

Study of Preparation, Properties and Applications of Graphene

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Abstract. As a two-dimensional nano-material with outstanding characteristics, graphene is mainly composed of carbon atoms organized in a honeycomb configuration. Numerous attempts have been made to produce substantial amounts of graphene using various chemical processes since the first isolation of graphene in 2004 by mechanical exfoliation from graphite. There is still a lot of potential applications remained undiscovered, particularly in strengthen heat resistance and toughness of the material. This paper summarized the preparation process of graphene, micro-morphology and macro performance of graphene in recent years. The mechanical properties, ways of toughening composites and mechanism of graphene on ultra-high temperature ceramic matrix were studied. In addition, the influence on thermal properties via different synthesis process, thermal shock resistance and oxidation resistance of graphene were explored.

Keywords: Graphene, Development, Applications.

1. Introduction

The Graphene was first prepared by using mechanical exfoliation method in 2004. Graphene is proved to be able to be isolated. Graphene is the world's thinnest two-dimensional material, it is valuable due to its high tensile strength, electrical conductivity, transparency, and transparency. Because of its distinct electrical, chemical, mechanical properties, flexibility and elasticity, graphene has been changing a variety of fields. Graphene still have the potential to be beneficial in a variety of applications, including flexible, transparent, and wearable electronics, energy storage devices, diagnostic and therapeutic tools, water purification systems, and hypersonic aircrafts.

2. Preparation process of graphene

Choosing appropriate process is essential to obtain ideal graphene in structure and performance. At present, graphene is mainly prepared by powder sintering densification process, graphene powder is prepared first, and then sintered and densified to obtain a block composite material with a certain density. It is a simple way to produce graphene with decent performance, and easy to modify the detailed performance. The dispersion of secondary phase will direct effect the preformation of the product.

3. Graphene performance studies

3.1. Mechanical properties

Graphene nanoplatelet have aroused great interest, because it can improve the mechanical performance of ultra-high temperature ceramic materials through a variety of mechanisms. Early research mostly revolves around the toughening effect of graphene on ultra-high temperature ceramic matrix. Many studies show that the adding of graphene increases the homogeneity and compactness of compacts, and the encapsulation of GNPs (Graphene nanoplates) significantly inhibits the grain growth. This internal mechanism and the interaction between graphene nanoplatelets and grains together lead to the crack suppression mechanism, and the phenomenon of crack deflection and crack bridging appears in the micro morphology, thus realizing the toughening effect on ultra-high temperature ceramic matrix.

Nieto et al [1] synthesized graphene nanoplatelet reinforced TaC composite, which confirmed that the introduction of graphene nanoplatelet inhibited the grain growth. It improved the density of TaC ceramic matrix, and significantly increased the fracture toughness of the matrix by nearly 100%.

Nieto et al [2] also found that the addition of GNPs would reduce the damping up to 300%. Yadhukulakrishnan et al [3] and Asl et al [4] also toughen the ZrB₂ ceramic system by adding graphene, and they obtained composites with density up to 97%. The bending strength and fracture toughness of the system have both significantly increased in terms of mechanical attributes. The toughen effect of graphene can be told by these two experiments, which is caused by such toughening effects as crack deflection also crack bridging of graphene.

Zhang et al [5] and An et al [6] added graphene into ZrB₂-SiC composites by thermal reduction of graphene oxide into multilayer graphene nanoplatelets. Under the synergistic effect of SiC whiskers and graphene nanoplatelets, the bending ability and fracture toughness of the composite are improved to varying degrees compared with those of pure ZrB₂ ceramics. The toughening mechanism was analyzed by observing the fracture microstructure and indentation crack growth path of the composite. The crack bridging and drawing of graphene nanoplatelets appeared on the fracture surface of ceramic composite, which promoted the crack propagation of its reinforced composite. Recent studies have found that the fracture toughness shows a linear increase trend with the increase of graphene nanoplatelets, even if different processes and different matrix systems are used. It is confirmed that graphene nanoplatelets wrapped around ceramic particles inhibit the growth of grains, and the main toughening method are crack bridging, crack arrest and crack deflection.

