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The Effect of Ion Irradiation Induced Defects on Mechanical Properties of Graphene/Copper Layered Nanocomposites

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Abstract: One of the miraculous functions of graphene is to use its defects to alter the material properties of graphene composites and, thereby, expand the application of graphene in other fields. In this paper, various defects have been created in graphene by using ion irradiation. Defective graphene is sandwiched between two copper layers. A numerical model of Graphene/Copper layered composites after irradiation damage was established by the molecular dynamics method. The effects of ion irradiation and temperature coupling on defective graphene/copper composites were studied. The results show that there are a lot of empty defects in graphene after irradiation injury, which will produce more incomplete bonding. Although the bonds between carbon atoms can be weakened, defective graphene still enhances the mechanical properties of pure copper. At the same time, the location and arrangement of defects have a great influence on the mechanical stability of graphene/copper composites, and the arrangement of empty defects has different effects on deformation behavior and the stress transfer mechanism. It can be concluded that the defects formed by radiation have an effect on the physical properties of two-dimensional materials. Therefore, irradiation technology can be used to artificially control the formation of defects, and then make appropriate adjustments to their properties. This can not only optimize the radiation resistance and mechanical properties of nuclear materials, but also expand the application of graphene in electronic devices and other fields.

Keywords: graphene/copper layered composites; ion irradiation; defects; temperature; mechanical properties

1. Introduction

Graphene sheets-one-atom-thick two-dimensional layers of sp^2-bonded carbon were prepared by Geim et al. in 2004 [1]. Graphene exhibits excellent physical and mechanical properties (Young's modulus is 1100 GPa, fracture strength is 125 GPa [2]), and its specific surface area can reach 2630 m^2/g [3]. Meanwhile, it has good thermal performance [4] and excellent electrical performance (band gap is about 0, carrier mobility is 2×10^5cm^2·V^{-1}·s^{-1} [5]).

The existence of defects is unavoidable in the preparation process of graphene. Due to the defects of graphene, its chemical and mechanical properties have changed [6–10]. Although these changes worsen the properties of graphene, defects are not all harmful [11,12]. Controllable defects can expand the application of graphene in sensors, electronic containers, and so on. In addition, the existence of defects may play a beneficial role in the interaction between graphene-reinforced matrix composites [13,14].

Graphene can be modified and cut during the particle irradiation, and, as a result, it can change the physical and chemical properties of graphene as needed [15,16]. Recent research shows [17–19] that the graphene and its composites can be tailored, modified, and structurally designed by using irradiation technology, which can achieve the purpose of precise control performance. For example, the effects of different ions, different incident angles, and different incident energies on the properties of graphene were studied, and the Monte Carlo method for the morphological changes of graphene during irradiation was established by Lehtinen [20]. The effect of ion irradiation on the deformation of graphene was studied by Terdalkar et al. [21] through molecular dynamics simulation. The results show that irradiation energy and irradiation angle play a key role in the type and quantity of defects.

Irradiation technology can be used to artificially control the formation of defects, and then make appropriate adjustments to their properties. Moreover, irradiation technology can open the band gap of graphene, and expand the application of graphene/metal composites in electronic devices and other fields. In addition, various defects can also be created by using ion irradiation, to modulate the electrothermal properties of graphene and graphene/metal composites.

Although atomic irradiation technology is an important means of graphene processing and modification, there is little research on graphene-reinforced metal matrix composites. What is the effect of temperature and ion radiation coupling on the mechanical properties of graphene/copper layered composites, whether decreasing or increasing, or keeping unchanged? Most importantly, how will various defects in the most important part of graphene/copper layered composites under the different temperatures affect the mechanical properties we expect to see? In this paper, various defects have been created in graphene by using ion irradiation, and defective graphene is sandwiched between two copper layers. A numerical model of irradiation damage of graphene/copper composites is established by the molecular dynamics method. The effects of ion irradiation and temperature coupling on defective graphene/copper composites were studied, which is helpful for understanding and controlling the mechanical properties of the composites.

2. Molecular Dynamics Model and Method

The model was simulated by using molecular dynamics software LAMMPS [22].

2.1. Irradiation Model and Method

Unfortunately, due to the limitation of the preparation technology of graphene and its composites, it is difficult to obtain perfect graphene/copper composites in actual production, and there are inevitably empty defects in the composites. These defects will affect properties of composites. Therefore, this paper uses ion irradiation to form various defects in composites in order to study the effect of irradiation-induced vacancy defects on properties of composites. The defect statistics include single empty space, double vacancy, and complex defects, and exclude adsorption defects.

