrated that the tensile strength of the simulated polycrystalline UNCD block increases when the initial compressive strain \(\varepsilon_0\) increases before the strength reaches its maximum value. Further increase of the initial compressive strain \(\varepsilon_0\) will lead to a lower tensile strength (Shen and Chen, 2006, 2007a). Previous MD simulations (Shen and Chen, 2007a) have shown that the critical initial compressive strains for UNCD Blocks 1–3 are 0.0921, 0.0661 and 0.0834, respectively. Therefore, in the following MD simulations, UNCD Blocks 1–3 are first compressed to their respective critical strain level, and uniaxial tension is then applied with different loading rates and temperatures until the final failure of the specimen.

Fig. 2 shows the stress–strain curves for UNCD Blocks 1–3 under loading rate of \(2 \times 10^9\) s\(^{-1}\) at temperature \(T = 0\) °C. The stress–strain curves of UNCD Block 1 at temperature \(T = 0\) °C under different loading rates are presented in Fig. 3. It appears from Figs. 2 and 3 that the initial elastic modulus is almost size- and rate-independent, while the tensile strength decreases with the block size and increases with the strain rate at \(T = 0\) °C. Similar size and rate effects have been found on the mechanical properties of single crystalline diamond (Shen and Chen, 2006, 2007b, in press). Fig. 4 demonstrates the stress–strain curves of Block 1 under loading rates of \(2 \times 10^8\) and \(2 \times 10^9\) s\(^{-1}\), and Block 3 under loading rates of \(2 \times 10^9\) and \(2 \times 10^{10}\) s\(^{-1}\) at different temperatures. As can be found from these figures, the initial elastic modulus and tensile strength of the pure UNCD decrease with increasing temperature regardless of the grain size and loading rate. Similar to the previous findings on single crystal diamond (Shen and Chen, in press), both the initial elastic modulus and strength of UNCD decrease with increasing temperature.

The simulated tensile strengths of UNCD Blocks 1–3 under various loading rates and temperatures are given in Table 2. Due to the limitation of current computing capability, simulations with larger specimen sizes and lower strain rates are not performed. As can be found from Table 2, the tensile strength of the simulated UNCD decreases with increasing temperature, and increases with the increase of the loading rate. Although the tensile strength of UNCD block does decrease with the increase of block size in most cases, there are some cases where the strength of Block 3 is larger than that of Block 2 under the same loading conditions. Since each UNCD block is formed with a GB which is largely affected by the randomness of the film.
growth mechanism, the material properties of UNCD are not only affected by the block size but also dependent on the nanostructure of the growth surfaces which determine the GB structure and eventually the strength of UNCD film.

The failure patterns of UNCD Block 1 under tensile loading rate of $2 \times 10^9 \text{s}^{-1}$ at different temperatures are presented in Fig. 5. It appears that the failure mainly occurs at the GB at all temperatures, which is different from the fact that failure could occur anywhere within a single crystalline diamond under tension (Shen and Chen, 2006, in press). It seems that the UNCD strength is mainly determined by the nanostructure of GBs. As can be found in Fig. 5, the size of failure evolution zone increases when the temperature increases from 0°C to 1500°C. It appears that there is a transition from brittle to ductile failure in UNCD films as the temperature increases. Fig. 6 shows the failure patterns of UNCD Block 1 under different tensile loading rates at $T = 0 \text{°C}$. As can be seen from Fig. 6, the failure pattern of UNCD is not sensitive to the loading rate.

3.2. N-doped UNCD under tension

To study the effect of N-doping on the mechanical responses of the simulated UNCD film under tension, different numbers of N atoms are randomly inserted into the GBs of UNCD Blocks 1 and 3. For the purpose of comparison, the number of doped N atoms is chosen so that for a given block size, three cases with the number of N atoms versus the number of C atoms within the GB region being 1:12, 1:6, and 1:3, respectively, are investigated. In this study, a representative GB width $W_{GB} = 0.357 \text{nm}$ is considered and the numbers of C atoms within the GB regions of Block 1 and Block 3 are 96 and 193, respectively.

