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ARTICLE

Advance in Properties of Graphene and Graphene/Metal Layered Composite After Irradiation Damage

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Abstract: With the continuous development of spacecraft, nuclear powered ships, nuclear fusion power generation and other technologies, it is required that the material does not only process excellent performance, but also work normally under extreme conditions (irradiation, high temperature, etc.). How to ensure the service life of materials under long time irradiation? The design and preparation of metal composite with strong radiation resistance has become a hot issue in the field of national defense and nuclear fusion. In addition, the structure evolution, performance changes and internal mechanism of metal and its composite materials under irradiation are also the key to the design and preparation of radiation resistant materials. Graphene has excellent anti-radiation ability. What new changes will happen when adding graphene to metals? This review summarized the sequential advancements made in research involving graphene/metal composites and irradiated graphene, including cutting, modified modification, structural design and industrial functionalization. The mechanism of graphene/metal composites after irradiation is further understood. It provides a theoretical basis for the application of graphene/metal composites in nuclear industry.

Key words: graphene; graphene/metal composites; irradiation damage; vacancy defects; a new type of radiation resistant material

Graphene with high strength, high radiation resistance, electrical and thermal properties, are considered as new strategic materials, and it will have very broad application prospects, especially in the field of nuclear energy, nuclear coating, and electronic devices [1-5]. Mother of all graphite forms are shown in Fig.1.

However, the zero band gap of graphene greatly restricts the application of graphene in nanoscale electronic devices, for example field-effect transistor and optoelectronic devices. The studies found [6-9] that band gap of graphene can be opened by chemical doping, adsorbing atoms, introducing periodic defects and introducing quantum confinement, but it will destroy the lattice or chemical structure of graphene. In addition, these methods are often limited in high technical requirements. Schematic of the chemical processing method for graphene nanomesh is shown in Fig.2. Therefore, based on the cost, effect and technology, how should we effectively process graphene or perform doping for graphene? It has become a difficult issue. The studies[10,11] show that ion irradiation technology is an effective way to achieve the above purpose.

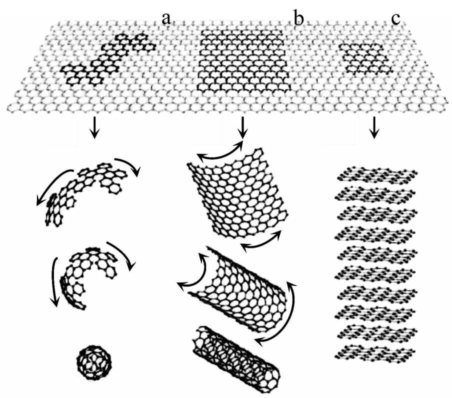

Fig.1 Mother of all graphitic forms: (a) fullerenes; (b) carbon nanotubes (CNTs); (c) graphene[1]

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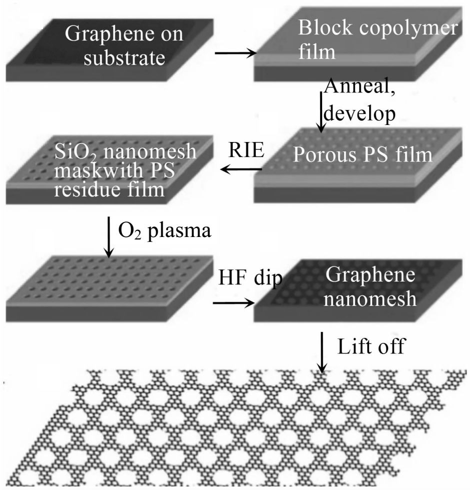

Fig.2 Schematic of the chemical processing method for graphene nanomesh[8]

One of the common misconceptions is that particle irradiation only has an adverse effect on the target material. The previous studies showed that fullerene can maintain good stability under γ radiations, it will not decompose or interrelate, and will not change crystal structure and produce defects[12]. With the in-depth study of carbon materials, it is gradually found that ion irradiation can change the crystal structure and properties of the target materials.

It is shown that single-walled nanotubes will produce uneven surface after irradiation, and the tube will become thinner. Although multi-walled nanotubes also cause some defects and damage to the structure, but the radiation resistance of multi-walled nanotubes is obviously higher than that of single walled nanotubes [13]. The study has shown that under the electron irradiation condition of 2.5 MeV, the paramagnetic defects of carbon nanotubes (CNTs) are more than that of the reference CNTs, and its conductivity was greatly improved [14]. Meanwhile, some nanostructures such as amorphous carbon and the link between tube walls were produced. It can improve the macro performance of CNTs. Dumitrica[15] also confirmed that irradiation can improve the macro performance of CNTs. A schematic of CNTs interconnected or merged under the condition of irradiation is shown in Fig.3.