The incident particles will collide with the target atom under irradiation conditions. If the collision energy reaches the departure threshold of the target atom, the target atom leaves the initial position and forms a vacancy defect. In this section, the graphene model was irradiated by carbon atoms. The size of monolayer graphene is 100 Å × 100 Å. Carbon atoms do not exist in graphene, while these carbon atoms are named group-1. In addition, carbon atoms exist in graphene, while these carbon atoms are named group-2. The carbon particle of group-1 is initially located 4 nm above the graphene. Carbon with 1 keV are vertically incident on graphene samples. The radiation model is achieved by collisions between incident particles and graphene. The interaction of group-1 and group-2 is described by the Tersoff/ZBL potential function. The Tersoff/ZBL potential function is a potential formed by smoothly connecting the multi-body Tersoff function [23] and the Ziegler-Biersack-Littmark (ZBL) universal shielding function [24]. It can describe the collision process between the incident particle and the target atom.

Eventually, for a more authentic irradiation process, the incident position of the particle is randomly generated by the computer, and then the particle occurs on the surface of graphene. After each incident particle is completed, the model relaxes by 1 pico-second (ps). The initial temperature of the model is restored to 300 K, and then the next particle is incident on graphene until the radiation dose is complete. In this paper, graphene is irradiated at random positions by 10, 20, 30, and 40 carbon atoms, respectively. After irradiation, many empty defects are formed in graphene, as shown in Figure 1.

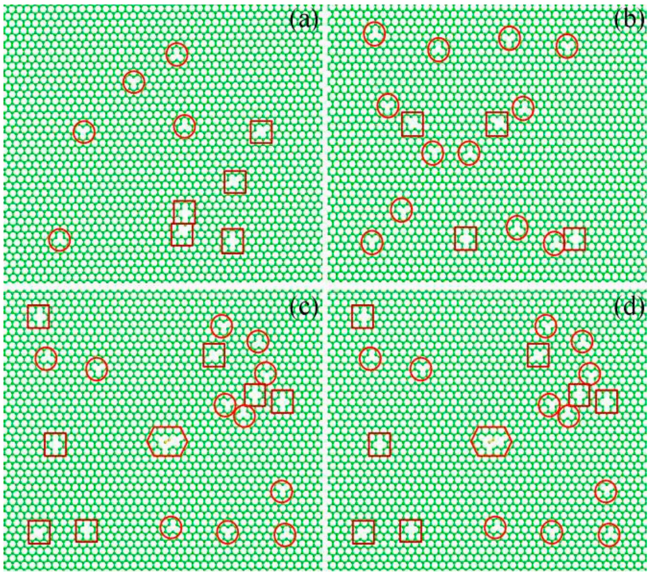
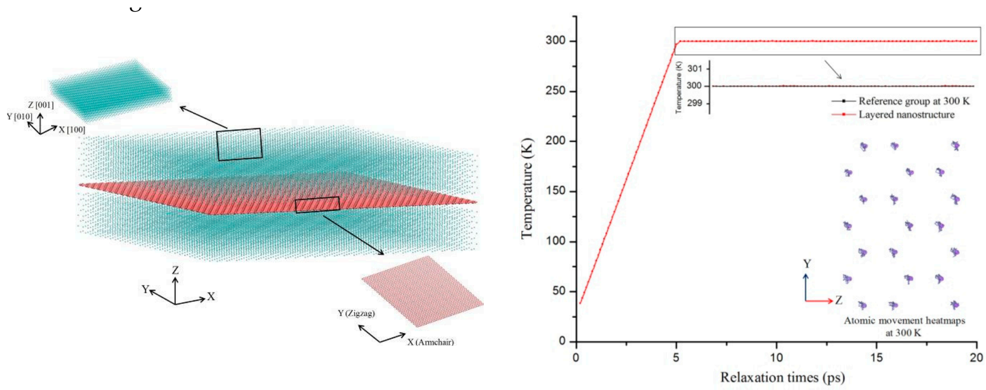


Figure 1. Configuration of graphene irradiated by a different number of incident carbon atoms (circular represents single vacancy (SV), square represents double vacancy (DV), and hexagon represents complex defects (CD)). (**a**) ion dose: 10 (SV: 5; DV: 5), (**b**) ion dose: 20 (SV: 12; DV: 4), (**c**) ion dose: 30 (SV: 11; DV: 7; CD: 1), and (**d**) ion dose: 40 (SV: 19; DV: 10; CD: 2).

2.2. Mechanical Models and Methods of Graphene/Copper Layered Composites

The perfect graphene/copper layered composites (referred to as PGC for simplicity) were prepared by inserting the perfect graphene reinforced material into the single crystal copper matrix, as shown in Figure 2. The size of graphene reinforced material is 100 Å × 100 Å. The thickness of graphene is 3.35 Å. The X end is the direction of the armchair, and the Y end is the direction of the Zigzag. The size of single crystal copper is 100 Å × 100 Å × 14.46 Å, and the crystal orientation index is [100], [010], and [001] in three directions of X, Y, and Z, respectively. Similarly, defective graphene is also sandwiched between two copper layers. All the cases are similar to the above section.