Recent experiments performed by some researchers (not published yet) have revealed by optical emission spectroscopy that nitrogen would come out of N-doped UNCD at high temperatures ($> 600 \text{°C}$). At very high temperature ($> 1000 \text{°C}$), the GBs are mostly free of nitrogen atoms. However, it is still very challenging to quantitatively establish the relationship between the amount of nitrogen atoms in the GBs and the temperature at this stage. Therefore, only the strengths of N-doped UNCD at temperature below 500°C are calculated in this study. Fig. 7(a)–(c) demonstrate the stress–strain curves of UNCD Block 1 doped with 8, 16, and 32 N atoms, respectively, under different temperatures and tensile loading of $2 \times 10^9 \text{s}^{-1}$. The stress–strain curves of UNCD Block 3 doped with 16 N atoms under different temperatures with a tensile loading of $2 \times 10^9 \text{s}^{-1}$ are shown in Fig. 7(d). As can be seen from these figures both the tensile strength and the initial elastic modulus of N-doped UNCD decrease with the increase of temperature regardless of the grain size and the number of doped N atoms.

To investigate the effect of strain rate on the mechanical responses of N-doped UNCD at elevated temperatures, MD simulations of N-doped Block 1 under tensile loading rates of $2 \times 10^{10}$, $2 \times 10^9$, and $2 \times 10^8 \text{s}^{-1}$ are performed at $T = 500 \text{°C}$. 

Fig. 2. Stress–strain curves of UNCD blocks under tensile loading with rate of $2 \times 10^9 \text{s}^{-1}$ and temperature $T = 0 \text{°C}$.

Fig. 3. Stress–strain curves of UNCD Block 1 under different loading rates at temperature $T = 0 \text{°C}$.
The corresponding stress–strain curves for Block 1 doped with 8, 16 and 32 N atoms are presented in Figs. 8–10, respectively.

As can be seen from these figures, the strength of N-doped UNCD increases with the increase of strain rate, while the initial elastic modulus is almost rate-independent regardless of the number of N atoms doped.

Tables 3 and 4 report the simulated tensile strengths for Blocks 1 and 3, respectively, doped with different numbers of N atoms under various tensile loading rates and temperatures. It appears from these two tables that the tensile strength of UNCD generally decreases as either the number of doped N atoms or the temperature increases, and the strength increases with the increase of loading rate.

The failure patterns of UNCD Block 1 doped with 8 N atoms under different tensile loading rates at $T = 0 \, ^\circ\text{C}$ are presented in Fig. 11. It appears from the figure that the size of the failure evolution zone increases, suggesting that the ductility increases as the loading rate decreases. This is different from what is found from the pure UNCD block under tension since...
the failure pattern of pure UNCD is almost rate-independent. The possible reason is that the C–N bonds in the N-doped UNCD are sensitive to the loading rate and tend to break easily under a low loading rate.

Fig. 12 shows the failure patterns of UNCD Block 1 doped with 8 N atoms under tensile loading rate of $2 \times 10^9 \text{s}^{-1}$ at different temperatures. The failure patterns of UNCD Block 1 doped with different numbers of N atoms under tensile loading rate of $2 \times 10^9 \text{s}^{-1}$ and $T = 0 \text{°C}$ are demonstrated in Fig. 13. As can be seen from the figure, the number of doped N atoms does not affect the failure pattern significantly.
4. Estimation of UNCD fracture strength

Based on the available experimental and computational results, an attempt has been made to formulate a hyper-surface in spatial, temporal and thermal domains to predict the combined size, rate and temperature effects on the material properties of pristine diamond (Shen and Chen, in press; Shen and Chen, 2008). In the proposed hyper-surface, the power scaling law (Bazant, 2002) which has been generally used to predict the size-dependent strength of materials has been adopted to model the size effect on the single crystal diamond (SCD) strength. A simple power-law type model motivated by the work of Schwaiger et al. (2003) is then used to describe the strain rate effect on the strength of SCD. To describe the temperature-dependent

Fig. 7. Tensile stress–strain curve of N-doped UNCD Block under different temperatures. (a) Block 1 doped with 8 N atoms. (b) Block 1 doped with 16 N atoms. (c) Block 1 doped with 32 N atoms. (d) Block 3 doped with 16 N atoms.

