Reactive Molecular Dynamics Simulations on Deformation and Fracture Mechanisms of Carbon Nanotube-reinforced Composite Materials towards Improving Their Mechanical Properties

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論文内容要約

Ceramics materials play an important role as structural materials in the industries of aerospace, automotive, and power plants because of their extraordinary strength and high hardness. However, from the perspective of safe utilization, it is vital to enhance the naturally low fracture toughness of ceramics materials. To improve the fracture toughness, it is suggested to add carbon nanotubes (CNTs) into the ceramics as the reinforcing agents. However, the CNT reinforcing effects investigated by past studies are still controversial in lack of an optimized composite design. The key issue to obtain the optimal design is to clarify the fracture mechanisms considering atomic-scale CNT/ceramics interfacial behavior[1]. To cope with the key issue, in this dissertation, the molecular dynamics (MD) method is applied to clarifying the deformation and fracture mechanisms of CNT/ceramics composites. Moreover, the reactive force field (ReaxFF) is adapted into MD simulations to discuss interfacial behaviors to calculate the generation and dissociation of bonds. SiC is employed as the ceramic matrix due to its frontier and wide applications. In the CNT reinforcement, the roles of CNT/SiC interfacial behaviors, interfacial interactions among walls of multi-walled CNT (MWCNTs), and structural factors of CNT orientation reinforcement are revealed. In addition, to provide promising instruction on structural materials design in applications, large-scale polycrystalline composite models are developed considering complicated reinforcing mechanisms, including CNT fracture and CNT bridging, as well as the applicated environments like water. These simulations capacitate the revelation of the fracture mechanisms focusing on interfacial interactions, CNT structural factors, and reinforcing mechanisms. This thesis consists of nine chapters.

Chapter 1 General Introduction

Chapter 1 introduces the background of CNT/ceramic composite materials, including an overview of past research, unsolved problems, and how MD can solve the according problems. The unique chemical bonding of CNT is highlighted, inherent by its unique multi-layer, hollow, and six-membered ring structures.

Chapter 2 Methodology

The basics of the MD method, ReaxFF potential, and tensile tests are introduced. Disadvantages of potentials other than ReaxFF and reported in past MD studies of CNT reinforcing composites are also summarized. Then, the advantages and significance of ReaxFF are explained.

Chapter 3 Competitive Mechanisms Underlying Annealing Temperature’s Effect on Tensile Properties of Carbon Nanotube (CNT)/SiC composite

Previous experimental study reveals that annealing could improve CNT/ceramics composite mechanical properties[2]. Besides, it is reported that annealing causes structural changes[3]. However, the mechanism of CNT structural changes affecting the mechanical properties of CNT/ceramics composite is unrevealed. Therefore, the purpose of this chapter is to elucidate how annealing affects the structures and mechanical properties of CNT/SiC composites. The composite models are conducted with annealing treatment, and then undergo tensile simulations as shown in Fig. 1. The tensile results show that Young's moduli (Fig. 2a) and tensile strengths (Fig. 2b) vary on annealing temperatures like a volcano. In search for the mechanism underlying the volcano pattern as annealing temperature rise, it has been discovered that the CNT stretching increases via increasing CNT/SiC interfacial bonds. Furtherly the cause for the mechanical property decreasing region is revealed to be CNT structural collapse, indicated by decreasing six-membered ring structures. To conclude the effect of annealing, it is discovered that coupled with CNT structural collapse and CNT stretching increases via stronger CNT/SiC interfaces led by annealing, contributing to a dependence of reinforcement to annealing temperature.

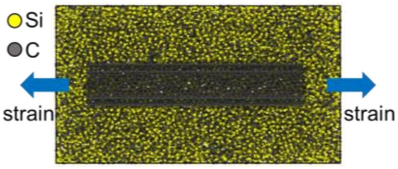

Fig. 1. Illustration of tensile simulation conducted on composite model.

