Atomistic simulation of the nanoindentation behavior of graphene/Al multilayered nanocomposites

Jia-Qi Zhu, Xia Liu and Qing-Sheng Yang

Department of Engineering Mechanics, Beijing University of Technology, Beijing 100124, China

1 Corresponding author, Tel./Fax: +86-10-67396333, E-mail: qsyang@bjut.edu.cn

Abstract. In this paper, the mechanical behaviour of graphene/aluminum multilayered nanocomposites (GAMC) was studied by conducting the nanoindentation simulations using molecular dynamics (MD) method. The reinforcement effect of graphene on aluminum was investigated by two different cases: the graphene layers are considered as the reinforcement and the coating materials respectively. The microscopic deformation mechanism is investigated through the study of a hemispherical diamond indenter indenting against the monocrystalline Al and GAMC. For the graphene-coated Al composite (GCA), it is found that graphene coating layers have an effect on the characteristics of dislocation slip in Al matrix and improve the load carrying capacity of the GCA significantly. In addition, graphene-reinforced Al composite (GRA) with different spacing-distance of the graphene layers was investigated. It is concluded that the GRA shows an increasing nanoindentation properties with reducing the thickness of Al layers. Although the present research is based on monocrystalline aluminum, the deformation mechanism here can be applied to other face-centered-cubic (FCC) monocrystalline metals structures.

Keywords: Graphene/aluminum; Nanoindentation; Molecular dynamics

1. Introduction

Graphene, a single atomic monolayer of graphite discovered by Novoselov et al. [1], is particularly promising for protective coating in many applications such as microelectronic components [2] due to its ultralow friction [3], chemically inert and easy-controllability of growing on an arbitrary surface [4]. Besides, the previous investigations have demonstrated that graphene have extremely high strength and high modulus [5-7]. These excellent properties make them ideal candidates as advanced enhancement materials in metal matrix composites.

Contact is the normal working state of some micro-electronic devices in many applications, and the important characteristics of the contact interface and the mechanical properties of the substrate materials are important factors affecting the service life of the equipment [8]. Therefore, it is of great importance to investigate the surface behavior of the substrates. Recently, many attempts have been made to the studies of graphene coating system [9,10]. For example, it is demonstrated by He et al. [11] that graphene-coating can protect metal substrate from contact damage during a contacting process by homogenizing the contact stress. An atomistic simulation conducted by Yan et al. [12]. It is suggested that, with the presence of graphene coating, the contact stiffness, elastic capacity and the load bearing capacity are obviously improved compared with bare nickle. Nanoindentation and scratching of graphene-coated Pt were carried out by Klemenz et al. [13] and it is revealed that graphene coating substantially enhanced the load carrying capacity of the Pt substrate. The intrinsic mechanical properties of bare substrate are recovered after the graphene rupture. Subsequently, Zhao et al. [14]...
explored image and misfit stresses, which act as a barrier to impede dislocations to slip out of the copper surface. They found that the graphene coating also plays a role in strengthening of the substrate after the break of graphene. Besides the investigation on graphene coating system, there are continuous efforts have been devoted to the graphene/metal or graphene/polymer multilayered nanocomposites. For instance, Feng et al. [15] performed uniaxial compression tests on graphene/Al multilayered composite. They highlighted the importance of micro-structure during the stiffening, strengthening, and toughening of composites. Alian et al. [16] suggested that the graphene have a significant reinforcement effect on Polyethylene (PE) substrate as both coating materials and reinforcements through nanoindentation simulations. Although extensive efforts have been made in the areas of graphene/metal multilayered composite of their mechanical properties, there remains a lack of detailed analysis of their microstructural evolution and the strengthening mechanism of both of the GCA system and GRA system. The main goal of the present work is to provide a comprehensive investigation of the surface mechanical properties of GCA and GRA during the nanoindentation processes based on the MD method.

The number of graphene coating layers is determined according to different applications [17] and it is crucial to control it to fully exploit the excellent properties of graphene. In this study, the nanoindentation tests on GCA with different coating number were carried out using an MD method in an effort to provide useful insights into the enhancement effect of graphene on the surface mechanical properties of GCA. In addition, the multilayered system of GRA have also been investigated with taking the different thickness of Al layers in consideration. The present work based on the GRA and GCA models is of great importance to a deeper understanding of the indentation behavior of GAMC.

