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Investigation on tensile behaviors of diamond-like carbon films

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ABSTRACT

The lubrication performance of diamond-like carbon films is significantly influenced by their deformations under loading. However, their deformation mechanisms are unclear so far due to their nanoscale thicknesses and complex microstructures. In this study, these mechanisms are explored by investigating the tensile response of the DLC films via molecular dynamics simulations. The atomic strain localizations are observed, and the regions where they occur are dominated by sp^2 clusters. These clusters relax the film at small tensile-strains by releasing its residual energies. The sp^3-sp^2 transitions are present at large tensile-strains and prefer to occur in the strain-localized regions. This preference significantly improves the graphitization level in these regions and thus promotes the sp^2 clusters to propagate. The propagation severely damages the sp^3 networks and leads to the failure of the film. This research suggests that reductions of heterogeneities such as existences of large-sized sp^2 clusters may be useful to delay the film failure by suppressing the initial strain localizations. It is demonstrated that the propagation of sp^2 clusters for the DLC films can be induced by their deformation besides the high friction temperature in their wear tests. This demonstration can help to improve the understanding of their trigological mechanisms.

1. Introduction

Amorphous solids are materials that lack the long-range order characteristics of crystals and thus exhibit disordered microstructures [1,2]. The linear defects and dislocations which support plasticity in crystals are inappropriate for interpreting the deformation mechanisms of amorphous solids. As a result, these mechanisms always attract attentions, and many significant discoveries have been made in the past decades [3–5]. It was found that amorphous solids exhibit localizations of atomic strains and atomic stresses when subjected to external forces. Domains in which the localizations occur are usually ill-packed and have high free-volumes due to low local densities and liquid-like properties [6–8]. Since the plasticity or localized shear transformations are initiated in these domains, they are commonly regarded as defects [5]. For metallic glasses, the evolutions of these domains can even induce the presence of shear bands which improve ductility of materials [9].

Diamond-like carbon (DLC) films are amorphous solids that combine carbon atoms by hybridized sp^3, sp^2, and sp bonds [10,11]. These films exhibit excellent mechanical properties and good wear resistances, and are widely used as solid lubrication films. Lubricities of DLC films are dominated by sp^3-sp^2 rehybridization transitions (also named graphitization) with the passivation of surface dangling bonds by other atoms or molecules [12–15]. Recent theoretical works showed that strains can largely induce the sp^3-sp^2 transitions and strain localizations are observed to play a crucial role in the lubricities of DLC films when the dangling bonds inside them lack efficient passivation [12,14,16–21]. Since both the strain-induced bond transition and the strain localization are closely related to structural evolutions of DLC films, these works indicate that the understanding of the film deformation mechanisms is of significant importance.

So far, few studies have been conducted on these deformation mechanisms, mainly due to the huge experimental difficulties in directly observing the microstructural evolutions of DLC films because of their nanoscale thicknesses [10,15,22]. Moreover, previous theoretical works mainly focused on the evolution of atoms at the sliding interface in the wear test [12,14,23] instead of the deformation of the whole film.

In view of the many similar properties such as the disorder distributions of atoms and the absence of dislocations shared by most of the amorphous solids, their common theories can provide useful points to investigate the deformation mechanisms of DLC films [3–5]. For example, the strain localizations may be used to understand the sp^3-sp^2 transitions [6], and the free-volume theory reminds that sp^2 atoms or clusters may act as defects due to their larger atomic volumes as compared with those of sp^3 atoms [7,8].

In the present study, the deformation process of DLC films under tensile loading is explored via molecular dynamics (MD) simulation. The evolutions of microstructures are studied in detail, and the effect of strains on the plasticity and graphitization is investigated. Since the

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DLC films are comprised of pure C atoms without other doping elements, the results are applicable for non-hydrogenated DLC films especially those with high fraction of sp^3 C atoms.

2. Modelling

The MD simulation is performed by the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [24]. Atomic interactions in DLC films are described by the Tersoff potential which is effective and accurate for carbon systems [25]. Its cutoff distance is set as 2.1 Å.

The initial atomic configurations of DLC films are generated by using the melting and quenching procedure, since it can help to easily obtain their realistic structures [26–29]. During this generation procedure, periodic conditions are applied along all three directions. At the beginning, a diamond-crystalline structure containing 29,504 atoms is created with a lattice parameter of 3.6 Å. The system is then heated from 300 K to the temperature above the melting point of crystalline diamond in the canonical NVT ensemble [30]. At the maximum temperature, the system is thermally equilibrated for 20 ps. It is cooled down with a quenching rate of 1000 K/ps to 300 K. This rate can promote the relaxation of the film structure and make it most realistic [26,31]. The systemic volume is subsequently adjusted at zero pressure by the isothermal–isobaric NPT ensemble to reduce the residual stress. The temperature in the NVT and NPT ensembles is adjusted by the Nose-Hoover method. The final dimensions of the system are 167.2, 74.6 and 15.6 Å along *x*, *y* and *z*-directions, respectively. The density of the obtained DLC film is about 3.02 g/cm^3.

