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Optical Coating on C_f/SiC Composites *via* Aqueous Slurry Painting and Reaction Bonding

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Abstract: A novel surface modification method for C_f/SiC composites is proposed with aqueous slurry painting together with reaction bonding. Stable slurries were obtained by dispersing SiC to carbon black in aqueous solution, under centain binder content and solid loading conditions. The results show that porous carbonaceous C/SiC tape with porosity of 49% could be obtained by aqueous slurry painting. Si/SiC coating with high density and strong bonding onto the substrate is realized by infiltrating liquid silicon into the as-prepared tape. A reaction layer of ~15 μm in thickness is formed between the coating and the substrate. This Si/SiC coating exhibits excellent mechanical properties, with HV hardness of (14.19 ± 0.46) GPa and fracture toughness of (3.02 ± 0.30) MPa·$m^{1/2}$. The coating is achieved fine surface of 2.97 nm RMS in roughness after precision grinding and polishing.

Key words: Si/SiC coating; C_f/SiC; aqueous slurry painting; reaction bonding

C_f/SiC composites have triggered great interest in various fields due to their excellent properties, such as low density, high fracture tolerance, excellent high temperature resistance and outstanding corrosion resistance[1-4]. Especially, their potential application in space optics enables them to be ideal materials as the next generation optical components[5-8]. However, realization of high-quality optical surface remains an unsolved challenge, which limits the application of C_f/SiC composites in space optics.

Surface modification of C_f/SiC composites is deemed to be an important tactic to solve this problem. To date, physical vapor deposition (PVD) and chemical vapor deposition (CVD) are two primary methods for the surface modification of C_f/SiC composites[9-11]. However, thick coating, which is necessary for achieving good optical surface by grinding and polishing, is hard to obtain for fully covering surface defects *via* both the above methods. What's more, large stress usually exists by these methods, causing the delamination of coating from the substrate. Therefore, the purpose of this work is to develop a new surface modification technique for C_f/SiC composites.

In the present work, a dense Si/SiC coating has been successfully prepared on C_f/SiC substrates *via* aqueous slurry painting and reaction bonding. The coating shows excellent mechanical properties as well as fine surface morphology. This study inspires a new and effective surface modification method for C_f/SiC composites.

1 Experimental

1.1 Material preparation

Commercially available α-SiC (Pingdingshan Yicheng New Material Co., Henan, China, purity > 99%), carbon black (Anyang Delong Chemical Co., Ltd., Henan, China, industrial grade) and Si powders (CNPC Power Group Co., Ltd., Shanghai, China, purity > 99.9%) were used as the starting materials. Tetramethylammonium hydroxide (TMAH) and polyvinylpyrrolidone (PVP) were selected respectively as the dispersants for SiC and carbon black in aqueous solution, while polyvinyl alcohol (PVA) was added as the binder. The raw materials were ball milled for 24 h using SiC media to ensure the homogeneity of the slurry. Afterwards, the slurry was applied for painting on the C_f/C preforms prepared in our lab. Porous tape was obtained after heat treatment at 1600℃ with a soaking time of 2 h in vacuum. At last, a dense Si/SiC coating on C_f/SiC was developed by liquid silicon infiltration at 1550℃ with 30 mins' dwelling time.

1.2 Test procedure

The zeta potential curves of SiC powers in the presence

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and the absence of TMAH, along with PVP-modified carbon black at different pH values were measured by zeta potential analysis (Zetaplus, Brookhaven Instruments Corp., Holtsville, NY). Rheological measurements were used to characterize the properties of slurries. The rheological test was conducted under steady shear condition by ascending and descending shear rate ramped from 0 to 1000 s^{-1} in 100 s, and from 1000 to 0 s^{-1} in 100 s, respectively, by the parallel-plate system on a Universal Stress Rheometer SR5 (Rheometric Scientific, USA) at various shear rates. The density, open porosity and mean pore size values of SiC/C tapes were measured by mercury porosimetry. Field emission scanning electron microscope (FESEM, Magellan 400) was used to observe the microstructures of porous tape and sintered Si/SiC coating. Hardness and fracture toughness were measured by indentation test on a Wilson-Wolpert Tukon 2100B (Instron, USA), with the load and holding time of 0.5 kg and 10 s, respectively. The fracture toughness was calculated from the method of Lawn[12]. The surface topography and roughness of the Si/SiC coating were tested by Atomic Force Microscope (AFM, Nanonavi Probe Station and Nanocute) in a 5 μm×5 μm region after precision grinding and polishing.

