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Atomistic simulation on nanomechanical response of indented graphene/nickel system

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ABSTRACT

Molecular dynamics (MD) simulations were carried out to study the nanoindentation mechanical properties of graphene/nickel system. The effects of indenter radius, loading speed, and number of graphene layers were investigated. The results show that the indentation response of graphene/nickel system includes elastic regime, plastic regime and graphene ruptures regime. The contact stiffness, elastic capacity and the load bearing capacity are visibly improved by graphene coverage. The indenter radius significantly influences the ultimate indentation depth and corresponding forces. The increasing number of graphene layers significantly enhances the elastic capacity and the ultimate forces of graphene/nickel system.

1. Introduction

Graphene, i.e., a single 2D sp2-hybridized carbon sheet with remarkable chemical and physical properties [1–6], has attracted considerable interests for both theoretical and applied researches since its discovery by Gein et al. [7,8]. Although graphene is lighter and more flexible than most materials, it is one of the strongest materials, with the highest-known intrinsic strength of 130 GPa and the Young's modulus of 1TPa [9–11]. Therefore, graphene has excellent potential applications for pressure sensing and material reinforcement in composite technologies [12,13].

The mechanical properties of graphene are very challenging to be measured because of uncertainty in the sample geometry, stress concentration at clamping points, structural defects, and unknown load distribution. Nanoindentation is the effective way to measure the mechanical properties of graphene, which is relatively easy to mount the membrane over a circular hole with a simple rigid boundary [14–16]. Using the nanoindentation technique on the basis of atomic force microscope (AFM), Frank et al. [17] and Lee et al. [3] measured the Young's modulus and ultimate strength of multiple layer and monolayer graphene. Zhang and Pan [18] determined the elastic properties of monolayer, bilayer and multiple-layer graphene sheets by using an instrumented nanoindenter. In order to further understand the experimental investigation, the theoretical and numerical studies of the graphene indentation response have developed [19–22]. The mechanical properties of graphene can be derived from the force-deflection relation of the clamped free-standing graphene sheet to a rigid indenter tip.

Graphene can enhance the load carrying capacity of the substrate [23]. Meanwhile, the graphene in the metal –graphene nanolayered structures can block dislocation propagation across the metal-graphene interface, which makes ultra-high strengths of the nanolayered composites [24]. Graphene-Ni multilayers were synthesized by CVD and etched many times, and the compression were tested and simulated, which revealed that graphene plays the role of the strength enhancer in the composites [24]. Nickel based composites have been widely adopted in automobile and aerospace industries because of their high specific strength, favorable corrosion resistance and toughness [25–27]. Graphene incorporated into the Ni matrix are expected to exhibit even higher hardness and strength. However, to the best of our knowledge, there are few reports on the nanoindentation mechanism of graphene/nickel system. This letter aims at reporting atomistic nanoindentation of graphene supported by a single crystal nickel substrate. Realistic substrates and a realistic interaction model for the graphene sheet were established. Our simulations employed the empirical interaction potential between nickel atoms, carbon atoms and graphene-nickel. The effects of loading speed, temperature, tip size and number of graphene layers were investigated.

2. Methods

In our simulations, models with a graphene sheet suspended on a face-centered cubic (fcc) Ni (1 1 1) surface and diamond spherical indenters were established. The structure of the spherical indenter

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is diamond. The spherical diamond indenters with radius of 1.0 nm, 2.0 nm and 3.0 nm were exploited. The nickel block is cubic cell with the side length of around 5 times the indenter radius, with a well-defined graphene supported on. The spherical diamond indenters were set to be rigid. The rigid indenters were located 1.0 nm on the top of the graphene center. The number of graphene layers varies from 1 to 4. The separation between the graphene layers is 3.5 Å. The bottom two layers of the nickel substrates are set as boundary atoms, which are unaffected during the simulation and remain fixed in their initial position, serving to reduce the boundary effects.

The accuracy of a potential function determines the reliability of Molecular dynamics (MD) simulation. Up to now, there are many types of force fields available, which have been parameterized to describe a variety of systems. The embedded-atoms method (EAM) potential developed by Mishin et al. [28] was used to describe the interaction between Ni atoms. Reactive empirical bond order potential (AIREBO) [29] was used to describe the intralayer carbon- carbon interaction of graphene, which gave a carbon-carbon bond length to be 0.142 nm, and agreed well with the experimental result [30]. Here, we adopted the classical Lennard-Jones (L-J) potential to describe carbon-nickel interaction between carbon atoms of diamond indenters and graphene and nickel substrate, with 0.023049 eV and 2.852 Å [31]. The van der Waals interaction between the graphene layers and indenter-graphene were modeled by the L-J interaction with 0.00284 eV and 3.4 Å [32].