Fig. 8. Tensile stress–strain curve of UNCD Block 1 doped with 8 N atoms under different loading rates at $T = 500^\circ$C.
strength model for SCD, the type of Johnson–Cook’s thermal softening model (Johnson and Cook, 1983) is adopted. In this study, by assuming that the temperature effect on material strength is rate- and size-dependent, the fracture strength of UNCD as a function of size, rate and temperature could be roughly estimated by using the available MD simulation results.

![Graph](image)

**Fig. 9.** Tensile stress–strain curve of UNCD Block 1 doped with 16 N atoms under different loading rates at $T = 500^\circ C$.

![Graph](image)

**Fig. 10.** Tensile stress–strain curve of UNCD Block 1 doped with 32 N atoms under different loading rates at $T = 500^\circ C$.

### Table 3

<table>
<thead>
<tr>
<th>$T$ ($^\circ$C)</th>
<th>Rate ($s^{-1}$)</th>
<th>Number of N atoms: number of C atoms within the GB</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$2 \times 10^{10}$</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>$2 \times 10^{8}$</td>
<td>8:96</td>
</tr>
<tr>
<td></td>
<td>$2 \times 10^{6}$</td>
<td>16:96</td>
</tr>
<tr>
<td></td>
<td>$2 \times 10^{4}$</td>
<td>32:96</td>
</tr>
<tr>
<td>0</td>
<td></td>
<td>106.2 108.2 107.6 102.1</td>
</tr>
<tr>
<td>500</td>
<td>$2 \times 10^{10}$</td>
<td>97.3 97.0 93.1 91.0</td>
</tr>
<tr>
<td></td>
<td>$2 \times 10^{8}$</td>
<td>93.0 88.6 85.6 84.2</td>
</tr>
<tr>
<td></td>
<td>$2 \times 10^{6}$</td>
<td>86.5 82.3 77.0 71.3</td>
</tr>
<tr>
<td>1000</td>
<td>$2 \times 10^{8}$</td>
<td>74.8</td>
</tr>
<tr>
<td>1500</td>
<td>$2 \times 10^{8}$</td>
<td>58.3</td>
</tr>
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</table>

### Table 4

<table>
<thead>
<tr>
<th>$T$ ($^\circ$C)</th>
<th>Number of N atoms: Number of C atoms within the GB</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>16:193</td>
</tr>
<tr>
<td></td>
<td>32:193</td>
</tr>
<tr>
<td></td>
<td>64:193</td>
</tr>
<tr>
<td>0</td>
<td>92.2 93.0 91.2 84.3</td>
</tr>
<tr>
<td>500</td>
<td>81.0 80.4 76.0 75.3</td>
</tr>
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<td>70.0</td>
</tr>
<tr>
<td>1500</td>
<td>58.1</td>
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</table>
Based on the procedure of formulating a hyper-surface in spatial, temporal and thermal domains to predict the strength of pristine diamond (Shen and Chen, in press), the fracture strength of UNCD as a function of loading rate $\dot{e}$ (in s$^{-1}$), size $D$ (in m) and temperature $T$ (in ºC) could be roughly expressed by

$$\log \sigma(\dot{e}, D, T) = \log \left( \sigma_o(D, T_0) \left( \frac{\dot{e}}{\dot{e}_0(D)} \right)^q \right) \times \left( k_1 \log D + b_1 \right) \times \left( k_2 \log \dot{e} + b_2 \right) \times \left( \frac{T - T_o}{T_{\max} - T_o} \right)^\beta$$

(4)
where \( \sigma_0(D, T_0) \) (in GPa) is the quasi-static tensile strength of UNCD with size \( D \) at temperature \( T_0 = 0 \, ^\circ C \), and \( \dot{\varepsilon}_o(D) \) is the size-dependent reference strain rate. \( T_{\text{max}} = 1500 \, ^\circ C \) is the maximum temperature for the proposed model, and \( k_1, k_2, b_1, b_2 \) are parameters to be determined. By analyzing the fracture strengths of pure UNCD from Table 2 using the procedure discussed in Shen and Chen (in press), the parameters have been obtained with \( a_0 = 0.2232, k_1 = 0.9288, b_1 = 6.4915, k_2 = -0.4247, b_2 = 4.950, q = 0.015 \) and \( \beta = 0.95 \).