(**a**) (**b**)

Figure 2. Graphene/copper layered composites. (**a**) Perspective side-view of graphene/copper layered composites model. Blue color represents copper atoms and red color represents carbon atoms. (**b**) Relaxation process of layered composites.

Perspective side-view of graphene/copper layered composites model and its relaxation process are shown in Figure 2.

Huang et al. [25] found that layered structures can effectively improve the mechanical properties and interfacial stability of graphene/copper composites. To avoid the initial dislocation or stress generation, the length of the analog box along the X and Y axes should be set to an integer multiple of the diameter of the graphene/copper composites, and the insertion position of graphene is the integer lattice constant of copper [26]. The X, Y, and Z directions are periodic conditions, the time step is 0.4 fs, and the fastest descent method is used to minimize the energy of the structure. Get the initial balance configuration of the model. Before stretching the simulation, the model is loosened by 20 ps using constant temperature and pressure (NPT), and the temperature is controlled by the Nosé-Hoover method. Then, the strain rate of 0.002 nm/ps is applied along the X direction, and the failure process under the conditions of 300 K, 600 K, 900 K, and 1200 K is simulated by the NPT ensemble. The interaction between Cu-Cu atoms is characterized by the Embeded-Atom Method (EAM) potential, which was investigated by Guo [27], Wu [28], and Duan et al. [29]. The interaction between carbon atoms in the graphene is characterized by tersoff potential, which was investigated by Iwata et al. [30]. Another point is that the interactions between copper and carbon atoms should be characterized by Lennard Jones (LJ) potential. In the previous study, Duan [29] and Liu [26,31] found that the LJ potential successfully described the characteristics of interactions between copper and carbon atoms. Table 1 shows parameters of the LJ potential for the interactions between copper and carbon atoms.

Table 1. Parameters of the LJ potential for the interactions between copper and carbon atoms.

Atoms	ε (eV)	σ (Å)	Reference
Copper-carbon	0.01996	3.225	[26,29]

3. Results and Discussion

3.1. Validation

To verify the simulation, Tables 2 and 3 show the results of previous work compared with the three mechanical values of single crystal copper and graphene/copper layered composites in this study.

Table 2. The results of previous work compared with the three mechanical values of the single crystal copper in this study.

Copper Types	Assessment Method (Potential)	Temperature (K)	Failure Strain	Failure Strength (GPa)	Young's Modulus (GPa)	Reference
single-crystal	Eam	300	0.124	6.19	51	Present study
single-crystal	Eam	293	-	10.83	59.78	Guo et al. [27]
single-crystal	Eam	300	0.115	7.11	62	Wu et al. [28]
single-crystal	Eam	300	0.133	5.5-5.8	42.16	Duan et al. [29]

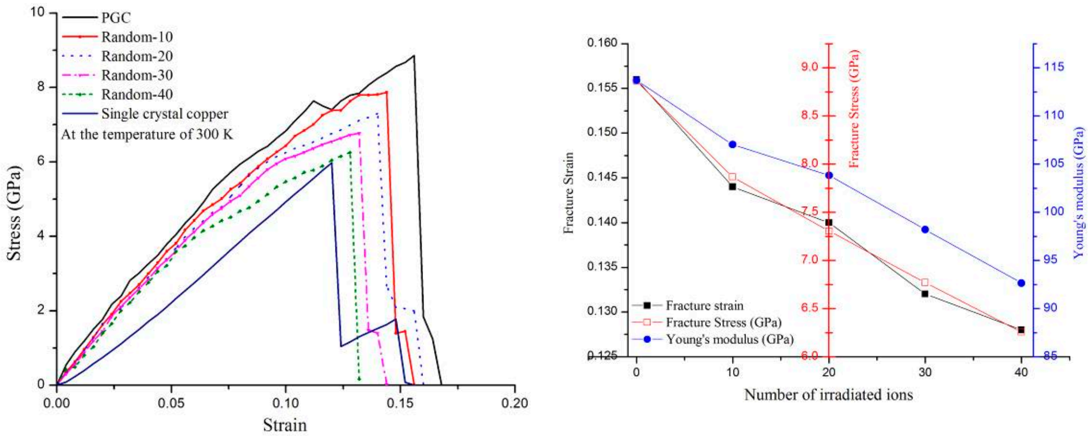
Table 3. The results of previous work compared with the three mechanical values of graphene/copper layered composites in this study.

Various Types of Graphene	Temperature (K)	Failure Strain	Failure Strength (GPa)	Young's Modulus (GPa)	Reference
AC	300	0.156	8.86	113.68	Present study
AC	300	0.12-0.13	10-11	-	Guo et al. [32]
AC	300	0.157	7.4	102.05	Duan et al. [29]
ZZ	300	0.2	10.24	111.81	

As shown in Tables 2 and 3, the comparison shows that the calculation method and the selection of the potential function are very reasonable, and the results obtained are also very consistent with previous work. For example, Young's modulus of graphene/copper layered composites in this study was found to be 113.68 GPa. This value in the study has approached the previous simulation value of 102.05 GPa. Again, fracture stress and strain in the study has also approached results from the previous work.

