Research Progress in SiC-Based Ceramic Matrix Composites

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ABSTRACT

SiC-based ceramic matrix composites show many advantages over their monolithic ceramic counterparts, which makes them potential candidates for applications in various fields. Depending strongly on the chemical composition and microstructure of the fiber reinforcement, matrix as well as the fiber/matrix interphase in the material, the properties of ceramic matrix composites (CMCs) are highly tailorable. In this paper, the latest progresses in the interphase design, matrix modification and fiber reinforcement decoration of CMCs are reviewed, their effects on the properties of the CMCs are introduced.

Key words : Ceramic matrix composites, Interphase design, Matrix modification, Fiber decoration

1. Introduction

Non-oxide ceramic matrix composites (CMCs) have attracted a lot of attentions in the past decades due to many of their advantages in properties, such as low density, high damage tolerance and high specific strength. The aforementioned advantages have ensured CMCs as potential candidates for a variety of applications in aerospace fields including rocket nozzles, heat shields and aircraft braking systems. Today, the most extensively studied CMCs are fiber reinforced SiC matrix composites, namely C/SiC, SiC/SiC and C/C-SiC composites. These CMCs are traditionally fabricated through chemical vapor infiltration (CVI),8,14-16 polymer infiltration and pyrolysis (PIP),17-23 hot pressing sintering (HP) methods. In addition, some hybrid fabrication processes have also been developed in order to take full advantage of the merits of traditional fabrication process but overcome their drawbacks.

The properties of CMCs, which show strong dependence on the consolidation state of the fiber performs, the matrix composition and the matrix/fiber interphase (and/or interface), can be systematically tailored through the application of proper fabrication process along with the modification of the composite matrix and/or interphase with some functional materials as well as decoration of fiber reinforcements. In this paper, the recent research progress in microstructure optimization and property tailoring of SiC-based CMCs is reviewed.

2. Design and Functions of the Interphases

The main advantage of CMCs over their monolithic counterparts lies in the fact that they are tough, despite that their constituents are intrinsically brittle, which endows CMCs with high reliability. In order to obtain CMCs with high fracture toughness, it is of great importance to design proper fiber/matrix interface, so that the formation of strong bonding between fibers and matrix can be avoided. This facilitates the microcrack arresting and deflecting at the interface, and prevents the early failure of the fibrous reinforcement. Nowadays, layer crystal structured pyrocarbon (PyC) and hexagonal boron nitride (h-BN) are generally used as interphase materials, although sometimes interphases composed of multilayered (PyC/SiC)n and (PyC/BN)n that are deposited parallel to the fiber surfaces are also used. Zhou fabricated (PyC/SiC)n multilayered interphases through forced pressure-pulsed chemical vapor infiltration process (FP-CVI) and analyzed the effect of deposition conditions on the microstructures of (PyC/SiC)n interphases, the microstructure of the as-fabricated (PyC/SiC)n interphases were shown in Fig. 1. Zhou also studied the effect of interphase on the mechanical properties of the C/SiC composites fabricated through vapor silicon infiltration (VSI). It was found that with the deposition of PyC/SiC interphase on carbon fibers, the composites show typical non-brittle fracture behavior and the average bending stress of the material increased from 67.4 MPa to 239.5 MPa as shown in Fig. 2. The positive effect of PyC/SiC interphase on mechanical properties of composites may be accounted by the following two reasons. Firstly, the existence of PyC/SiC interphase can act as diffusion barrier during the later stage of composite fabrication process, which can effectively prevent the diffusion of silicon toward carbon fiber and the strength of fiber...
reinforcements can be well retained. Secondly, the weakly bonded interphases can arrest and deflect the matrix cracks, thus protect the fibers from early failure through notch effect. Fig.3(a) shows the siliconization of carbon fibers when no interphases were applied, Fig.3(b) shows the deflection of cracks along the PyC/SiC interphase.