In Eq. (4), \( \sigma_0(D, T_0) \) is calculated using the following equation:

\[
\log \sigma_0(D, T_0) = \log \sigma_l + \frac{1}{2} \left( \frac{D}{D_L} - 1 \right) \left( \frac{\log \sigma_u - \log \sigma_l}{\log D_L - \log D_S} \right) \quad \text{for } D_S < D < D_L
\]

with \( \sigma_u = 96.9 \, \text{GPa} \) being the ultimate strength for \( D \leq D_S = 5.53 \, \text{nm} \) based on this study, and \( \sigma_l = 3.92 \, \text{GPa} \) being the size-independent macro-scale strength for \( D \geq D_l = 0.5 \, \text{mm} \) based on the experimental data for diamond (Field and Pickles, 1996).

The reference strain rate \( \dot{\varepsilon}_o(D) \) is size-dependent and takes the form of

\[
\frac{\log \dot{\varepsilon}_o(D) - \log \dot{\varepsilon}_{oL}}{\log \dot{\varepsilon}_{oS} - \log \dot{\varepsilon}_{oL}} = \frac{1}{2} \left( \frac{D}{D_L} - 1 \right) \left( \frac{\log \dot{\varepsilon}_{uS} - \log \dot{\varepsilon}_{oL}}{\log D_L - \log D_S} \right) \quad \text{for } D_S < D < D_L
\]

with \( \dot{\varepsilon}_o = \dot{\varepsilon}_{oL} = 1 \times 10^{-5} \, \text{s}^{-1} \) for \( D \geq D_L \), and \( \dot{\varepsilon}_o = \dot{\varepsilon}_{oS} = 2 \times 10^7 \, \text{s}^{-1} \) for \( D \leq D_S \) (Shen and Chen, in press).

Using Eq. (4), it is possible to estimate the fracture strength of pure UNCD block of different sizes under different loading rates and temperatures. For example, the fracture strength of pure UNCD specimen with 2 \( \mu \text{m} \) size under loading rate of \( 1 \times 10^{-5} \, \text{s}^{-1} \) and temperature \( T = 0 \, ^\circ C \) is estimated to be 18.0 GPa, which is about 4 times larger than the experimentally measured strength of 4–5 GPa for micro-scale UNCD specimens (Espinosa et al., 2003a). It is believed that the difference between the theoretically estimated and experimentally measured UNCD strengths is mainly due to the effect of defects in real UNCD specimens. Although the preliminary results illustrate the potential of the proposed procedure in linking different spatial and temporal scales in a unified multi-scale modeling framework, there are still several critical issues to be addressed before it could be applied to general cases.

5. Conclusions and future work

In this study, a simple procedure is applied to form a polycrystalline UNCD block with an artificial grain boundary. The mechanical properties of the resulting UNCD film are then investigated by applying displacement-controlled tensile loading.
in the MD simulation. It appears that the initial elastic modulus of UNCD block is size- and rate-insensitive, while it decreases as the temperature increases. The maximum strength of pure UNCD increases as the specimen size decreases or as the strain rate increases, but it decreases as the temperature increases. From the failure pattern of UNCD block under tension, it appears that there is a transition from brittle to ductile failure as the temperature increases. However, the failure pattern is not sensitive to the loading rate.

By randomly inserting different numbers of N atoms into the GB of the polycrystalline UNCD films, N-doped UNCD films can be formed. The tensile strength of N-doped UNCD decreases as the temperature or the number of doped N atoms increases, although it increases as the loading rate increases. The ductility of N-doped UNCD increases as the loading rate decreases which is different from the rate-insensitivity of pure UNCD. On the other hand, the number of doped N atoms does not affect the failure pattern significantly.

Based on the previous study of the effects of size, rate and temperature on the material properties of single crystal diamond, the fracture strength of pure UNCD as a function of loading rate, size and temperature is estimated. Due to the effect of defects in real UNCD specimens, however, the estimated UNCD strength is about 4 times larger than the experimentally measured strength of microscale UNCD specimens.

Due to the simple procedure used to form both pure and N-doped polycrystalline UNCD blocks, the artificial GB nano-structure developed in the MD self-assembly process might be different from those experimentally measured. An integrated analytical, experimental and numerical effort is therefore required to further improve the simulation procedure for UNCD growth and to advance our knowledge in the mechanical properties of pure and N-doped UNCD.

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References