3.2. Effects of Different Doses of Ions Irradiation Induced Defects

Stress-strain curves and mechanical values of graphene/copper layered composites and single crystal copper are shown in Figure 3. It is noted that the failure strength of the PGC is 8.86 GPa at 300 K, while the failure strength of pure copper is 6.19 GPa in the same condition. Compared with pure copper, the failure strength of is increased by 43.13%. Clearly, graphene as a reinforcement material greatly improves the strength of monocrystalline copper. However, graphene is prone to defects in the preparation process. Therefore, it is necessary to study the effect of defective graphene on the properties of composites. In this section, different locations and types of defects are produced in graphene by using different doses of ionic radiation, including 10, 20, 30, and 40 carbon atoms. Graphene with various defects is then inserted between two copper blocks as reinforcement material. It should be noted that the mechanical values of random −10, −20, −30, and −40 with temperature changes are obtained by an average of three sets of data, respectively.



(**a**) (**b**)

Figure 3. Mechanical properties of graphene/copper layered composites. (**a**) Stress-strain curves and (**b**) mechanical values of graphene/copper layered composites and single crystal copper (Random −10, −20, −30, and −40 represent graphene/copper layered composites with various defects, which are created by using 10, 20, 30, and 40 doses of atoms, respectively.).

It is observed that mechanical properties of graphene/copper layered composites show a decreasing trend with an increase in the number of defects (increase in the dose of ion irradiation). When the dose of ion irradiation increases from 0 to 40, the fracture strength decreases from 8.86 to 6.25 GPa with a 29.46% reduction at 300 K. The fracture strength of Random-40 is very close to that of a single crystal copper (6.19 GPa). Another important point is that defects have the greatest influence on the fracture stress of PGC, which is followed by the fracture strain and Young's modulus, when the dose of ion irradiation increases. For example, fracture strength of graphene/copper layered composites varies from 8.86 to 6.77 GPa with a 23.59% reduction when the dose of ion irradiation is increased from 0 to 30, at 300 K. At the same time, the fracture strain and Young's modulus of composites decreased by only 15.39% and 13.61%, respectively.

Figures 4 and 5 show the fracture process and stress distribution of PGC and Random-20 under single-axis tensile loads at 300 K temperature, respectively. Clearly, the existence of defects reduces the nature of PGC. At the same time, it was observed that, when the hexagonal elements of graphene were damaged or broken by tensile loads, the composite system was also destroyed. Therefore, we can conclude that graphene plays a key role in the mechanical properties of composite systems. In addition, it should be mentioned that there is a significant difference between the fracture process and the original model of the defective graphene/copper layer composites after irradiation. The graphene/copper layer composites (PGC) break from the edges and extend inward along a straight line. However, the initial fracture position and fracture direction of the defective graphene/copper composite composites after irradiation are closely related to the location of a defect band and atomic lattice vacancies in the defect band.

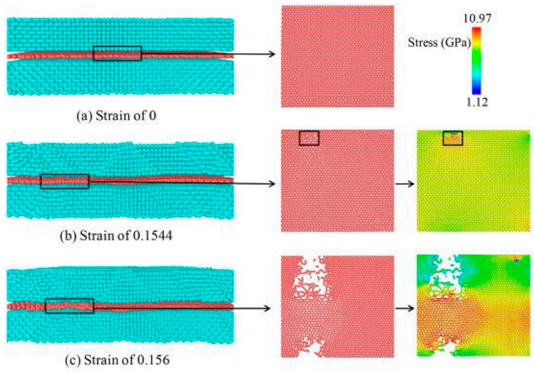


Figure 4. Fracture process and stress distribution of PGC under uniaxial tensile loading at the temperature of 300 K. (**a**) ε = 0 before the load is applied. (**b**) ε = 0.1544 before reaching the stress limit. (**c**) ε = 0.156 after Fracture Failure.