An energy minimization process was carried out to avoid overlaps in the positions of the atoms after models completed. The periodic boundary conditions were employed in the transverse directions (XY directions). A Nose/Hoover thermostat was applied to maintain the temperature of 300 k. The equations of motion were integrated using the Verlet algorithm [33] with a time step of 10^{-15} s. The system was stabilized for 100 ps to make the system reach equilibrium. The indenters were moved at a constant speed along the z-direction until to the preset indentation depth. The indent speeds varied from 5 to 100 m/s. The forces acting on the indenter were obtained by summing the forces contributed by the graphene and substrates. The snapshots of the nanoindentation were recorded.

3. Results and discussions

Fig. 1a shows the calculated load-displacement of graphene supported on nickel substrate. Analogous indentation simulations with bare nickel system were also performed in Fig. 1a as a reference. It can be observed from Fig. 1(a) that when the indenters are in vicinity of the surface of graphene/nickel or nickel system (as shown in Fig. 2a), the vertical load is negative due to van der Waals attraction. When the indentation depth is less than 1.52 nm, the load-displacement of the graphene/nickel system and the nickel system are almost coincident, which reveals that the graphene bears no surface tensile stress and has no effect on the indentation. It also suggests the flexural rigidity of graphene can be neglected. After an initial elastic regime, plasticity in the nickel substrate sets in leading to small sawtooth shaped steps in load that reflect the dislocation activity below the indenter. For the single nickel system, the onset of plastic deformation and dislocation slip occurs at the depth of 1.52 nm thus reducing the vertical load. For the graphene/nickel system, the vertical load increases with the increasing of the indentation depth until the first plastic deformation and dislocation slip occurs at the depth of 1.77 nm. Which reveals that graphene bearing surface tensile stress improves the contact stiffness and elastic capacity. With the increasing of the indentation depth, the load-displacement of two systems distinguishes visibly. The vertical load of nickel system tends stability due to the contact area between indenter and nickel substrate being unchanged at the critical indentation depth (3.0 nm), while the load of graphene/nickel system increase until graphene ruptures at depth of 4.2 nm. For this instant, a straight crack occurs in the graphene accompanied by an instantaneous drop in normal force by 1104 nN. Interestingly, the further indentation normal forces of the graphene/nickel system approach the load-displacement curve measured on nickel system after the graphene ruptured. Consequently, the indentation response of graphene/nickel system can be divided into three stages: elastic stage (as shown in Fig. 2b), plastic stage (as shown in Fig. 2c) and graphene ruptured stage (as shown in Fig. 2d). Covering the nickel surface with graphene delays the onset of plasticity, which extends the Hertz behavior to larger indentation depths. Most importantly, the loads of graphene/nickel system are obviously higher than that of the single nickel system at the same penetration depth in the plastic regime. The load carrying capacity of graphene/nickel system is almost 9 times higher than that of pure nickel system.

The indentation load-displacement of graphene/nickel system are analyzed with the Hertz contact theory. The function between load and indentation depth is presented in Eq. (1) [34]. The indentation hardness is defined as Eq. (2).

$$P = \frac{4}{3}E^{*}R^{\frac{1}{2}}h^{\frac{3}{2}} \tag{1}$$

$$\mathrm{H} = P_{max}/A_c \tag{2}$$

where P is the sum of the atom forces in the vertical direction of the indent, E^{*} is the elastic modulus, R is the radius of indenter, h is the indentation depth. $P_{\max}$ is the critical load from elastic stage to the onset of plasticity. And A_c is the projected contact area. For spherical indenter, $\mathrm{A_c}$ is defined as $A_c = \pi a^2$, where $\mathrm{a} = (2Rh - h^2)^{\frac{1}{2}}$. The elastic modulus and hardness of graphene/nickel system and bare nickel system calculated are presented in the Table 1. The experimental results of the elastic modulus and the hardness of graphene/nickel composites and the pure nickel were compared [35]. The elastic modulus and hardness of graphene/nickel system are significantly improved than that of bare nickel system, the increments of elastic modulus and hardness are 48% and 285% for 1 nm indenter, 45.5% and 313.2% for 2 nm indenter, 48.6% and 289.7% for 3 nm indenter, respectively, which suggests that graphene coverage significantly improves the elastic modulus and hardness of metallic substrate. The calculated elastic modulus and hardness of bare nickel system and graphene/nickel system decrease with the increase of indenter sizes. The elastic modulus of single nickel system and graphene/nickel system decreases slightly with the increase of the indenter sizes, and agree well with that from the experimental study, while the hardness values decrease significantly with the increase of indenter sizes, and have discrepancy with that from experimental study. With the increase of the indenter size, the contact area will increase, while the calculated hardness values reduce. The indenters used in the experiments is much larger than that used in the simulations, making the contact area be much larger than that in the simulations, which may lead the hardness values from experiments to be smaller than that from the simulations. The time and space scales of molecular dynamics simulation is much smaller than that of the nanoindentation experiments, which will also lead the values of the elastic modulus and hardness obtained from simulations and experiments to be not consistent. In addition, the contact area between indenters and single nickel system or graphene/nickel system will be affected by the atomic vibrations in the molecular dynamics simulations, which makes it difficult to calculate the actual contact area and accurate hardness values. It may also be the reason of the difference between the simulated hardness and