3.2. Effect of graphene on dynamic mechanical and tribological properties

By the dynamic response of ceramic materials is weak, which is related to the rigid covalent bond or ionic bond in its microstructure. Although traditional fiber additives enhance its dynamic response, due to its heterogeneous dispersion and structural damage, the dynamic response is still limited to a threshold, which seriously restricts the wide application of ceramic materials. However, graphene is generally considered to be a good alternative strength material because of its excellent internal force in plane. Zhang et al [7] developed an expandable process to manufacture ZrB₂-SiC/graphene composites and studied their dynamic mechanical properties. Compared with data before the addition of graphene, the dynamic strain of ZrB₂-SiC/graphene composite increased from 0.095% to 0.226%, and the dynamic stress increased from 1.50 GPa to 1.92 GPa, an increase of 28%. They used finite element method to simulate the localization of dynamic stress distribution, crack morphology and fracture process, and analyzed the toughening mechanism of graphene. This work provides a reference for preparing graphene reinforced ceramic composites with strong dynamic response.

The mechanical properties of heterogeneous interfaces are critical to the performance of graphite reinforced composites. Zhang et al [8] set graphene between two stable layers and made 12 interface models ZrB₂ surfaces. Using density functional theory, they systematically studied the structure, adhesion, cleavage and sliding of heterogeneous interfaces between ZrB₂ matrix and graphene nanoplates, and compared them with existing data. The results show that the surface chemical properties of ZrB₂ matrix materials largely determine the properties of interface structure and interface interaction, and the interface bonding mechanisms of the two interface types are different. Zr-C interface has strong chemical bonding, so it has high resistance to crack growth and interface sliding, and its response to mechanical stress was significantly affected by graphene wrinkle. Through weak π - π superposition, B-C interface is prone to interface debonding and shear deformation, showing similar characteristics to two-dimensional material heterostructure. The results of this research provide a reference for the interface bonding mechanism of graphene and an effective design scheme for the synthesis of ceramic composites.

Asl et al [9], and Nguyen et al [10] added graphene nanoplates into ZrB₂-SiC and TiC ceramic systems, and studied the nano indentation characteristics of the composite, especially the sudden wave in the load displacement curve. The research shows that graphene is helpful to obtain a finer microstructure, and improves the bending strength of the sample. Koval č í kov á et al [11] studied the

effects of different graphene nanoplates additions on the microstructure, mechanical properties and tribological properties of $\text{TiB}_2\text{-SiC}$ ceramic matrix materials. It was found that the addition of GNPs also significantly improved the friction resistance, but had a decrease in the hardness. Ocak et al [12] found the same phenomenon in the study of ZrC-TiC-GNP system.

3.3. Thermal Performance

Graphene has excellent electrical and thermal performance, with a thermal conductivity of $5.3 \times 10^3 \text{ W/(m}\cdot\text{K)}$ [13]. In ultra-high temperature ceramic materials, the addition of graphene will raise the heat conductivity of the matrix material, cool down the overheating area faster, thus extending the working life of the material. Simonenko et al [14] added 2% graphene composite into $\text{HfB}_2\text{-30% SiC}$ material system, with overall thermal conductivity ranging from $113 \text{ W/(m}\cdot\text{K)}$ to $164 \text{ W/(m}\cdot\text{K)}$, increased by about 45%. The study of Cheng et al [15] shows that the $\text{ZrB}_2\text{-SiC}$ with inclusion of graphene will significantly improve the thermal conductivity, specific heat capacity, and thermal diffusion coefficient of ceramic matrix. Excessive addition will lead to the attenuation of the thermal conductivity of the composite. Caused by the thermal conductivity of graphene decreases due to agglomeration, and the ceramic matrix grain decreased in size and porosity increases. Graphene will produce thermal conductivity interface in the process of composite with ceramic matrix, and build three-dimensional high heat transfer path, so it can be used as an excellent thermal interface material to enhance the thermal conductivity and thermal conductivity of the matrix material. In addition, graphene brings effect in phonon transmission paths, so the thermal conductivity will increase with the adding of graphene.