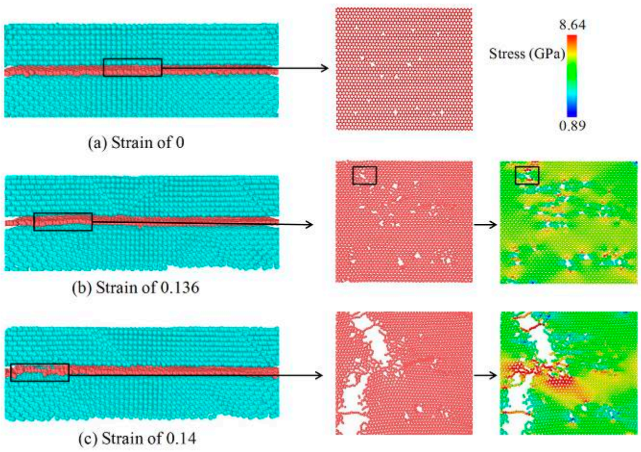


Figure 5. Fracture process and stress distribution of Random-20 under uniaxial tensile loading at the temperature of 300 K. (**a**) ε = 0 before the load is applied. (**b**) ε = 0.136 before reaching the stress limit. (**c**) ε = 0.14 after fracture failure.

3.3. Coupling Effect of Ion Irradiation and Temperature

What is the effect of temperature and ion radiation coupling on the mechanical properties of graphene/copper layered composites, whether decreasing or increasing, or keeping unchanged? Most importantly, how much is the effect of the coupling of radiation and temperature on the mechanical properties of composites? Hence, we explore temperature and ion radiation coupling on the mechanical properties of graphene/copper layered composites.

Figure 6 shows the effect of ion irradiation and temperature coupling on mechanical properties of graphene/copper layered composites in different cases. It is observed that the mechanical properties of graphene/copper layered composites decrease with the increase of temperature (when the temperature increases from 300 K to 1200 K). In addition, it should be mentioned that, with the increase of temperature and the ion irradiation dose, the mechanical properties of defective graphene/copper composites decreased sharply, and the extent of the decrease for defective graphene/copper layered composites was higher than that of defect-free graphene/copper layered composites. Graphene contains a large number of vacancy defects after irradiation damage. These "defective carbon atoms" are in a semi-active state. With the increase of temperature, carbon atoms are more likely to exceed constraints of binding energy, and break away from the stable state. As a result, the more carbon atoms are eliminated after radiation damage, the more the mechanical properties of graphene/copper composites are reduced and decreased when the temperature increases from 300 K to 1200 K.