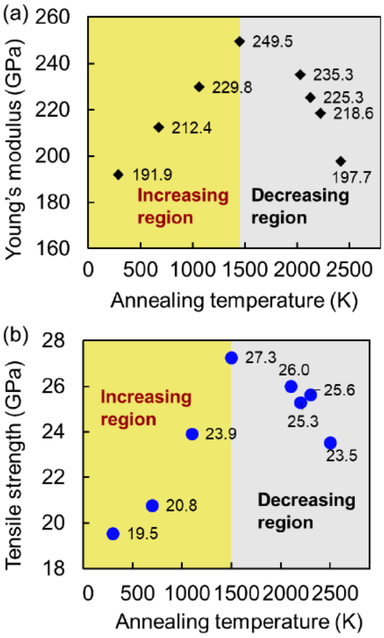

Fig. 2. Plots of (a) Young’s moduli and (b) tensile strength of composites annealed at different temperatures.

Chapter 4 Effect of Si-Dopes on the Reinforcement in Crystalline SiC: Different Reinforcing Mechanisms with Different Doping Position

It is reported that doping on CNT improves the properties of CNT reinforcing composites[3, 4]. However, the mechanism underlying the improvement regarding toughness is not yet clarified. Therefore, this chapter aims to investigate the effect of Si-doping on the CNT reinforcement and the underlying mechanism. For the discussion on the influence of different CNT structures, tensile simulations are conducted on double-walled CNTs (DWCNTs) /SiC composite models with Si doping on the inner CNT and outer CNT. As a result, it is found that Si doping facilitates the formation of bonds between the inner and outer CNTs. Furthermore, the contribution of Si doping on the inner CNT is more significant in the increase in interwall bonding, whereas Si doping on the outer CNT contributes more to the outer CNT/SiC interfacial interaction. Toughness is investigated to represent crack resistance and is calculated as the area surrounded by the stress-strain curve. By comparing the toughness of the composite with Si doping on the inner CNT and doping on the outer CNT, it is understood that the DWCNT reinforcement is better with doping on the inner CNT. Therefore, it is concluded that better reinforcement is achieved from the CNT interwall bonding than the CNT/SiC interfacial interaction.

Chapter 5 Orientation-dependent Reinforcing Mechanisms of CNT in SiC: Discovery of Two Mechanisms with Crystalline Models

In general, when a certain volume fraction of CNT is added to ceramics, the reinforcing result has been reported to be only 20% of the ideal prediction, which is thought to arise from the random orientation of CNT in the matrix[6]. However, the underlying mechanisms are still elusive due to the difficulties of experimental measurements of composites nanostructures. By conducting tensile simulations on crystalline models with varying angle (θ) between CNT axial direction and tensile direction, two reinforcing mechanisms are discovered. One is CNT axial stretching, referring to the CNT stretches axially to bear load and reinforce SiC, and it determines the tensile strength of composites. The other is CNT bridging, which refers to CNT surviving and connecting two grains after SiC cracks, and it determines the toughness of composites. Moreover, the typical "sword in sheath" failure of CNT is observed, referring to the CNT fracture mechanism where the outer tube of CNT breaks and the inner tube is pulled out from the outer tube. As the θ increases, CNT bridging effect increases and the axial stretching effect decreases. The strength of the CNT/SiC composite increases as it depends on CNT axial stretching effect. The toughness of the CNT/SiC composite is determined by both CNT axial stretching and CNT bridging effects. Hence, an optimal balance between the two effects exists, resulting in a volcano-type (firstly increase to the peak at 45°, then decrease) dependence of toughness to θ, as shown in Fig. 3. The conclusion for this chapter is that the orientation affects CNT reinforcement regarding strength and toughness via two mechanisms, CNT axial stretching and CNT bridging.

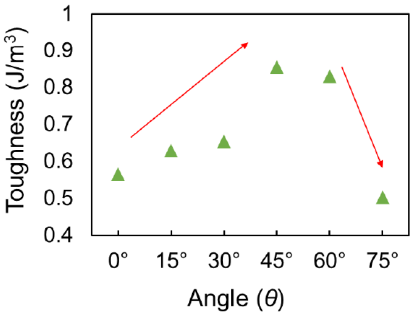

Fig. 3. Plots of toughness of composites models with different angle θ.

Chapter 6 Large-Scale Simulation on Polycrystalline CNT/SiC composites: How Does Volume Fraction Affect Composites' Fracture Behaviors?

