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Short communication

A hot-pressing reaction technique for SiC coating of carbon/carbon composites

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Abstract

A hot-pressing reactive sintering (HPRS) technique was explored to prepare SiC coating for protecting carbon/carbon (C/C) composites against oxidation. The microstructures of the coatings were analyzed by X-ray diffraction and scanning electron microscopy. The results show that, SiC coating obtained by HPRS has a dense and crack-free structure, and the coated C/C lost mass by only 1.84 wt.% after thermal cycles between 1773 K and room temperature for 15 times. The flexural strength of the HPRS-SiC coated C/C is up to 140 MPa, higher than those of the bare C/C and the C/C with a SiC coating by pressure-less reactive sintering. The fracture mode of the C/C composites changes from a pseudo-plastic behavior to a brittle one after being coated with a HPRS-SiC coating.

Keywords: A. Hot pressing; A. Sintering; D. SiC

1. Introduction

Oxidation resistance is a key requirement for carbon/carbon (C/C) composites for applications in an oxygen-containing environment at high temperature [1–3]. To prevent C/C composites from oxidation, SiC coating was widely used due to its excellent oxidation resistance and good compatibility with C/C composites [4,5]. Presently, SiC can be coated on the surface of C/C composites by several methods, such as pack cementation [6], chemical vapor deposition (CVD) [7] and laser-induced chemical decomposition (LICD) [8]. Among these methods, pack cementation was usually used for providing a strong interface bonding between SiC coating and C/C composites [9]. However, cracks will be formed inevitably in this coating during the cooling process from high temperature to room temperature due to the mismatch of thermal expansion between SiC and C/C composites, which offer entrance channels for oxygen and result in the failure of the coating [5,7].

Hot-pressing reactive sintering (HPRS) is a technique in which both the chemical reactions of the starting materials and densification occur in single step. This technique can be economical due to low cost starting powders and relatively low sintering temperature, and it also leads to the possibility of densifying the materials without additives [10,11]. As far as the authors know, no literature has been published about using HPRS technique to prepare ceramic coatings for C/C composites. Though HPRS technique is not practical to prepare coatings for complex shaped C/C composites, it can be applicable to regular shaped ones by designing suitable moulds. In the present work, HPRS technique was proposed to prepare SiC coating for C/C composites. The microstructures and oxidation protective ability of the coatings were investigated, and the effect of SiC coating on the flexural property of the coated C/C composites was also studied.

2. Experimental

The substrates were cut from bulk 2D C/C composites with a density of 1.75 g/cm^3. Powder compositions for the HPRS process were 65–80 wt.% Si and 20–35 wt.% graphite. These powders were mixed by a blender for 2 h. C/C specimens were packed by these mixtures in a graphite crucible, and were pressed by a graphite pressing head. The pressure was controlled by 250 kPa. Then the graphite crucible was heated to 1873–2073 K and held at that temperature for 2 h under

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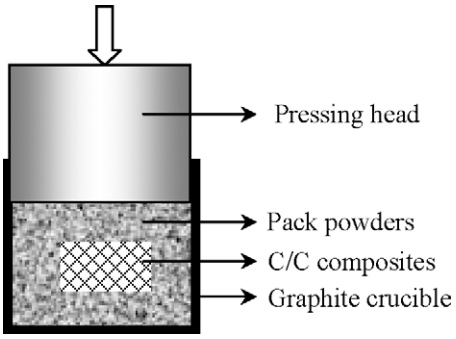

Fig. 1. Sketch of preparing SiC coating for C/C composites by HPRS.

slight argon flow. During this process, Si will melt and react with C/C composites to form SiC coating. The sketch of preparing SiC coating for C/C composites by HPRS is shown in Fig. 1. For comparison, another kind of SiC coating was prepared by pressure-less reactive sintering (PRS) with the same starting powders and heat-treatment temperature.

To investigate the thermal stress resistance of the coatings, the thermal cycling test between 1773 K and room temperature was performed. The samples were weighed at room temperature by electronic balance with a sensitivity of ±0.1 mg during thermal cycling tests. To evaluate the mechanical properties of the samples, three-point bending tests were carried out in a servohydraulic machine of 8871 (INSTRON CO., Ltd., USA). The span was 40 mm and the crosshead speed was 0.5 mm/min. Five samples for each kind of sample were tested and the final flexural properties were obtained by computing the average values of five samples.