Both fullerenes and CNTs in carbon nanomaterials can be seen as a single graphene. So is it possible to change the structure and properties of graphene by particle irradiation? Teweledebrhan et al[17] found that irradiated graphene was prepared by using electron beams, the crystalline structure can be changed into nanocrystalline and amorphous state. The structure and properties of graphene under gamma ray irradiation were studied by Dume et al[18]. It was found that low dose of γ rays can help reduction and oxidation of

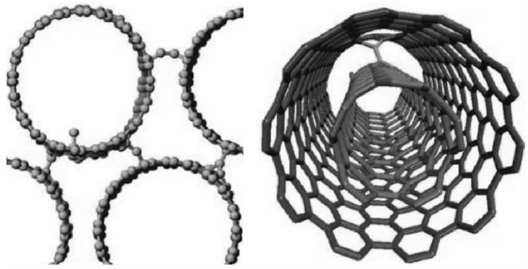

Fig.3 A schematic of CNTs interconnected or merged under the condition of irradiation[16]

graphene, while high dose of γ rays can seriously damage graphene structure.

The effect of particle irradiation on the structure and properties of carbon materials such as graphene is not all harmful, but it is also beneficial. Theoretical study shows [19] that the band gap of graphene can be opened by particle irradiation, but defects will be produced. Thus, a problem has been derived. Whether graphene can be modified and cut through particle irradiation? According to application of materials, its physical and chemical properties were changed and modified.

This review summarized the sequential advancements made in research involving graphene/metal composites and irradiated graphene, including cutting, modified modification structural design and industrial functionalization. The mechanism of graphene/metal composites after irradiation is further understood, which provides a theoretical basis for the application of graphene/metal composites in nuclear industry.

1 Properties of Irradiated Graphene

1.1 Experimental studies of irradiated graphene

The zero band gap of graphene brings great limitations to the application of nano-electronic devices. Therefore, introducing defects into graphene and opening band gap is of great significance for application of graphene. Lee et al[20] found that the defect of graphene was produced by the proton incident, and the variations of the defect with increasing the proton energy were studied. Zeng et al [21] studied that the defects of graphene were irradiated by fast heavy ions and high charge ions, and the variations of the defects with increasing the ion doses were discussed. In addition, the studies [22, 23] have shown that defects of graphene can also be modified or introduced by irradiation of electron beams and inert gas ions.

In fact, no matter which means to introduce these defects, they have a great influence on the electronic transport properties of graphene. Therefore, the study of the defects and doping of monolayer or multilayer graphene is particularly important for understanding and predicting the properties of graphene. However, there are few reports on the irradiation effect and modification analysis of graphene.

Recently, Chen et al[24] studied that the graphene was irradiated by He and Ne ions. The results show that the defects of graphene were generated, and then these defects would lead to interalloy scattering, and the electron mobility of graphene was greatly reduced. Tapaszto et al[25] also confirmed that the electronic structure of graphene can be regulated by ion irradiation. It is more surprising that the defects produced by irradiation, also affect mechanical properties and thermal conductivity of graphene. Ng et al[26] found that Stone-Wales defects of graphene can reduce the 50% thermal conductivity of graphene. It is also found that the combination of radiation and heat treatment will have many beneficial effects on the nanostructured materials[27].

1.2 Theoretical analysis and numerical simulation of irradiated graphene

In the field of nanomaterials, transmission electron microscopy (TEM) can not only observe defects of nanomaterials, but also make it possible to understand how defects affect the properties of nanomaterials. Therefore, the visualization of the defect results is realized by TEM. However, because it occurs on the scale of the picosecond, it is not conducive to analysis and observation[28].

Atomic computer simulation has become an important supplement method for experimental study of nanomaterials. It can provide the radiation damage of nano-material in detail, and characteristics and defects in the nanostructure. The most important is that it can effectively control irradiation defects and provide the real-time information [29].

The relationship between incident particles and steady state stress was firstly established by Marks et al [30]. Then the effect of ion irradiation on the deformation of graphene is investigated by molecular dynamics (MD) [31]. The result shows that the irradiated energy and the angle of irradiation have an important influence on the type and quantity of the formation defects of graphene. After that, the MD method is used to study the performance of the irradiated graphene. The effects of different types of ions, different incidence angles and different incident energies on the cutting of graphene were studied by Lehtinen et al [32]. The morphological changes of graphene in the irradiation process were also established using Monte Carlo method. In addition, the formation of nanopores in the graphene and variety of nanopores were studied by the classical MD. The result shows that, compared with the incidence of Si and C ions, Au ions are more suitable to form relatively perfect nanopores of graphene with smooth edges[33].