2. MD Model and Method of GAMC

2.1. MD models during simulations

The schematic of the nanoindentation model of monocrystalline Al with a FCC (face centered cubic) structure and the hemispherical indenter with a diamond structure are shown in Figure 1 and the initial distance between Al substrate and the indenter tip is 1 nm which is larger than the cut-off radius of the potential energy of 0.9 nm. To save time of the calculation and improve computational efficiency, we used a rigid [11] hemispherical indenter with a 3.0 nm radius and the wall thickness is set to 0.5 nm by deleting the central-part atoms. The size of the Al substrate is 15.89 nm×15.79 nm×11.69 nm which is about five times the tip radius [13]. Actually, graphene can be coated in any crystal surfaces by using the chemical vapor deposition (CVD) method. But only on the Al (111) can graphene have a relatively perfect structure [18]. Therefore, the graphene grown on the Al (111) substrate with different coating number is modelled in the present studies which are shown in Figure 2. In addition, the MD models of GRA nanocomposite with different Al-layer thickness are shown in Figure 3. The total thickness of Al substrate is kept constant while the number of graphene layers and the Al-layer thickness are varied. As shown in Figure 3, the Al-layer thickness are 11.69 nm, 5.85 nm and 3.90 nm, respectively with the number of reinforcing graphene layers ranged from one to three.

Figure 1. MD simulation model: (a) Schematic of the nanoindentation model of monocrystalline Al (b) the hemispherical indenter
Figure 2. Graphene layers are considered as coating materials: GCA with mono-, bi-, and tri-layers of graphene coating.

Figure 3. Graphene/Al multilayered composite system in which graphene layers are considered as reinforcements in aluminum.

2.2. MD simulations
All the MD simulations for the GCA and GRA composites were carried out using a Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS). During the simulations, interactions between Al atoms were modelled using the embedded atom model (EAM) potential [19]. The adaptive intermolecular reactive empirical bond order (AIREBO) potential [20] was used to model the graphene sheets and the diamond indenter. In addition, the van der Waals interactions were modelled using the 12-6 Lennard-Jones (LJ) potential [21]. The relevant parameters are \( \varepsilon=0.035078 \text{ eV} \) and \( \sigma=3.0135 \text{ Å} \) for the C-Al interface [21] and \( \varepsilon=0.00286 \text{ eV} \) and \( \sigma=3.47 \text{ Å} \) for the interactions between indenter and graphene layers [22]. The function of these potentials were briefly introduced as follows.

In terms of the EAM potential, the total energy \( E_i \) was given by

\[
E_i = F_\alpha \left( \sum_{j\neq i} \rho \beta(r_{ij}) + \frac{1}{2} \sum_{j\neq i} \phi \alpha \beta(r_{ij}) \right)
\]

(1)

where \( F \) is the embedding energy, \( \rho \) is the electron density, \( \phi \) is the pair potential interaction, and \( \alpha \) and \( \beta \) are the element types of atoms \( i \) and \( j \), respectively. The multi-body nature of the EAM potential is a result of the embedding energy term. Both summations in the formula are over all neighbors \( j \) of atom \( i \) within the cutoff distance.

For the AIREBO potential, the total energy consists of three terms:

\[
E = \frac{1}{2} \sum_i \left( E_i^{\text{REBO}} + E_i^{\text{LJ}} + \sum_k \sum_{i\neq j} E_{ij}^{\text{TORSION}} \right)
\]

(2)

The standard 6-12 Lennard-Jones potential was used to compute the interactions between Al and carbon atoms, which was given by

\[
E = 4\varepsilon \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \quad r < r_c
\]

(3)

where the parameters \( \varepsilon \) and \( \sigma \) are introduced above and the cutoff distance \( r_c \) is 8.5 Å [23].

During the MD simulations, periodic boundary conditions were applied along x and y directions and the free boundary was applied along z direction. First, the whole system was subjected to an energy-minimization process with a specified energy and the force tolerance of 1x10-12 by iteratively adjusting the atom coordinates. Then, a relaxation process (50 ps) was conducted using an NPT ensemble (Nose/Hoover isobaric-isothermal ensemble). The system temperature is kept at 1 K to avoid the effect of thermal fluctuation. The time step for one integration was set to 0.001 ps. The
microstructure of the MD models was optimized when the system potential energy converged. During indentation, the Al atoms in the bottom three layers are fixed to prevent the movement of the substrate. Then, the indenter moves down and penetrates into the Al substrate, the GCA and GRA system at a NVE ensemble at a speed of 0.1 nm/ps with a maximum displacement of 4 nm. Finally, the indenter moves up to the initial position with the same speed.