2 Results and discussions

2.1 Surface properties of SiC and carbon black

The Zeta potential is commonly used as a parameter to describe the surface charging behavior of the particles in suspensions. The stabilization of the particles is contributed to the effect of steric hindrance as well as the electrostatic repulsion forces[13]. TMAH and PVP have been proved to be effective dispersants for the aqueous dispersion of SiC and carbon black[14]. Figure 1(a) shows the Zeta potential curves of SiC and carbon black with and without dispersants. The surfaces of SiC are electronegative during the whole pH region, regardless of the presence of TMAH or not. It is a result of dissociation of oxide layers according to Ganesh and Li's reports[15-16]. The absolute value of zeta potential increases with pH increasing from 2 to 10. In the presence of TMAH, the absolute value of zeta potential receives an increment of ~4.8 mV at pH 10, which is beneficial to improve the stability of SiC powers in aqueous suspensions. It is known to all that carbon black has a poor wettability with polar water molecule (H_2O) due to its nonpolarity and large specific surface area. As shown in Fig. 1(b), zeta potential curve of PVP modified carbon black together with the molecular structure of PVP are presented. At around pH 10, the absolute value of zeta potential reaches a maximum. Therefore, stable aqueous SiC-C suspensions could be obtained at around pH 10. PVP plays an important role in the aqueous dispersion of carbon black. It is possible that the hydrophilic acyl groups were absorbed onto the surface of carbon black and steric hindrance took effect. Thus, well-dispersed aqueous solution was obtained at the presence of PVP.

2.2 Rheological properties of the aqueous SiC/C suspensions

Figure 2 presents the rheological properties of 35vol% solid loading suspensions with different PVA (binder) content. It could be found from Fig. 2(a) that the slurries show typical shear-thinning behavior and the viscosity increases with increasing the PVA content. The viscosity of the suspensions is 0.15–0.35 Pa·s at the shear rate of 1000 s^{-1}, which is suitable for painting. The shear stress shows the same tendency from Fig. 2(b).

Figure 3 displays the rheological properties of 6wt% PVA content suspensions with different solid loadings. It is obvious that the slurries show typical shear-thinning behavior, similar with Fig. 2. Both the viscosity and shear stress increase with high solid loading. Thicker pre-coating could be obtained after drying with higher solid loading. It needs to be noted that the viscosity of the slurry suitable for painting should be neither too thick nor too

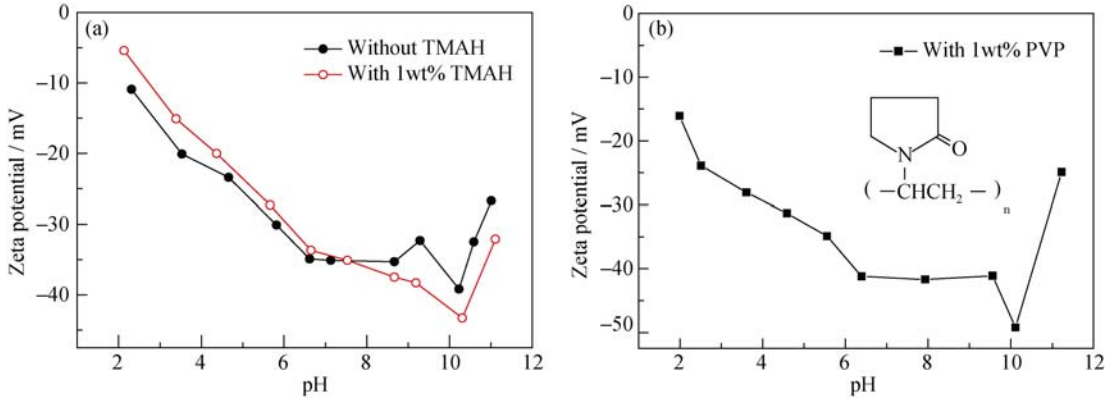

Fig. 1　Zeta potential curves of SiC with and without TMAH (a) and PVP modified carbon black (b)