The morphologies and crystalline structures of the coatings were analyzed by JSM-6460 scanning electron microscopy (SEM) and Rigaku D/max-3C X-ray diffraction (XRD).

3. Results and discussion

Fig. 2 shows XRD patterns of the surface of the coated samples. From Fig. 2(a), the diffraction peaks of graphite and cubic β-SiC are detected from the surface of the coating obtained by PRS. Graphite is corresponding to the C/C substrate, and β-SiC comes from the coating. Fig. 2(b) displays that a new phase of Si was generated in the coating by HPRS.

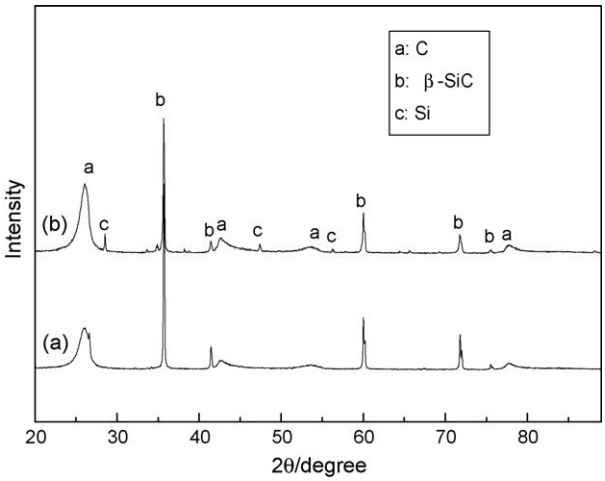

Fig. 2. XRD patterns of the surface of the C/C samples with coatings prepared by PRS (a) and HPRS (b).

During the preparation of coating, melted Si will react with C/C to form SiC coating. Under pressure, some of liquid Si in the pack powders was congregated to the surface of the samples and left in the SiC coating, which is advantageous to relax the stress at the end of the cracks and heal up the cracks in the coating.

Fig. 3(a) displays SEM image of the coating prepared by PRS. This coating has a porous structure with some microcracks, resulted from bigger coefficient of thermal expansion of SiC coating than that of C/C composites. Due to its loose structure, this coating might provide a poor oxidation protective ability for C/C composites. From Fig. 3(b), the as-received coating prepared by HPRS possesses a dense and crack-free structure. With pressure, the coatings will have compressive stress, which can effectively make up for the tensile stress induced by the shrinkage of SiC coating during the cooling process from high temperature to room temperature. The thermal stress in SiC coatings can be relaxed by the introduction of pressure.

SEM images of the cross-section of the SiC coated samples are shown in Fig. 4. From Fig. 4(a), there are large numbers of holes in the SiC coating prepared by PRS, owing to the difficult sintering of SiC ceramic without pressure. From Fig. 4(b), SiC coating prepared by HPRS is denser than that without pressure,

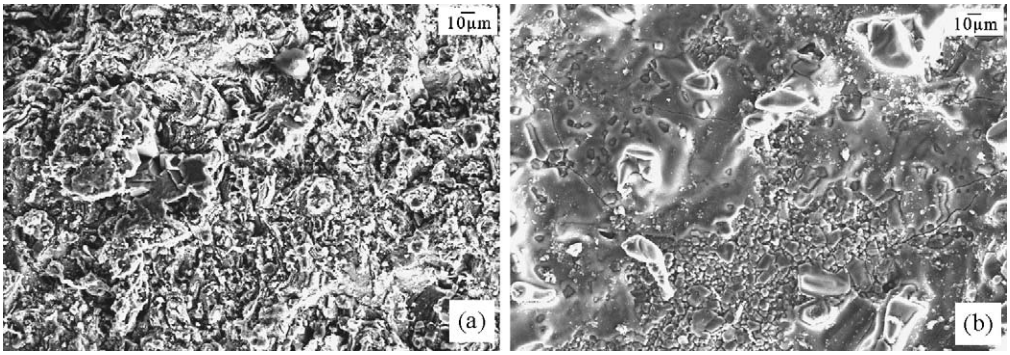

Fig. 3. SEM images of the surface of the coatings prepared by PRS (a) and HPRS (b).