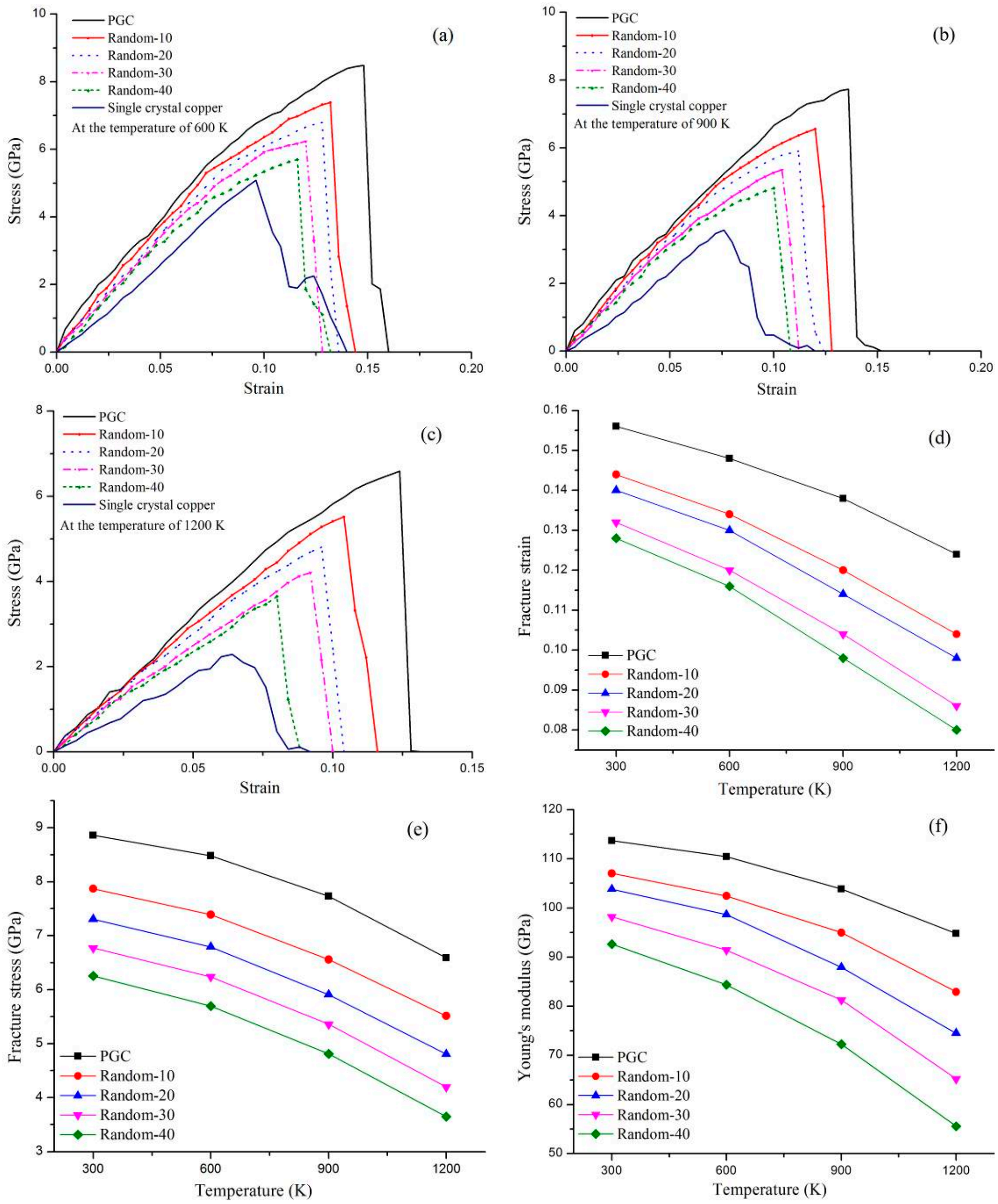


Figure 6. Effect of ion irradiation and temperature coupling on mechanical properties of graphene/copper layered composites in different cases. Stress-strain curve of the simulated model at (**a**) the temperature of 600 K, at (**b**) the temperature of 900 K, and at (**c**) the temperature of 1200 K. (**d**–**f**) Variations of fracture strain, fracture stress, and Young's modulus values of graphene/copper layered composites at different temperatures.

3.4. Coupling Effect of Defects Distribution and Temperature

The random defects (Random-20) in the previous section are replaced by the centerline, the eccentric line, and block corner defects, in the same conditions. Centerline, eccentric line, and block corner defects are created in graphene/copper layered composites, and we studied the effect of defect distribution on mechanical properties of graphene/copper layered composites. Figure 7 shows the local side view of graphene with various defects inserted into copper.

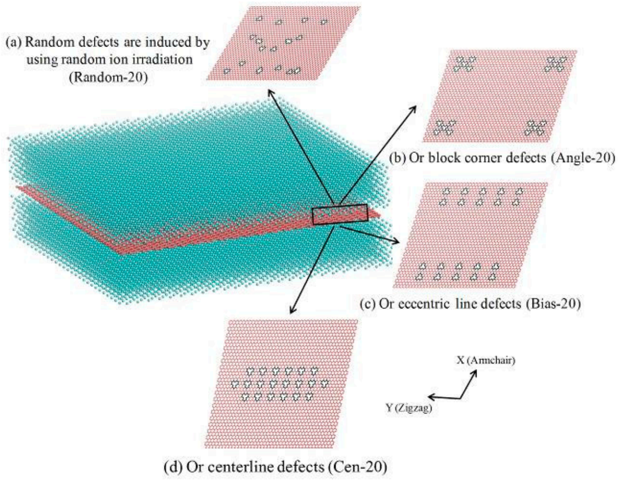


Figure 7. Local side view of graphene with various defects inserted into copper. (**a**) Random defects are induced by 20 randomly ions irradiation. (**b**) Block corner, (**c**) eccentric line, and (**d**) centerline defects are created in graphene by using 20 directional ions irradiation.

Figure 8 shows mechanical value of graphene/copper layered composites with different types of defects at different temperatures. In order to ensure the reliability of random defects (Random-20), random defects are obtained from the average of three groups, which is different from random-20 in the previous section.

It is found that, regardless of the types of defect distribution, the effect of defects on fracture stress of composites is the greatest, followed by fracture strain and, lastly, Young's modulus. For example, compared with graphene/copper layered composites, the fracture stress of Angle-20 decreases from 8.86 to 7.379 GPa with a 16.72% reduction when the temperature is 300 K, while the Young's modulus and fracture strain of Angle-20 are decreased by only 6.56% and 10.26%. When the temperature is from 300 K to 1200 K, the Young's modulus, fracture strain, and stress of Angle-20 are decreased by 25.34%, 20.16%, and 16.54%, respectively, relative to that of graphene/copper layered composites in the same condition. Besides, graphene/copper layered composites with other types of defects distribution do follow the trend. Another focus is that random defects are most affected by temperature, while central defects are the least affected by temperature. For example, the fracture stress of Cen-20 decreased by 87.03%, while the fracture stress of Random-20 decreased by 82.5% compared with PGC when the temperature was K. As the temperature rises, this trend becomes more pronounced. Therefore, if graphene is used as a metal reinforcement material, defects occur in graphene, and random or blocking angle defects should be avoided.