After the simulations, the Open Visualization Tool (OVITO) [24] was used to reveal and analyse the dislocation movements within the deformed structures.

3. Results and discussion

3.1. Nanoindentation on GCA with different number of graphene coating layers.

Figure 4 shows the indentation force-displacement curves of GCA with different graphene coating layers. During the simulations of GCA system, it can be clearly seen that the GCA system shows a better indentation behavior with the number of the graphene coating layers increases. The indentation resistance of GCA system is much higher than that of bare Al due to the presence of graphene layers. The first drop of the indentation force curves mean the transition from the elastic stage to the plastic stage caused by the generation of the dislocations. The indentation forces of the bare Al, mono-, bi- and tri layers GCA at the end of the elastic stage are 44.84 eV/Å, 121.97 eV/Å, 193.43 eV/Å and 231.36 eV/Å, respectively – corresponding to points a-d in Figure 4. The maximum indentation force are 237.29 eV/Å, 534.33 eV/Å, 786.02 eV/Å and 968.52 eV/Å, respectively, corresponding to points e to h in Figure 4. Figure 5 shows the atomic configuration of the deformed GCA structure – corresponding to points a to h in Figure 4. The coloring of the Al atoms is according to the different atomic structure: Green represent for the FCC structure, red represent for the HCP structure and white represent for the other structure. The Al atoms with perfect FCC structure were deleted to obtain a clearer observation of the dislocation expansion. It can be seen from the Figure 5(a)-(d) that the resistance of dislocation nucleation in the GCA system is higher than that of bare Al which caused a longer elastic stage compared with bare Al. As can be seen in Figure 5(e-h), dislocations occurred beneath the indenter and dislocation loops continuously moved to the interior of Al substrate. While in the GCA system, the most obvious difference is that dislocations glide on the slip plane parallel to the interface between Al substrate and graphene.

![Figure 4. Indentation force-displacement curves of GCA with different number of graphene coating layers.](image-url)
Figure 5. Atomic configurations of the deformed GCA structure: (a) bare Al at D=12 Å, (b) monolayer GCA at D=14 Å, (c) bilayer GCA at D=16 Å, (d) trilayer GCA at D=17 Å, (e-h) bare Al, mono-, bi- and tri-layer of GCA at the maximum displacement (D=40 Å).

The top view and the cross-section of the displacement distribution of Al atoms at D=3 nm are shown in Figure 6 and Figure 7, respectively, where blue represents zero displacement and red represents the maximum displacement. It is obvious that the most displaced Al atoms are under the indenter within bare Al while a larger area of Al atoms displaced due to the presence of graphene coating layers. In theoretically, part of the strain energy will be relaxed if dislocations are near a free surface. Thus, dislocations tend to slip out of the surface in order to reduce energy which means that free surfaces are attractive to dislocations. Therefore, the dislocations are easily to slip out of the surface during the indentation of bare Al and the Al atoms piled up around the indenter as shown in Figure 7(a). But it is difficult for dislocations to release at the interface between Al and graphene layers. This is because the interactions between the dislocations and the interface which is called image stress. The shear modulus mismatch between Al and graphene caused the image stress which will affect the movement of dislocations. With the addition of graphene coating layers, the dislocations within the Al substrate need to conquer the barrier stress, image stress, to slip out of the surface, that’s one of the strengthening mechanism of graphene coating layers on Al substrate.

Figure 6. Top view of the displacement distribution of Al atoms at D=3 nm. (a) bare Al, (b) monolayer graphene-coated Al, (c) bilayer graphene-coated Al, (d) trilayer graphene-coated Al.

Figure 7. Cross-sectional displacement distribution of Al atoms at D=3 nm. (a) bare Al, (b) monolayer graphene-coated Al, (c) bilayers graphene-coated Al, (d) trilayer graphene-coated Al.
3.2. **Nanoindentation on GRA with different Al-layer thickness.**