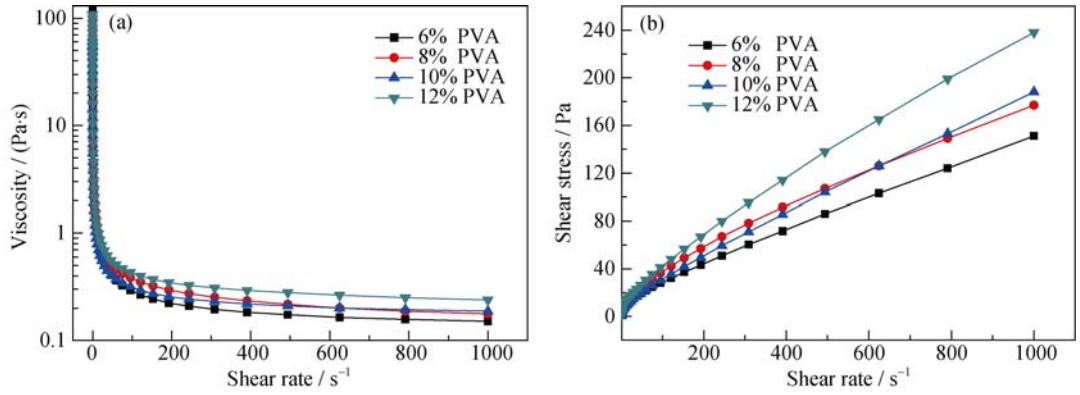

Fig. 2 Viscosity (a) and shear stress (b) of 35vol% solid loading suspensions with various PVA contents at different shear rates

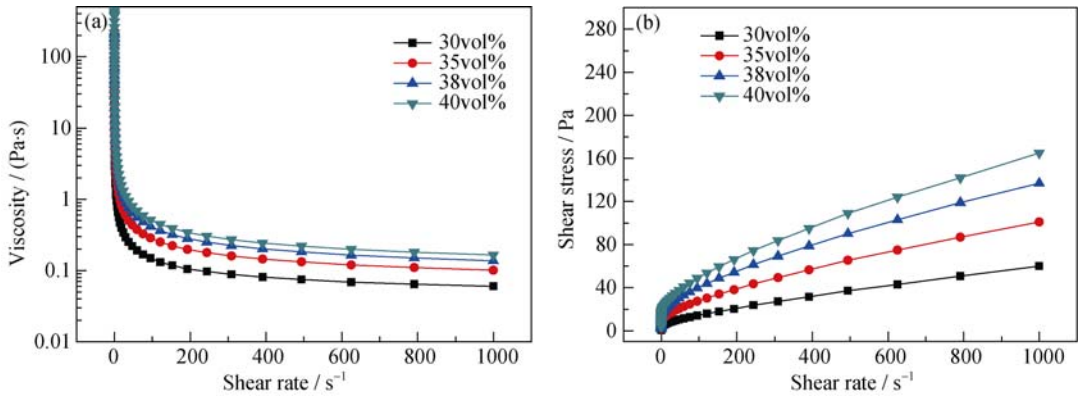

Fig. 3 Viscosity (a) and shear stress (b) of 6wt% PVA content suspensions with various solid loadings at different shear rates

thin. In the present work, the optimal solid loading is 35vol%.

2.3 Microstructure of the SiC/C green tapes

Figure 4 shows the macroscopic photograph and SEM image of the porous green tape after binder removal. It is observed that the prepared green tape is smooth without any obvious defects such as holes or cracks. Silicon carbide, carbon black and pores are homogeneously distributed as arrowed in Fig. 4(b). The pores in the tapes are found to be interconnected. The mean pore size of the tape is ~0.16 μm and the porosity is ~49%, which are measured by mercury porosimetry method.

2.4 Microstructure of the sintered Si/SiC coating

Figure 5 presents the microstructure of the sintered Si/SiC coating. The dense coating is consisted of Si and SiC, in which Si (pale phases) and SiC (dark phases) are homogeneously distributed. From Fig. 5(b), it could be found that the Si/SiC coating is strongly bonded with the substrate. A reaction layer of ~15 μm in thickness is formed between the coating and substrate by reaction between the liquid silicon and carbon. The interface between the coating and substrate is not quite clear due to the formation of this layer. Though a small amount of carbon fibers are corroded in the substrate, the formation of this reaction layer is helpful for realizing strong bonding between the coating and substrate.