3.4. Thermal and shock resistance

The serious problem of low thermal shock resistance limits the extensive application of aerospace, especially the components made by ultra-high temperature ceramic. In extreme environments such as high temperatures and a significant temperature gradient during a high-speed re-entry into the atmosphere is out of the capability of ultra-high temperature ceramic. The excellent mechanical and thermal properties of graphene can strength the toughness and thermodynamic properties of ceramic matrix composites. Zhang et al [16] built a hierarchical structure through electrostatic assembly bionics, and found that the shock resistance of $\text{ZrB}_2\text{-SiC}$ composites can be enhanced and toughening it. Graphene has formed a weak grain boundary interface and an optimal thermal conductivity path in the composite. Compared with pure $\text{ZrB}_2\text{-SiC}$ composite, the residual strength after thermal shock at 400°C and 500°C increased by 74.8% and 304.4% respectively. Cheng et al [17] obtained isotropic toughened $\text{ZrB}_2\text{-SiC}$ ceramics with weak interfaces by building an equiaxed structure. As $\text{ZrB}_2\text{-SiC}$ -graphene is the weak interface, they achieved multiple ways of toughening of $\text{ZrB}_2\text{-SiC}$ ceramic materials. In addition to the design of coaxial structure, they achieved exceptional thermal shock resistance with a critical thermal shock temperature differential of up to 861°C after improving the damage tolerance and critical thermal shock temperature difference of the composite.

To avoid thermal aggregation of graphene oxide during heating and drying, Cheng et al [15] synthesized three-dimensional graphene oxide/ $\text{ZrB}_2\text{-SiC}$ composite foam by electrostatic self-assembly and liquid nitrogen assisted freeze-drying process. $\text{ZrB}_2\text{-SiC}$ ceramic particles were evenly embedded on the wall of graphene net. After sintering, $\text{rGO/ZrB}_2\text{-SiC}$ ceramics with different microstructures and properties were obtained by adjusting the volume content of reduced graphene oxide, which were $20\text{rGO/ZrB}_2\text{-SiC}$, $25\text{rGO/ZrB}_2\text{-SiC}$ and $30\text{rGO/ZrB}_2\text{-SiC}$ respectively. Although the bending resistance has reduced, its thermal conductivity, fracture toughness, fracture work and thermal shock resistance have been improved by the adding of graphene. The critical thermal shock temperature difference of $30\text{rGO/ZrB}_2\text{-SiC}$ ceramics is 650°C , which is much higher than 340°C of $\text{ZrB}_2\text{-SiC}$ ceramics, 410°C of $20\text{rGO/ZrB}_2\text{-SiC}$ ceramics and 410°C of $25\text{rGO/ZrB}_2\text{-SiC}$ ceramics.

Wang et al [18] studied the thermal shock properties of sharp leading edges (SLEs) of graphite platelets modified $\text{ZrB}_2\text{-SiC}$ ceramics through scanning electron microscope (SEM) observation and finite element simulation analysis. The results show that the thermal shock is related to the wedge

angle θ Sensitive, when θ from 12° to 9° , the critical failure temperature decreases by about 35%. The increase of tip curvature radius and tip thickness will lead to the decrease of thermal shock resistance. Cracks formed by thermal shock usually initiate near the midpoint of the leading edge and propagate mainly along the cooling direction. This work is helpful to further understand the thermal shock characteristics of SLEs, and lays a theory for the future engineering design and application of advance components in hypersonic area.

3.5. Oxidation resistance

The key of making ultra-high temperature ceramic matrix suitable for engineering applications is to strengthen its mechanical properties, also the resistance of oxidation. Under the condition of high enthalpy supersonic flight, the hot end of the new spacecraft will be subject to severe ablation damage under the coupling effect of multiple factors such as heat, force and oxygen, which will cause serious mechanical peeling of the surface of ultra-high temperature ceramic materials, reduce the structural integrity, and weaken the ultra-high strength of materials to a certain extent. Therefore, the advancement of oxidation behavior is an important research direction of ultra-high temperature ceramic materials under extreme environmental service. The Nieto research team [19] was the first to carry out the research on oxidation resistance. They prepared graphene nanoplates reinforced TaC composites by SPS, and used atmospheric plasma oxidation ablation experiments to prove that graphene can significantly reduce the surface ablation temperature of the materials, thus greatly improving the oxidation resistance of the composites.