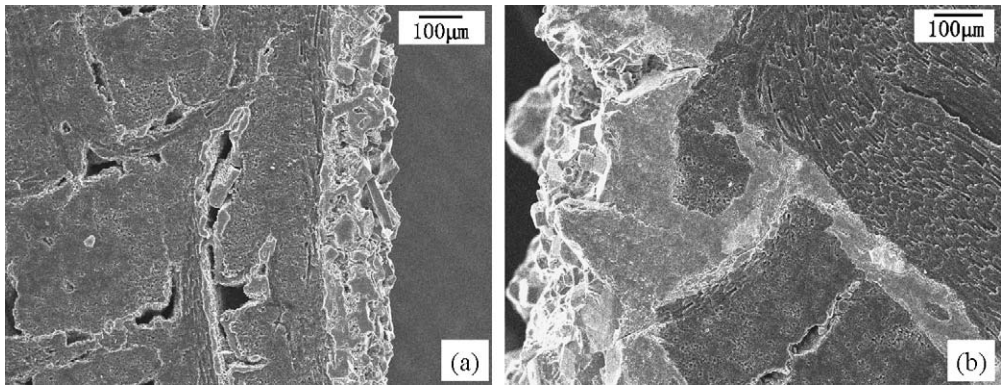

Fig. 4. SEM images of the cross-section of the samples with SiC coatings prepared by PRS (a) and HPRS (b).

and the coating materials are existent at the edges of the holes in C/C composites near the coating. At the processing temperature, the silicon powders in the original pack mixtures melted and possessed strong infiltration ability. The liquid Si would infiltrate deeply to the inside of the C/C composites through the holes and cracks in these composites and react with C/C, which is advantageous to the bonding between coating and C/C composites.

Fig. 5 shows the percent mass losses of the samples during thermal cycling between 1773 K and room temperature. Bare C/C composite specimen has a poor oxidation resistance, and its mass loss percentage is up to 70 wt.% after thermal cycling for only 10 times. With a SiC coating prepared by PRS, the sample loses mass for about 17.6 wt.% after 15-time thermal cycles. Compared with the SiC coating by PRS, the SiC coating prepared by HPRS exhibits a better thermal shock and oxidation resistance, and the mass loss of the C/C sample with this coating is only 1.84 wt.% after 15-time thermal cycles. The SiC coating obtained by HPRS has a dense and crack-free structure, so it has a better oxidation protective ability for C/C composites.

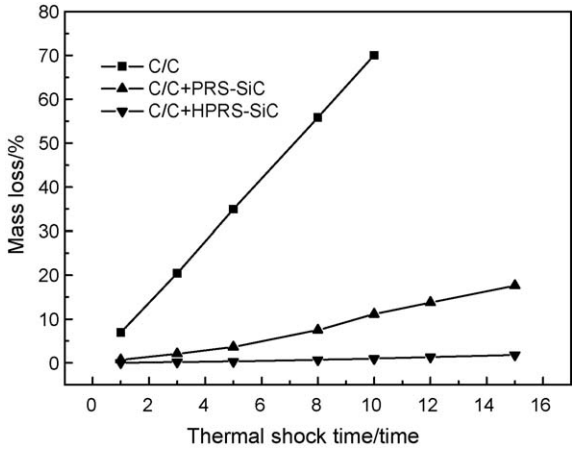

Fig. 5. Percent mass losses of samples during thermal cycling between 1773 K and room temperature.

Table 1
Flexural properties of the as-tested samples.

Samples	Strength/MPa	Modulus/GPa
C/C	89 ± 7	11 ± 1
C/C + PRS-SiC	105 ± 10	12 ± 1
C/C + HPRS-SiC	140 ± 12	27 ± 3

The flexural property parameters of C/C and coated C/C composites are shown in Table 1. The flexural strength of C/C, PRS-SiC coated C/C and HPRS-SiC coated C/C are 89 ± 7, 105 ± 10 and 140 ± 12 MPa, respectively. Compared to the bare C/C composites, the SiC coated C/C composites have higher strength and modulus for the reason that SiC coating can eliminate some defects in C/C composites near their surface. These defects consist of microcracks resulted from the machining of C/C and holes left in C/C substrate during their preparation. More defects will be eliminated by the stronger infiltration ability of Si under pressure. So, the sample with a HPRS-SiC coating exhibits higher mechanical property than that with a PRS-SiC coating.

