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Interfacial strengthening and self-healing effect in graphene-copper nanolayered composites under shear deformation

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ABSTRACT

The mechanism of interfacial strengthening and self-healing effect in graphene-copper nanolayered (GCuNL) composites under shear deformation is investigated at a theory and quantitative level. It is found that the interfacial constraining effect between graphene and copper layer highly improves the shear strength and toughness of GCuNL composites. The interlayer distance between graphene monolayers and the crystal stacking orientation of copper layers plays an important role in the shear yield strength of composites. The shear toughness of composites is jointly determined by the crystal orientation of copper layer and the chirality of graphene. The shear failure strain of zigzag-based composites is remarkably higher than that of armchair-based composites, while the shear failure stress of (100)-stacking composites is larger than that of (111)-stacking composites due to rotation of slip bands. Furthermore, we find a remarkable self-healing effect in GCuNL composites by interfacial trapping dislocations. The self-healing ability is determined by the interlayer distance between graphene monolayer. Synthesizing both the strengthening and self-healing effect, the optimum distance between graphene monolayers is ranging from 5 to 15 nm.

1. Introduction

Though graphene has a high intrinsic strength of 130 GPa and a Young's modulus of 1.0 TPa [1], it is still challenging to use graphene as structural materials due to its two-dimensional structure [2]. In addition, hybrid composite nanomaterials provide an attractive and versatile material platform for numerous emerging nano- and biomedical applications by offering the possibility to combine diverse properties which are impossible to obtain within a single material [3]. Thus, three-dimensional graphene composites become a study hotspot in recent years [4–6]. Graphene is considered as a promising strength enhancer in composites [7,8]. It has been demonstrated that graphene fragments can improve the strength and toughness of composites even without ordered arrangement [9,10]. In 2013, Kim *et al.* realized the synthesis of graphene-metal (copper and nickel) nanolayered composites [11]. It is expected that graphene interfaces in nanolayered composites can increase resistance against dislocation propagation as an incoherent interface system [12,13]. In addition, this composites is closely related to the flaw tolerance at the nanoscale, which serves to increase strength and promote self-healing. Gao *et al.* found that materials become insensitive to flaws at nanoscale [14], and hierarchical structures can highly improve the strength of nanomaterials [15]. Furthermore, there is an optimal hierarchy of load-bearing these nanomaterials [16]. Moreover, the graphene interfaces has a strong/weak duality to strengthen and self-heal nanolayered composites under shock loading [17]. However, compared to tensile loading, the mechanical resistance of graphene interfaces is quite weak under in-plane compression due to a low bending stiffness [18,19]. As we are aware, the mechanical response of graphene interfaces in composites under complex stress states has not been reported, especially under that with an in-plane compressed component [20].

As a primary deformation of structural materials, the shear response of nanomaterials was investigated due to important applications in engineering [21,22]. Though graphene has a theoretical in-plane shear strength of over 50 GPa, the structural buckling

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due to in-plane instability highly decreases the shear strength of suspended graphene [23]. High nonlinearity induced by structural buckling limits the utilization of graphene as structural materials [24]. Moreover, the chirality-dependent mechanical behaviors of graphene under compression such as bending [25], buckling [19] and twisting [26] have been observed, which is crucial in the design of anisotropic nanomaterials [27]. The metal layers in nanolayered composites can be considered as nanomaterials divided by graphene interfaces, whose shear strength is close to the theoretical limit at the nanometer scale [28–30]. In addition, it is found that interfaces in nanolayered composites can trap dislocations [31]. Thus, it is expected that graphene will improve the mechanical properties of graphene-metal nanolayered composites under shear deformation.

In this work, molecular dynamics (MD) and theoretical analysis are used to investigate the mechanical properties of graphene-copper nanolayered (GCuNL) composites under shear deformation. Our results reveal that the shear strength and toughness of GCuNL composites can be highly improved with less than 5 wt% graphene. This is resulted from a interfacial strengthening effect between graphene and copper layer. On one hand, the copper layers are constrained by graphene monolayers, which impedes the nucleation of dislocations and improves the shear strength of composites. On the other hand, the structural buckling of graphene is impeded by copper layers, which improves the shear toughness of composites due to the high in-plane strength of graphene. We studied the shear behaviors of GCuNL composites with different crystal orientation of copper layers and chirality of graphene monolayers, and an analytical analysis was performed to reveal the underlying mechanism. We found a self-healing effect induced by graphene during release process, and there was an optimum range of the interlayer distance between graphene monolayers in composites for strengthening and self-healing the GCuNL composites. It is expected that the strengthening and self-healing mechanism in this work would provide a valuable guideline for design and implementation of graphene composites.