SiC exists in the polycrystalline form in nature. Therefore, a large-scale polycrystalline model is built to simulate the natural deformation of composites, and furtherly develop a simulation method for structural materials for industrial applications. Moreover, the controversial influence of CNT volume fraction on the reinforcement in ceramics has been reported[7]. To investigate the effect of volume fraction on polycrystalline composites' fracture and CNT reinforcement, models with different numbers of CNTs aligned in the SiC crack tip area at the same distance from the crack tip are constructed. As the results of tensile simulations, it is discovered that a large CNT volume fraction makes the crack tip area too strong, and the model fractures quickly along a concentrated crack, which is formed spontaneously in the unreinforced area. Therefore, the large CNT volume fraction results in unsatisfying reinforcement. Meanwhile, when the volume fraction is relatively low, the optimal reinforcement is attained. This is because the CNT-reinforced crack tip area and the unreinforced area are almost equally strong, resulting in the stress distributed into multiple small cracks. This phenomenon is defined as "crack dispersion". From further observation on the CNT reinforcing mechanisms, it is also revealed that "crack dispersion" occurs when the "sword in sheath" (as one of the CNT fracture mechanisms) and CNT bridging both occur (Fig. 4). Therefore, the conclusion of this chapter is as follows: in the CNT/polycrystalline SiC composites, the best reinforcement is achieved by a relatively low CNT volume fraction, as multiple small cracks propagating together.

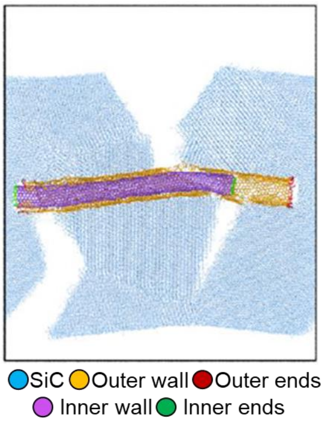

Fig. 4. Occurrence of CNT bridging and CNT fracture as "crack dispersion" appears.

Chapter 7 Effect of High Temperature Water on CNT Reinforcement in Polycrystalline SiC

For the goal to apply the composites as structural materials in corrosive environments like high temperature water environment, it is important to study the effect of oxidation by high temperature water on the CNT reinforcement. Therefore, the purpose of this chapter is to investigate the effect of high temperature water environment on CNT reinforcement in a polycrystalline model. Large-scale SiC and composite models in vacuum and water environments are constructed. As the result of tensile simulations, it is revealed that CNTs reinforce SiC in water via two mechanisms: one is that even in a corrosive environment, reinforcement is achieved without CNT corrosion; the other is that CNT prevents water from contacting with SiC at the crack tip, result in suppressing the further corrosion of SiC at the crack tip. Hereby, the CNT reinforcement in high temperature water environment is confirmed.

Chapter 8 How Do CNTs' Relative Position Influence the Reinforcing Result in High Temperature Water Environment

In actual applications, CNTs are more likely to be distributed with random relative positions than being aligned at the same distance from the crack tip. Therefore, it is necessary to confirm whether the reinforcement is valid with any CNTs' relative positions. Two large-scale CNT/SiC composite models are constructed, each with CNTs inserted in different relative position patterns. One model (pattern 1 model) has one CNT in the crack tip area and one CNT in the area far away. Another model (pattern 2 model) has two CNTs aligned in the crack tip area. Results of tensile simulations show that in the pattern 1 model, shear stress formed along the crack propagation path cuts the further CNT, whereas both CNTs in the pattern 2 model remain intact and stop critical crack propagation. Furthermore, reinforcement appears in either of the relatively positioned models in terms of toughness. In the conclusion, it is confirmed that reinforcement is achieved by both relative position patterns of the CNTs.

Chapter 9 General Conclusion

The effects of CNT/SiC interfacial bonding and CNT interwall interaction on reinforcement are clarified in Chapter 3 and Chapter 4, respectively. The role of structural factors like orientation is revealed in Chapter 5. Moreover, to achieve the purpose to provide references for industrial composite design, large-scale CNT/polycrystalline SiC composite models are adapted in Chapter 6. For the understanding of chemical reactions with applicated environments, the influence of water molecules on CNT reinforcement in polycrystalline composite models is investigated in Chapter 7. Finally, in Chapter 8, effective reinforcement by two typical patterns of CNTs' relative positions in the water environment is confirmed, indicating the universality of CNT reinforcement in applicated conditions. This doctoral thesis illuminates the fracture mechanisms of CNT/SiC composites considering interfacial behaviors, structural factors, and applicated conditions. It is reckoned to assist future experimental studies by showing the optimal reinforcing conditions.

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