A tensile test of the obtained DLC film is performed along the *x*-direction at 300 K, as shown in Fig. 1. Periodic conditions are applied along the *x* and *z*-directions. During the tensile test, the strain rate is set as 0.002 ps^{-1}. The molecular visualization is conducted by using the software VMD and OVITO [32,33]. The structural properties of the DLC film are studied by evaluating its radial distribution function (RDF), pair distribution function (PDF) and bond angle distribution [32,34]. Moreover, the coordination numbers of atoms are calculated based on a cutoff distance of 1.90 Å by regarding four-fold and three-fold atoms as being sp^3 and sp^2 bonded, respectively [26]. This distance corresponds to the first minimum in the RDF of DLC films.

In the deformation of amorphous solids, their structural changes commonly occur in regions where atomic volume strains and atomic shear strains localize [3,9]. Due to the significance of these two strains, they are evaluated as in the reference [35] to interpret the microstructural evolutions of DLC films. The effect of atomic strains on the film structure is further investigated by the clusters analysis.

3. Results

3.1. Stress-strain curves and potential energy evolution

Fig. 2 shows the obtained stress vs. strain curve. When the tensile-strain initially increases, the stress increases linearly, indicating a linear and reversible elastic deformation process. The slope of the linear curve gives the elastic modulus, as about 539 GPa which agrees well with those reported in the experimental study [36]. As the tensile-strain increases, the stress-strain curve becomes nonlinear and exhibits a decreasing slope. The nonlinear deformation also called inelasticity is usually irreversible. As the strain increases further to about 0.21, the stress reaches a maximum value, i.e., the ultimate tensile strength of the DLC film, after which it fractures immediately.

Stress-strain curves of reverse tests which are conducted by compressing DLC films from tensile-strains of 0.05 and 0.16 are also presented in Fig. 2, respectively. The stress in the reversed test is lower than that in the tensile test at the same strain. This reveals that the film microstructures change during the tensile tests.

The potential energy evolutions of the DLC films in the tensile test as well as in the reversed tests are shown in Fig. 3. In the tensile test, when the tensile-strain increases initially, the potential energy increases slowly. However, it increases rapidly at high tensile-strains. This rapid increase is attributed to that the huge tensile stress causes the atoms to deviate far from their balanced locations in the potential landscape [37]. When the ultimate tensile strength is reached, the maximum potential energy is obtained, followed by a sharp drop due to the film failure.

In the reversed tests, the potential energy is lower than that in the tensile tests at any given strain. The lower potential energy is usually caused by microstructure relaxation or transformation, depending on the initial tensile-strains. At a small initial tensile-strain of 0.05, the potential energy of the film monotonically decreases as it is compressed and reaches a minimum value at zero tensile-strain where the potential energy for the tensile test is also the minimal. The monotonic decrease of the potential energy during the reverse test for the initial tensile-strain of 0.05 indicates that small initial tensile-strains can only cause the structural relaxation of films instead of their structural transformations [38,39]. On the contrast, at a large initial tensile-strain of 0.16, the potential energy of the DLC film first decreases and then increases as it is compressed, showing a nonmonotonic behavior. Minimum of the potential energy is reached at the tensile-strain of about 0.03 rather than at the zero tensile-strain. Such nonmonotonic behavior indicates there is a microstructure transformation caused by the large initial tensile-strain. Such transformation will be further illustrated below. The potential energy evolutions of DLC films

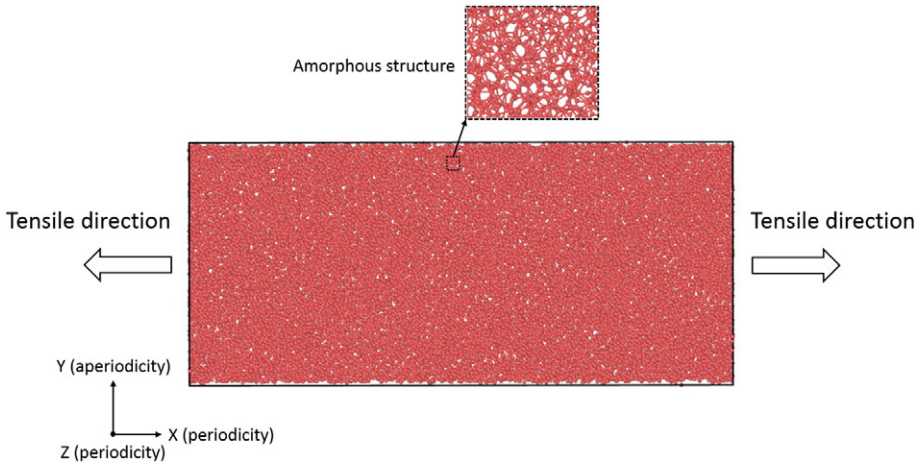

Fig. 1. Illustration of MD models for tensile test of DLC film.