In order to investigate the indentation performance of the GRA with different Al-layer thickness, the indentation simulations are carried out on GRA consisted of different number of graphene/Al layers. Figure 8 shows the nanoindentation force-displacement curves of GRA with different Al-layer thickness. It can be clearly seen that the indentation resistance increases significantly due to the reinforcing effect of graphene. While at the maximum indenter displacement, the indentation force of the bare Al, monolayer system of GRA, bilayer system of GRA and trilayer system of GRA are 237.29 eV/Å, 534.33 eV/Å, 592.15 eV/Å and 610.39 eV/Å, respectively. Meanwhile, the indentation behavior of the GRA is better with a smaller Al-layer thickness. Bare Al under indentation entered plastic stage at D=12 Å while the GRA with of Al-layer thick of 11.69 nm, 5.85 nm and 3.90 nm entered the plastic stage at about D=13.7 Å, D=14.1 Å and D= 14.7 Å, respectively – corresponding to points b-d in Figure 8, which are all later than that of bare Al – corresponding to point a in Figure 8. This means that the elastic stage of the GRA under nanoindentation will increases with the decrease of the Al-layer thickness. To further confirm the reinforcing effect of graphene layers, the atomic configurations of the deformed GRA structure at D=14 Å are shown in Figure 9. It is obviously that dislocations nucleated at the surface of the bare Al and a fewer dislocations occurred at the surface of Al in the monolayer GRA system while there is no dislocation nucleation in the bilayer and trilayer GRA systems. This indicates that the multilayered GRA system with a smaller Al-layer thickness is still at the elastic stage which is consistent with the previous conclusion mentioned above.

![Figure 8. Indentation force-displacement curves of GRA with different Al-layer thickness.](image)

An important strengthening mechanism in the multilayered GRA system is the dislocation-blocking effect [25] caused by graphene layers. The atomic configurations of the deformed GCA structure at D=35 Å are shown in Figure 10. The dislocations move freely in the Al substrate without the effect of graphene which will cause a small indentation resistance, as shown in Figure 10(a). While in the GRA multilayered system, the first layer of graphene affected the movement of the dislocations as discussed before. In addition, the graphene layers embedded in Al substrate can block the dislocations and confine the dislocations at the first layer of Al substrate. Then the dislocations piled up and interacted with each other which are the main reason for the strengthening effect of graphene layers as shown in Figure 10(c) and (d). As the decreasing of the Al-layer thickness, both the indentation force on the second graphene layer and the dislocations density of the first Al layer are increased because the continuous increase of the indentation displacement and the much pile-ups of dislocations at the
interface between the Al substrate and the graphene reinforcements. It can be inferred that if the Al-layer thickness within the GRA system continues to decrease, new dislocations will nucleate beneath the second graphene layer and expand to the interior under the same indentation loading.

![Figure 9](image)

**Figure 9.** Atomic configurations of the deformed GRA structure at D=14 Å: (a) bare Al, (b) monolayer GRA, (c) bilayer GRA, (d) trilayer GRA.

![Figure 10](image)

**Figure 10.** Atomic configurations of the deformed GCA structure at D=35 Å: (a) bare Al, (b) monolayer GCA, (c) bilayer GCA, (d) trilayer GCA.

4. Conclusions

In this study, the surface mechanical properties of the GCA system and GRA system were studied by nanoindentation simulations using a molecular dynamics method and revealed the mechanism of the strengthening effect of graphene on Al.

1. There are many pile-ups of Al atoms around the indenter during the indentation on bare Al but not in the GCA system. The presence of graphene coatings caused a great difference of dislocation expansion compared with bare Al, that is, dislocations expanded parallel to the interface. Nevertheless, the image stress between graphene coatings and Al substrate caused by the shear modulus mismatch can affect the movement of the dislocations. It can hinder the dislocations to slip out of the surface which can increase the indentation resistance and then lead to a better indentation behavior of GCA.

2. It can be concluded that the indentation properties of GCA improved with the increase of the number of graphene coating layers. The GCA with more graphene coating layers has a longer elastic stage and larger indentation resistance.

3. During the nanoindentation simulations of the multilayered GRA system, it is proved that the presence of graphene layers can block the dislocations and confine many dislocations in one layer of Al substrate which contribute to the strengthening effect of graphene on Al. Moreover, the graphene/Al nanocomposite with a smaller Al-layer thickness shows a better indentation properties.

Acknowledgment

This work is supported by the Natural Science Foundation of China (11472020, 11772012, 11872079 and 11632005), and the General Program of Science and Technology Development Project from Beijing Municipal Education Commission (KM201810005002).

References

[1] Novoselov KS, Geim AK, Morozov SV, Jiang D, Zhang Y, Dubonos SV, et al. 2004 Electric field effect in atomically thin carbon films. *Science*. **306** 666-9.

[2] Prasai D, Tuburquia JC, Harl RR, Jennings GK, Bolotin KI. 2012 Graphene: Corrosion-inhibiting coating. *Acs Nano*. **6** 1102-8.