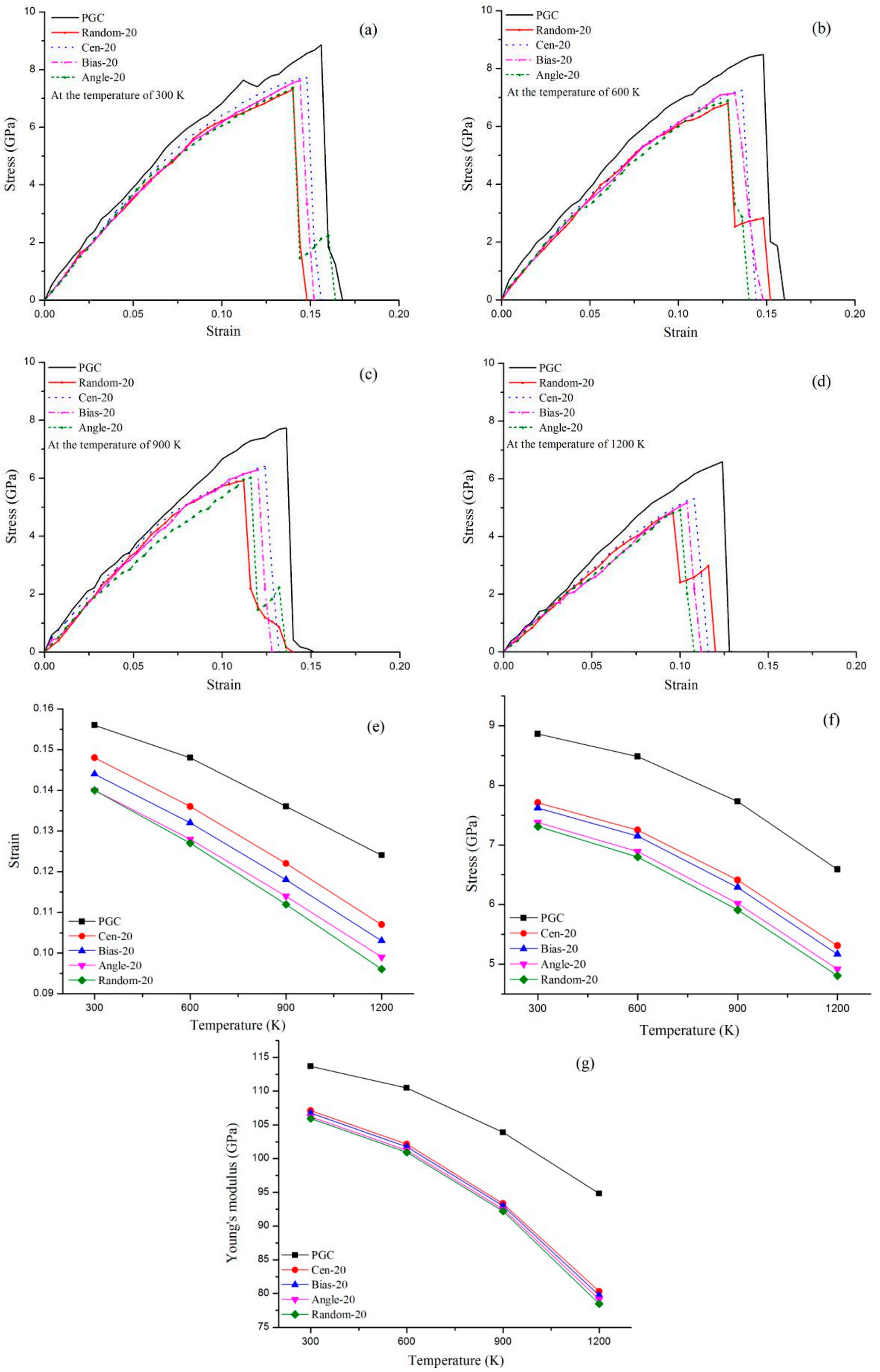


Figure 8. Stress-strain curve of graphene/copper layered composites with different types of defects at (**a**) the temperature of 300 K, at (**b**) the temperature of 600 K, at (**c**) the temperature of 900 K, and at (**d**) the temperature of 1200 K. (**e**)–(**g**) are mechanical values of graphene/copper layered composites with different types of defects at different temperatures.

Figure 9 shows the fracture process and stress distribution of graphene/copper layered composites with different types of defects at 300 K. It is observed that defects distribution has a significant effect on mechanical properties of graphene/copper layered composites. Random-20 has a negative effect on mechanical properties than the other three groups. When composite materials contain various types of defects distribution, the best mechanical values are Cen-20, and the lowest mechanical values are Random-20. This can be attributed to the fact that complex defects can be produced on graphene by using random ion irradiation methods. These complex defects are more likely to form crack defect bands, which make the six-square lattice elements incomplete. This reduces the mechanical properties of graphene/copper composites. However, when the defects are in the center distribution (Cen-20), Cen-20 can withstand more stress than other defective graphene/copper layered composites, and delay the time of defects propagation and penetration, which slows down the degradation degree of mechanical properties.