2. Methods and models

The in-plane mechanical resistance of graphene is very strong, while the out-of-plane mechanical resistance of graphene is quite weak [18,19]. Meanwhile, the slip interfacial strength of GCuNL composites is very low (see the supplementary). Thus, it is expected that increasing the in-plane load percentage of graphene interfaces in GCuNL composites can lead to strengthening effect. The ideal shear strength of pure copper, which is the minimum shear stress to cause permanent deformation in a material without imperfections, is obtained in the close-packed (111) plane along the $[11\bar{2}]$ direction [29]. In addition, the strength of copper can be close to the theoretical limit at nanoscale, which is influenced by crystal orientations [32]. The chirality of graphene can be well controlled experimentally, while it is challenging to accurately control the crystal orientation of copper layers in GCuNL composites [11]. Thus, the strongest [100](100) and the weakest $[11\bar{2}]$ (111) stacking planes are both taken into account in this work. Besides, it has been demonstrated that the chirality plays an important role in the mechanical behaviors of graphene [19,23,33], which should also be taken into account. The two shear planes ((100) and (111)) of copper and the chirality (armchair and zigzag) of graphene are illustrated in Fig. 1a. Thus, there are four assemblies of GCuNL composites with different crystal stacking between graphene and copper layers: (100)-armchair, (100)-zigzag, (111)-armchair and (111)-zigzag.

Molecular dynamics (MD) simulations were performed using the publicly available simulation code Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [34]. The interactions between carbon atoms were described by adaptive intermolecular reactive empirical bond order (AIREBO) potential [35] with a cutoff of 2.0 Å for the Reactive Empirical Bond Order (REBO) part [36], and that between copper atoms were described by embedded atom model (EAM) [37]. Lennard-Jones (LJ) potentials were used to describe the interactions of carbon-copper [38]: the well-depth and size cross LJ parameters are 0.019996 eV and 3.225 Å. The LJ potential has been demonstrated suitable for studying the quasi-static [39] and shock loading [17] of GCuNL composites. The timestep was set as 1.0 fs. Visualization was performed using OVITO [40]. Before all shear simulations, initial configurations of graphene, copper and GCuNL composites were relaxed for 100 ps at 300 K in an isothermal-isobaric (NPT) ensemble to reach equilibrium state. Periodic boundaries were applied along x-, y- and z-axes in relaxing simulations. Thus, as shown in Fig. 1a, the length along x- and y-axes of simulation box should be proper to simultaneously include an integral number of periodic units of four types of GCuNL composites to avoid initial dislocations or stress. Additionally, for the GCuNL composites, the interlayer distance between graphene layers λ in composites should be integral multiple of copper crystal lattice ($\lambda = n \times$ Cu lattice) as illustrated in Fig. 1b, which is ranging from several to hundred nanometers experimentally [11].

To study the ideal shear behavior of GCuNL composites, infinite shear model [23] was simulated in our work. This infinite model is widely used to study the shear response of materials including heterostructures with interfaces [41]. As shown in Fig. 1c, the shear properties of bulk material were calculated by implementing the deformation-control method in a simulation box with periodic boundaries [30]. It has been demonstrated that MD results of this model for graphene are not sensitive to the strain rate [42]. For copper, the shear strain rate plays an important role in the critical stress and dislocation initialization. A discussion of shear strain rate in detail is given in the Supplementary: the load-release simulations of (111)-stacking copper under different shear strain rate are performed. As shown in Fig. S2, the percentage of residual dislocation atoms under 0.0001 ps^{-1} is same with that under shear strain rate of 0.001 ps^{-1}, and the slip bands in copper layers under 0.0001 ps^{-1} and 0.001 ps^{-1} are similar. When the shear strain rate is 0.01 ps^{-1}, the percentage of residual dislocation atoms increases to 9.3% as shown in Fig. S2c. Heino *et al.* demonstrated that the processes of dislocation initiation and propagation were independent of strain rate at least for time scales short enough to neglect creep and long enough with respect to the speed of sound and the system size when the shear strain rate was decreased to 30% in 200 ps (0.0015 ps^{-1}) [43]. Thus, here we applied the strain increment with strain rate of 0.001 ps^{-1} after every 1000 time steps in NVT ensemble at 300 K [23,30]. Li *et al.* found that the compressive nucleation stress of copper under 10^{-3} s^{-1} and 10^{8} s^{-1} was 1.3 GPa and 2.5 GPa [44]. It seems that the variation of critical stress with strain rate is not very sensitive (10^{11} times difference of strain rate while only 2 times difference of critical stress). We report the results with this shear strain rate, which is typical for MD simulations and consistent with previous theoretical results [28] and first-principle simulations [29]. The shear strain γ was calculated as δ_x/L_y, where δ_x is the displacement of deformation along x-axe and L_y is the length of simulation box along y-axis.

3. Results and discussion

3.1. The mechanical behavior of GCuNL composites under large shear deformation

To analyze the shear behavior of GCuNL, it is necessary to