[3] Liu Z, Yang J, Grey F, et al. Observation of microscale superlubricity in graphite. 2012 *Phys Rev Lett*, **108** 205503.
[4] Li X, Cai W, An J, Kim S, Nah J, Yang D, et al. 2009 Large-Area Synthesis of High-Quality and Uniform Graphene Films on Copper Foils. Science. 324 1312-4.
[5] Lee C, Wei X, Kysar JW, Hone J. 2008 Measurement of the elastic properties and intrinsic strength of monolayer graphene. Science. 321 385-8.
[6] Wang L, Yang Z, Cui Y, Wei B, Xu S, Sheng J, et al. 2017 Graphene-cooper composite with micro-layered grains and ultrahigh strength. Sci Rep-Uk. 7 41896.
[7] Zhu Y, Murali S, Cai W, Li X, Sük JW, Potts JR, et al. 2010 Graphene and graphene oxide: synthesis, properties, and applications. Adv Mater. 22 3906-24.
[8] Toler BF, Coutu RA, McBride JW. 2013 A review of micro-contact physics for microelectromechanical systems (MEMS) metal contact switches. J Micromech Microeng. 23 103001.
[9] Nine MJ, Cole MA, Tran DNH, Losic D. 2015 Graphene: a multipurpose material for protective coatings. J Mater Chem A. 3 1258-62.
[10] Qi Y, Liu J, Zhang J, Dong Y, Li Q. 2016 Wear resistance limited by step edge failure: the rise and fall of graphene as an atomically thin lubricating material. Acs Appl Mater Inter. 9 1099-106.
[11] He X, Bai Q, Shen R. 2018 Atomistic perspective of how graphene protects metal substrate from surface damage in rough contacts. Carbon. 130 672-9.
[12] Yan Y, Zhou S, Liu S. 2017 Atomistic simulation on nanomechanical response of indented graphene/nickel system. Comp Mater Sci. 130 16-20.
[13] Klemenz A, Pastewka L, Balakrishna SG, Caron A, Bennewitz R, Moseler M. 2014 Atomic scale mechanisms of friction reduction and wear protection by graphene. Nano Lett. 14 7145-52.
[14] Zhao Y, Peng X, Fu T, Zhu X, Hu N, Yan C. 2018 Strengthening mechanisms of graphene coated copper under nanoindentation. Comp Mater Sci. 144 42-9.
[15] Feng S, Guo Q, Li Z, Fan G, Li Z, Xiong D, et al. 2017 Strengthening and toughening mechanisms in graphene-Al nanolaminated composite micro-pillars. Acta Mater. 125 98-108.
[16] Alian AR, Dewapriya MAN, Meguid SA. 2017 Molecular dynamics study of the reinforcement effect of graphene in multilayered polymer nanocomposites. Mater Design. 124 47-57.
[17] Yao Y, Li Z, Lin Z, Moon K, Agar J, Wong C. 2011 Controlled growth of multilayer, few-layer, and single-layer graphene on metal substrates. J Phys Chem C. 115 5232-8.
[18] Tao L, Lee J, Chou H, Holt M, Ruoff RS, Akinwande D. 2012 Synthesis of high quality monolayer graphene at reduced temperature on hydrogen-enriched evaporated copper (111) films. Acs Nano. 6 2319-25.
[19] Daw MS, Baskes MI. 1984 Embedded-atom method - derivation and application to impurities, surfaces, and other defects in metals. Phys Rev B. 29 6443-53.
[20] Brenner DW, Shenderova OA, Harrison JA, Stuart SJ, Ni B, Sinnott SB. 2002 A second-generation reactive empirical bond order (REBO) potential energy expression for hydrocarbons. J Phys-Condens Mat. 14 783-802.
[21] Silvestre N, Faria B, Canongia Lopes JN. 2014 Compressive behavior of CNT-reinforced aluminum composites using molecular dynamics. Compos Sci Technol. 90 16-24.
[22] Wang W, Peng Q, Dai Y, Qian Z, Liu S. 2016 Distinctive nanofriction of graphene coated copper foil. Comp Mater Sci. 117 406-11.
[23] Zhu J, Yang Q, He X, Fu K. 2018 Micro-mechanism of interfacial separation and slippage of graphene/aluminum nanolaminated composites. Nanomaterials. 8 1046.
[24] Stukowski A. 2010 Visualization and analysis of atomistic simulation data with OVITO-the Open Visualization Tool. Model Simul Mater Sc. 18 2154-62.
[25] Zhang JY, Liu G, Sun J. 2013 Strain rate effects on the mechanical response in multi- and single-crystalline Cu micropillars: grain boundary effects. Int J Plasticity. 50 1-17.