The defect types, layer effect, ribbons and chiral types of graphene are considered, and the model is established. The effect of radiation on the properties of graphene has also been reported. On this basis, how will the properties of graphene change under the interaction of multiple factors (heat, electricity, magnetic field and irradiation)? Li Dongbo et al[34] studied correlation of tensile mechanical properties of graphene irradiated by C atoms with temperature. It can be concluded that compared with perfect graphene, the tensile mechanical properties of irradiated graphene are more sensitive to temperature change. With the increase of temperature, the tensile ultimate strength decreases obviously, and the ultimate tensile strain and elastic modulus decrease differently.

2 Effect of Irradiation on the Properties of Graphene/Metal Composites

2.1 Effect of irradiation on the properties of metal based materials

With the continuous development of spacecraft, nuclear powered ships, nuclear fusion power generation and other fields, we not only require the material to possess excellent performance, but also require it to work normally under extreme conditions (irradiation, high temperature, etc.). For example, in fusion reactor engineering, materials will undergo high dose of neutron radiation, and then large amounts of transmutation helium will be generated inside the material. They will gather inside the material and eventually form helium bubbles. These helium bubbles will reduce the mechanical properties of materials, and seriously affect the service life of materials. The study also shows that the mechanical properties of metal materials will change, and new phenomena appear (such as irradiation brittleness, irradiation hardening and irradiated creep, etc.) after long time irradiation[35-37]. Li et al[38] studied that the tensile simulation of irradiated single crystal copper. The results show that the tensile modulus of single crystal copper decreases after irradiation. Ma et al[39] studied the cracks of single crystal nickel propagate after irradiation. It can be concluded that irradiation defects will promote the propagation of cracks with increasing the temperature.

How to ensure the service life of materials under long time irradiation? The design and preparation of metal composite with strong radiation resistance has become a hot issue in the field of national defense and nuclear fusion. In addition, the structure evolution, performance changes and internal mechanism of metal and its composite materials under irradiation are also the key to the design and preparation of radiation resistant materials.

The radiation resistance of single metal is limited. Metal composite material is another potential anti-radiation material. The excellent anti-radiation ability of graphene has been introduced. What will be the new change in the introduction of graphene into the metal? Previous studies have shown that introducing graphene into polymers can enhance the anti-radiation ability of polymers [40-43]. Kolanthai et al [44] studied the properties of polyethylene composites modified with irradiated graphene using 25 kGy and 50 kGy doses. The experimental results showed that polyethylene composite coating retained the hardness and mechanical strength of the composites, and meantime the graphene could maintain the crosslinking degree of the polyethylene matrix in the irradiated environment, and reduce the effect of the gamma ray on composites.

These studies also provide reference for the study on radiation resistance of graphene/metal composites.

2.2 Effect of irradiation on the properties of graphene/ metal layered composites

In the early preparation of graphene composites, there was an idea that the excellent mechanical properties of graphene can be introduced into polymers. It has been proved that incorporation of single graphene into composite materials, i.e. polymer composites, will lead to the best mechanical properties. Later, Kim et al[45] thought that the excellent mechanical properties of graphene can effectively limit the dislocation movement, and help to improve the strength of metal. Based on the special properties of graphene/ metal composites, the anti-shockwave properties of metal/ graphene composites were studied by numerical simulation. It is found that the grain boundary in the composite has the ability to adsorb defects[46]. It can be concluded that graphite/metal composite materials may attract the point defects produced at the initial stage of radiation under irradiation conditions, and graphene/metal composites are expected to become new anti-radiation materials.

During the nuclear reaction, core materials under the condition of high-energy radiation will generate vacancies and interstitials, which evolve into defect clusters, dislocation and grain boundaries with time. The results will lead to grain boundary embrittlement, swelling, surface roughening and foaming. Finally, the mechanical properties of core materials will decrease. Therefore, it is necessary to carry out the study of irradiated graphene/metal composites [47].

Huang et al[47] studied that the interface stability of graphene/copper composites under irradiation environment, and a model of graphene/copper composite structure was constructed. The composite structure model impacted by the PKA atoms with different initial energies and different distances, and then the number of point defects near the interface of the composite structure under different temperatures was analyzed. It can be concluded that the interface of composite structure can enhance the anti-radiation performance, but with the increase of PKA energy, the graphene is also damaged by irradiation. Copper on the top or bottom of graphene may recrystallize, and form columnar structure through graphene, resulting in the weakening of interface stability, and radiation resistance of composite materials also decreases.