Fig. 6 shows the load-displacement curves of the samples. It can be seen that the bare C/C sample exhibited a bit pseudo-plastic fracture behavior. With a PRS-SiC coating, the toughness of the sample was reduced evidently. While the HPRS-SiC coated sample experienced a bit of brittle fracture mode.

Fig. 7 shows the fracture surface of the samples after flexural tests. From Fig. 7(a), carbon fibers were pulled out from

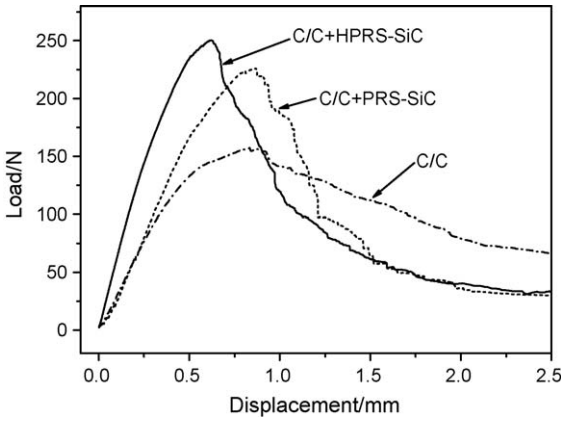

Fig. 6. The load-displacement curves of the samples.

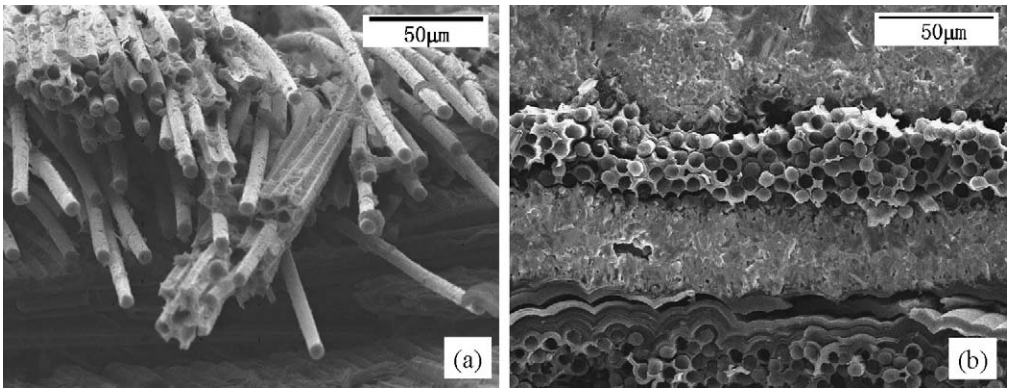

Fig. 7. Fracture surface micrographs of the samples after flexural tests. (a) C/C and (b) HPRS-SiC coated C/C.

pyrocarbon evidently, which is advantageous to the ductility of the sample. From Fig. 7(b), the HPRS-SiC coated C/C sample had an even fracture surface, accordant with its brittle fracture characteristic. It is well-known that, defects, such as holes and cracks, are generally existent at the interface between carbon fiber and carbon matrix. By HPRS-SiC coating, these defects will be eliminated partially, and the interface bonding between fiber and matrix will be improved largely. Therefore, the fracture mode of the C/C sample changed from a pseudo-plastic fracture behavior to a brittle one after being coated with a HPRS-SiC coating.

4. Conclusions

HPRS technique can be applied to obtain a dense and crack-free SiC coating for C/C composites. The HPRS-SiC coating can infiltrate into C/C substrate deeply, resulting in excellent thermal shock and oxidation resistance between 1773 K and room temperature. The flexural property of the HPRS-SiC coated C/C sample is higher than those of the bare C/C and the PRS-SiC coated C/C sample. The fracture mode of the C/C sample changes from a pseudo-plastic behavior to a brittle one after being coated with a HPRS-SiC coating.

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