Wang\textsuperscript{21,28} studied the effect of interphases on the mechanical properties of C/SiC-ZrC composites fabricated by slurry impregnation and PIP densification using polycarbosilane as precursor. They found that the mechanical properties of the material could be significantly improved only with the introduction of proper interphases. In other words, a matching effect existed between the fiber reinforcements and interphases, which showed a strong influence on the mechanical properties of composites. When M35JB carbon fibers were used as the reinforcements, composites with PyC interphase possessed the highest bending stress. In comparison, when T700SC carbon fibers were used as the reinforcements the composite with PyC/SiC interphase possessed the highest bending stress. In addition, it is found that the introduction of interphases will hinder the infiltration of ceramic particles in the slurries to the intra-bundle zones, as shown in Fig. 4, which may be ascribed to the tight structure of fiber bundles after deposition of interphases.

3. Matrix Modification Potential for Different Applications

It is well-known that CMCs can be applied in a variety of fields. However, different requirements have to be met for a specific application. When applied as engine components, the long-term oxidation properties at intermediate and low temperatures have to be considered. When applied as some thermal structure components in hypersonic vehicles, since the components have to face the environments with ultrahigh temperatures and high velocity, special attentions should be paid to the ablation behaviors. For some other application, low fabrication costs and short manufacturing periods should be considered. In order to meet the different requirements for applications, matrix modification has been proved to be a feasible method.

To overcome the drawbacks of large volume shrinkage accompanied with PIP process, active filler controlled pyrolysis(AFCOP) process has been developed by Greil\textsuperscript{29}. In AFCOP process, the volume expansion occurred in the chemical reaction of active filler will compensate the volume shrinkage caused by the pyrolysis of organic precursors, which will greatly increase the processing efficiency. Zhu\textsuperscript{30-32} takes Al as active filler for the rapid fabrication of SiC-based composites. The density as well as the mechanical proper-
ties can be increased, as shown in Fig. 5. In the fabrication process, the active filler Al will react with the decomposition products, the matrix can be strengthened as a result of the in situ formation of Al₄Si₃, Al₄C₃ and AlN. Meanwhile the filling of some pores by the newly formed phases will account for the increase of density.

Wang tried to fabricate carbon fiber reinforced SiC-based composites by applying boron as active filler and observed the microstructure evolution process. It is found that, with the application of active filler, the densification process can be accelerated. The density of C/SiC composites fabricated by traditional PIP process decreased from 1.92 g/cm³ to 1.77 g/cm³, while that of composites with boron particles increased from 1.71 g/cm³ to 1.77 g/cm³ after the nitridation process. When nitridated at 1800°C in N₂ atmosphere, the SiOC phases existed in the matrix of composites will decompose to gaseous SiO and CO, resulting in the decrease of density. However, when active filler boron is incorporated, it will react with N₂ to h-BN and the weight gain accompanied will compensate the weight loss of SiOC phases decomposition. As the micro-pores and micro-cracks will act as the diffusion paths for N₂ gases, the diffusion of N₂ to active filler boron particle is a key factor for the conversion of boron into h-BN. Therefore, the h-BN phases formed may grow along the micro-pores and micro-cracks, as shown in Fig. 6(b). The filling of microcracks and micro-pores will lead to the increase of density. After the modification of SiC matrix with h-BN, the oxidation resistance of composites improved obviously, as shown in Fig. 7. This phenomenon has proved the self-sealing effect of boron-bearing materials when operated at low and intermediate temperatures.

Considering it is hard to get composites with homogenous microstructures through slurry impregnation as shown in Fig. 4, Li tried to synthesis ZrC-SiC nanocomposites through heat-treatment of ZrC precursor and polycarbosilane mixtures, and extended this method to the fabrication of C/ZrC-SiC composites. ZrC was synthesized from precursor-derived ZrO₂ and carbon by carbothermal reduction reaction. The ZrC precursor and polycarbosilane can be dissolved in the same solvent, and the precursor solution can fill all open pores existing in the composites. Therefore, the volume content and the phase uniformity are greatly increased. It can be concluded from Fig. 8 that only a small amount of pores can be found in the as-fabricated composites, the ZrC and SiC phases are mixed in nano-scale. Hereby, high efficiency modification of SiC-based composites is realized through the co-solved precursor. With the increase in ZrC content and the uniformity of CMCs, it is believed that the ablation properties of the material can be greatly enhanced.