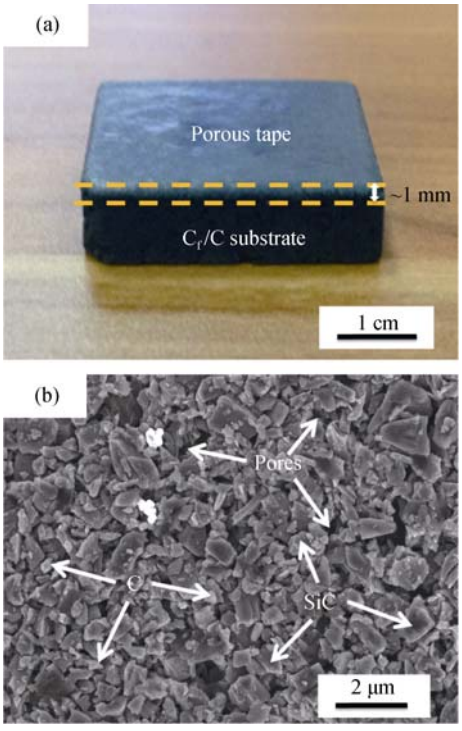

Fig. 4 Macroscopic photograph of as-prepared sample (a) and SEM image of the porous green tape (b)

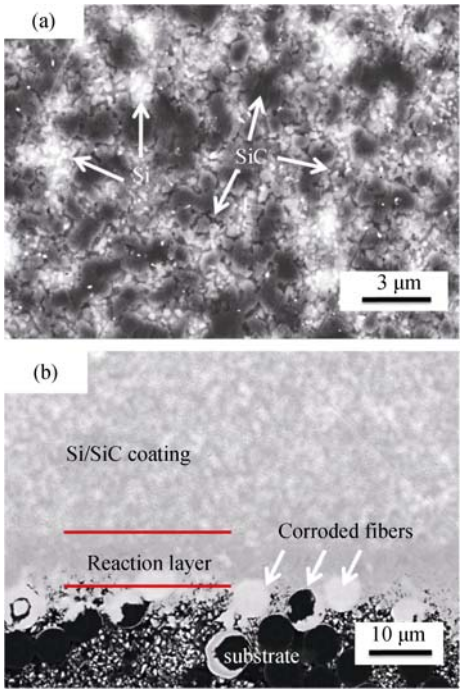

Fig. 5　SEM images of the sintered Si/SiC coating (a) and its interface between the coating and the substrate (b)

2.5　Surface roughness and mechanical properties of the sintered Si/SiC coating

The surface topography and roughness of the Si/SiC coating are displayed in Fig. 6(a)-(b). It could be found that there are some steps between Si and SiC. It is due to the different polishing rate between Si and SiC. The P-V (peak-to-valley) value of the surface roughness is 17.61 nm. There are no defects such as large holes or protuberances in the test region, indicating super smooth feature of the surface. In the present work, fine surface with roughness as low as 2.97 nm RMS has been achieved after precision grinding and polishing. Importantly, the surface roughness obtained from this method is comparable to those from PVD-Si or CVD-SiC method[11, 17], which would presumably meet the requirements for the application in space optics. Furthermore, it is a flexible and cost-effective technique, promising for preparing high-performance C_f/SiC composites. Fig. 6(c) shows indentation test on the polished surface of the sintered coating. It could be seen that the coating is not shattered by indentation and the shape of indenter is well kept, indicating that uniform structure could be obtained by aqueous slurry painting and reaction bonding. In the present experiment, the HV hardness and fracture toughness are (14.19 ± 0.46) GPa and (3.02 ± 0.30) MPa·m$^{1/2}$, respectively.