Yang et al[48] answer the above question from another angle. Based on the first principle of density functional theory, they studied the formation and migration of point defects near the graphene/copper interface, and analyzed the effect of graphene on the point defect behavior of copper based materials. It has been shown that the interface of copper/graphene composites have a strong capture effect on the point defects of copper. The defects are captured and annihilated, which leads to the reduction of the total number of defects. From another point of view, the introduction of graphene may enhance the anti-radiant ability of the graphene/metal composite. However, the interface between copper and graphene is a weak interface, how to enhance the radiation resistance of the strong interface between graphene and metal (Ni, Co, Ru and so on)? Can graphene prevent the development of metal dislocations? It is worth our expectation.

3 Conclusion and Prospect

Particle irradiation has become an important role in the processing and modification of graphene and its composites in the application of graphene. However, the study on the radiation resistance of graphene/metal composites is still in the initial stage. Further study on the irradiation mechanism of graphene/metal composites is needed. The present paper provides a theoretical basis for the application of graphene/metal composites in the nuclear industry.

1) The radiation resistance in the existing researches depends on changes of point defects in composites materials. The number of point defects in the outer region of graphene is less than that in pure metal. Therefore, it is concluded that the composite has good radiation resistance. But the radiation resistance of metals depends on many factors[47], e.g., the number of point defects produced by displacement cascade, and the diffusion of defects. Therefore, we need to study the mechanism of irradiated graphene/metal composites, and further to study the following three questions. How does graphene affect the number of point defects in metal composites? How does graphene affect the migration behavior of point defects in metal composites? How does the incorporation of graphene affect the radiation resistance, the degree and the mechanism of metals? It provides new ideas for graphene/metal composites in the development of nuclear industry.

2) The interface of copper/graphene composites have a strong capture effect on the point defects of copper, which leads to the reduction of the total number of defects. In addition, the introduction of graphene may enhance the anti-radiant ability of the graphene/metal composite. However, the interface between copper and graphene is a weak interface, what is the radiation resistance of the strong interface between graphene and metal (Ni, Co, Ru and so on)? Can graphene prevent the development of metal dislocations? It's worth our expectation.

3) The properties of graphene after radiation have been studied by scholars. In general, the perfect graphene is usually chosen. However, in the actual preparation and application, the large area graphene produced by the CVD method inevitably contains the grain boundary and other topological

defects, such as the Stone-Wales defect[49]. Then it derives a problem. What are the changes in the properties of graphene with Stone-Wales defect by ion irradiation? Are these previous results expected to predict the effect of particle irradiation on the mechanical properties of graphene with Stone-Wales defect? Will the mechanical properties and failure mechanism of irradiated graphene with Stone-Wales defect produce new changes? These new changes are worthy our expectation in the future research.

4) The incident particles will collide with the material during the irradiation. When transmitted energy of incident particle reaches the threshold energy of the target atom during the impact, the target atom will leave the position in the crystal. When the incident particle cannot transfer to the enough energy of target atom, the incident atom is adsorbed in the crystal. The defects in the irradiation process are mainly adsorption defects, vacancy defects and complex defects[50]. However, it is usually to study the radiation damage behavior of graphene under once ion irradiation. Actually, there are also twice radiation effects and many radiation effects. That is to say, the defect structure is formed by once irradiation. It will collide again and again with energetic ions, so it may form a new defect structure[51]. What new phenomena will change the properties of graphene/metal composites still needs further exploration.

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石墨烯及石墨烯/金属层状复合材料辐照损伤研究进展

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摘　要：随着航天器、核动力船舶、核聚变发电等工业的不断发展，不仅要求材料拥有优异的性能，还要求材料在极端条件下（辐照、高温等）仍能正常工作。那么如何保证材料在长时间辐照条件下的使用寿命？设计和制备抗辐照性能优异的金属复合材料已成为国防领域和核聚变发电的热点问题，此外，金属及其复合材料在辐照条件下的结构演化、性能变化及内在机理也是设计、制备抗辐照材料的关键所在。石墨烯具有优异的抗辐照能力，将石墨烯加入金属中又将会产生什么新变化呢？本文综述了离子辐照技术在石墨烯/金属复合材料及石墨烯的裁剪、修饰改性、结构设计及产业功能化等方面的研究进展。进一步理解石墨烯/金属复合材料辐照后的变化机理，为石墨烯/金属复合材料在核工业的应用提供理论依据。

关键词：石墨烯；石墨烯/金属复合材料；辐照损伤；空位缺陷；新型抗辐照材料

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