4. Fiber Reinforcement Decoration for Multi-functional Enhancement Mechanism

In the past decades, a lot of attention has focused on the
studies of CMCs, especially SiC-based composites, and almost all composites with fibers as reinforcements, such as carbon fibers and SiC fibers. Though great progresses have been made in industrial application of CMCs, no state-of-the-art materials can meet all requirements for industrial applications, some properties need to be optimized. For example, with the development of hypersonic vehicles, emphasis on thermal properties of these materials is becoming more prevalent. It is favorable for CMCs with high thermal conductivity to divert heat from hot zone to the cold zone when used as hot-structural materials, which will lower the temperature in the hot zone. Although the thermal conductivities of their main constituents (fiber reinforcements and matrix phases) are very high in the pure state, CMCs possess a relatively low thermal conductivity, normally lower than 20 W/mK. This phenomenon may be caused by the thermal barriers in CMCs induced by the defects such as interfacial debonding, delamination, micro-pores and micro-cracks. As the thermal conductivity strongly relies on the compositions and microstructures of CMCs, it can be enhanced by introducing some phases with very high thermal conductivity and well connection to each other. CNTs have been recognized as ideal nano-reinforcements for ceramics, and some applications have been realized. For high-temperature applications, the high thermal conductivity of CNTs suggests that their incorporation in CMCs, even at low volume fractions, might provide the thermal transport needed to reduce material operating temperatures and improve thermal shock resistance. In our work, CNTs have been introduced into CMCs for both mechanical and thermal properties improvement of the material through a multi-functional enhancement mechanism.

There are a variety of methods for the fabrication of CNTs. However, considering the future application of CNTs decorated carbon fibers as the reinforcements in composites, which requires large quantity production of carbon nanotubes in an economical manner, catalyst vapour-assisted chemical vapor deposition method (CVD) has been used for the direct growth of CNTs on carbon fibers. After getting CNTs-decorated carbon fibers, SiC-based CMCs were developed through polymer infiltration and pyrolysis process. Fig. 9 shows the SEM micrographs of carbon fibers before and after the in-situ growth of CNTs on their surfaces. From Fig. 9(b), it can be observed that there is a high volume fraction of CNTs grown on the fiber surface through catalyst-assisted CVD process and CNTs fill the gaps among fiber filaments. It can also found from the magnified graphs shown in Fig. 9(c) that the CNTs connect to each other, which is beneficial for heat transfer through the high thermal conductivity CNTs.

Fig. 10(a)-(c) show the effect of CNTs on the fracture behavior of SiC-based composites. It can be deduced from these figures that the incorporation of CNTs in the composites significantly strengthens the matrix of the materials, according fiber bundle pull-out is observed in them (Fig. 10(b),(c)). Instead, fiber pull-out is observed in the conventional CMCs (Fig. 10(a)) due to its relatively weak matrix. Furthermore, owing to the incorporation of CNTs, the thermal conductivity of the composite is increased by about 50% in comparison with that of the composite without CNTs. It is believed that with the proper control of CNTs/fiber as well as CNTs/matrix interphases, the synergetic effect of the carbon fiber CNTs reinforcements can be fully utilized and high performance SiC-based CMCs can be developed.
5. Conclusions

Some progresses have been made concerning property tailoring of CMCs through interphase design, matrix modification and reinforcement decoration. For obtaining high performance CMCs, special attention should be paid to the composition and microstructure optimization of the material, together with the development of special fabrication process.

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