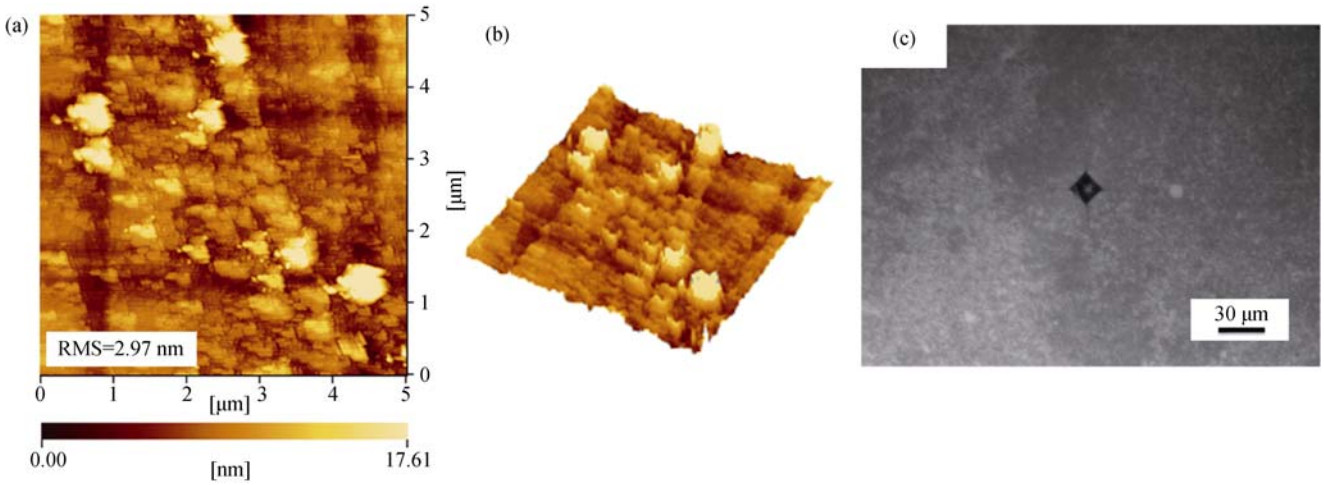

Fig. 6　Surface topography and roughness of the Si/SiC coating (a, b) and indentation image on the polished surface of the sintered coating (c)

3　Conclusions

A novel surface modification method is proposed for C_f/SiC composites: combination of aqueous slurry painting and reaction bonding. The conditions for preparation of stable aqueous SiC/C slurries are optimized. The optimal pH value and solid loading are ~ 10 and 35vol%, respectively. Porous carbonaceous tape with mean pore size of ~ 0.16 μm and porosity of ~ 49% is prepared by aqueous slurry painting method. A reaction layer of ~15 μm in thickness is formed due to the reaction between liquid silicon and carbon, which in turn ensures the strong bonding. This Si/SiC coating exhibits an excellent mechanical property with HV hardness of (14.19 ± 0.46) GPa and fracture toughness of (3.02 ± 0.30) MPa·m$^{1/2}$. Smooth surface with roughness (RMS) as low as 2.97 nm, which is comparable to the traditional CVD or PVD techniques, has been achieved after precision grind-

ing and polishing. Overall, this research offers an effective and low-cost approach for the surface modification of C_f/SiC composites, and further opens a new perspective for the development of space optics.

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水基浆料涂覆结合原位反应制备 C_f/SiC 复合材料表面光学涂层

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摘 要: 本研究提出一种 C_f/SiC 复合材料表面改性新方法为水基浆料涂覆结合原位反应烧结工艺。系统研究了 SiC 和炭黑在水基浆料中的共分散、粘结剂的量和浆料固含量对浆料流变性能的影响、涂层的微观结构和性能等。研究结果表明: 采用水基浆料涂覆工艺可在基材表面制备一层气孔率达 49%的多孔 C/SiC 预涂层; 通过液相渗硅原位反应工艺, 多孔预涂层转变为高致密、与基材强结合的光学涂层, 并且在涂层与基材间形成了~ 15 μm 的化学反应过渡层; Si/SiC 涂层的维氏硬度为(14.19 ± 0.46) GPa, 断裂韧性为(3.02 ± 0.30) MPa·$m^{1/2}$; 经过精细研磨抛光, 涂层的表面粗糙度可达 2.97 nm RMS。

关 键 词: Si/SiC 涂层; C_f/SiC; 水基浆料涂覆; 反应烧结

中图分类号: TQ174 **文献标识码:** A