The location and arrangement of defects have great influence on the mechanical stability of graphene/copper layered composites, and the arrangement of vacancy defects has a different influence on the deformation behavior and stress transfer mechanism. It can be concluded that defects formed by irradiation have an effect on the physical properties of two-dimensional materials. Therefore, irradiation technology can be used to artificially control the formation of defects, and then to make appropriate adjustments to their properties. This can not only optimize the radiation resistance and mechanical properties of nuclear materials, but also expand the application of graphene in electronic devices and other fields.

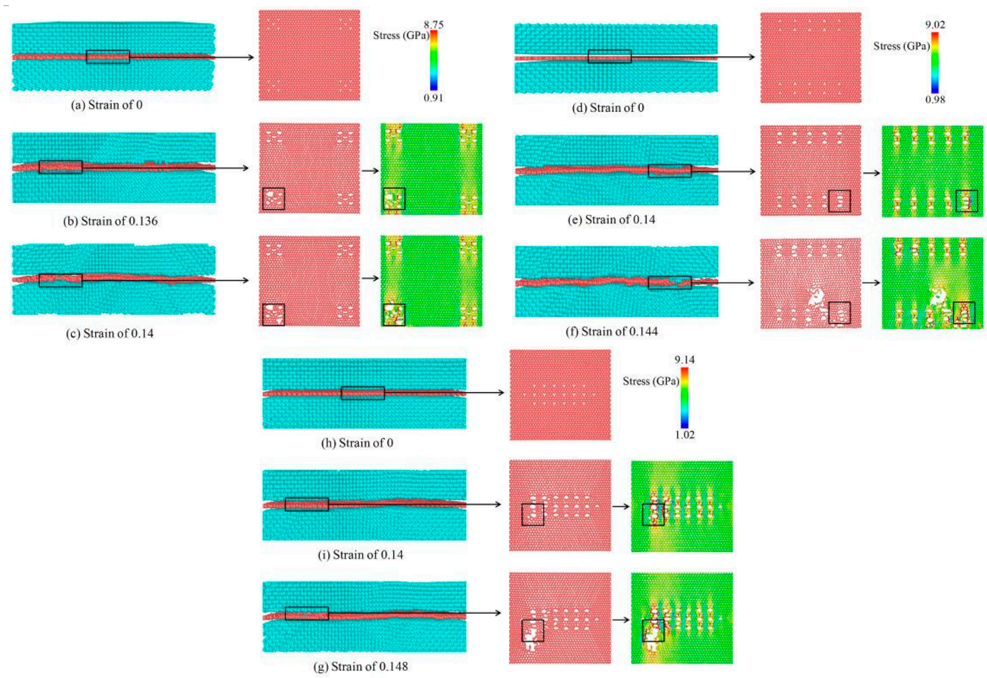


Figure 9. Fracture process and stress distribution of graphene/copper layered composites with (**a**–**c**) centerline, with (**b**–**f**) eccentric line, and with (**h**–**g**) block corner defects at the temperature of 300 K. (Before the load is applied, before reaching the stress limit, and after fracture failure).

4. Conclusions

Today, graphene-reinforced metal matrix composites have attracted more attention due to their excellent properties. However, graphene is prone to defects in the process of preparation. Therefore, it is necessary to study the effect of defective graphene on the properties of composites. In this paper, a numerical model of graphene/copper layered composites after irradiation damage was established by molecular dynamics simulation. The effect of ion irradiation and temperature coupling on defective graphene/copper layered composites was investigated. It is found that the fracture process of the defective graphene/copper layered composites after irradiation and the fracture process of the original model are significantly different. Graphene/copper layered composites (PGC) breaks from the edge and extends inward along a certain straight line. However, the initial fracture location and fracture direction of defective graphene/copper layered composites after irradiation are closely related to the location of the defect band and atomic lattice vacancies in the defect band. In addition, it should be mentioned that, with the increase of temperature and ion irradiation dose, the mechanical properties of defective graphene/copper composites decreased sharply, and the decrease of defective graphene/copper composites was higher than that of non-defective graphene/copper composites. This is because graphene contains a large number of empty defects after radiation damage. These "defective carbon atoms" are in a semi-active state. As the temperature increases, the carbon atom is more likely to exceed the binding energy constraints and is out of a stable state. Although the bonds between carbon atoms can be weakened, defective graphene still enhances the mechanical properties of pure copper. At the same time, the location and arrangement of defects have great influence on the mechanical stability of graphene/copper composites, and the arrangement of empty defects has different effects on deformation behavior and the stress transfer mechanism. It can be concluded that the defects formed by radiation have an effect on the physical properties of two-dimensional materials. Therefore, irradiation technology can be used to artificially control the formation of defects, and then make appropriate adjustments to their properties. This can not only optimize the radiation resistance and mechanical properties of nuclear materials, but also expand the application of graphene in electronic devices and other fields.

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