Akarsu et al [20] found that after the introduction of GNP, the thickness of $Zr_{0.25}Ti_{0.75}B_2$ outer oxide layer was $130\mu m$ down to $100\mu m$ ($1100^\circ C$, oxidation for 180 min) and from $220\mu m$ down to $200\mu m$ ($1200^\circ C$, oxidized for 180 min), which is due to the encapsulation of graphene nanoplates leading to grain sealing and enhancing its oxidation resistance, and inhibiting the influx of oxygen through the grain boundary.

After graphene is added into the ceramic matrix, the thermal gradient of the composite exposed to the plasma flow is significantly reduced, bring with the thermal conductivity increase, thus enhancing the diffusion and conduction of heat and avoiding local overheating [14, 19]. Moreover, graphene makes it difficult for oxygen to diffuse through the grain boundary by wrapping, winding grains and interpenetrating between grains, and even sealing the oxidation grain boundary and diffusion path. The toughening effect of graphene also inhibits the generation and propagation of cracks, thus preventing the rapid penetration of oxygen. Cracks are crucial to retard the oxidation rate. In addition to the above physical ways, graphene will also consume oxygen through chemical reactions, weaken the corrosion of oxygen on ceramic matrix, play a protective role, and thus enhance the oxidation resistance of ceramic matrix. In the carbide ceramic system, graphene also provides the carbon source required for reducing oxides to carbides, and inhibits the formation of oxide layer by inducing local reduction.

4. Problems existing

The uniform dispersion of graphene in the ultra-high temperature ceramic matrix has been proved to have a significant strengthening and toughening effect. The oxidation resistance, thermal shock resistance and other properties of the composite have also been improved. However, the application of graphene in ceramic materials is only a start, there are still many problems that need to be studied.

4.1. Optimization of preparation process

The uniform dispersion of graphene is crucial for an ideal graphene. Due to the strong chemical insertion between the two phases and the weak van der Waals interaction, it is difficult to achieve the uniform dispersion of graphene in the ceramic matrix. When the adding large amount of it, the problem of agglomeration is particularly serious, and the mechanical, electrical, also thermal mechanical performance of the composite are reduced. In order to further maximize its positive effect,

the effective dispersion of graphene and the appropriate interface between matrix and graphene are key factors. The dispersion of graphene can be improved by chemical methods such as in-situ polymerization and functional modification, or by physical methods such as adding additives, charge attraction, and strengthening mechanical mixing. Secondly, it is easy to reduce the performance it should get. In the preparation and processing of ultra-high temperature ceramic materials, which will have a huge impact on the properties of composites. For now, during the sintering process, there are few studies on the change of graphene itself, its role in controlling the grain size of ceramic matrix and other mechanisms, and the mechanism is not completely discovered. In addition, plasma sintering is mostly used in the process. In the future, it is necessary to explore other sintering processes such as low-temperature densification sintering, and further study the control methods of micro morphology.

4.2. Mechanism of graphene

The research on graphene improving the oxidation resistance and thermal shock resistance of matrix is still few. The synergistic effect of multiple mechanisms is still unclear. There are still a lot of unknown mechanisms to explore, and many practical problems need to be overcome. But this is crucial for understanding the role of graphene in the system and further optimizing the system performance.

4.3. Insufficient verification and assessment of extreme environmental performance

The high temperature mechanical strength and thermal protection ability of ultra-high temperature ceramic materials are key status to evaluate their performance. The existing research mainly focuses on the mechanical properties of graphene/ultra-high temperature ceramic composites at room temperature and the oxidation resistance and ablation ability at medium and high temperatures. In order to reach the requirements of the next generation of spacecraft at higher speed, it is necessary to carry out the verification research on the ultra-high temperature mechanical strength and anti-oxidation ablation performance of new graphene reinforced ultra-high temperature ceramic composites above 2000°C.

5. Conclusion

In recent years, it is a hot spot of graphene composites of the material science. The excellent properties of graphene have great potential. It is widely used in many areas due to its excellent properties such as wrapped grains, crack deflection and crack bridging on the ceramic matrix. The oxidation process of the matrix is suppressed by the physical and chemical effect, the thermal shock resistance of the matrix is improved by influencing the mechanics and thermodynamics of the matrix. At present, the research is poor on certain area, and there are still many problems to be solved, which makes the scientific research in this field of great practical meaning. It is believed that with the further exploring of the potential of graphene, the application direction of graphene ultra-high temperature ceramics will be greatly enhanced in the future.

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