

Double SiC Oxidation Protective Coating on C/C Composites Prepared by Spark Plasma Sintering

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Abstract

Easy oxidation of carbon limits applications of carbon-carbon composites in an oxygen-containing environment. In this study, a two-layer SiC coating was prepared on carbon-carbon composites by a Spark plasma sintering technology at 1350°C for 1 min. The coating was mainly composed of β -SiC and Si and well bonded with the substrate. The double SiC coating could effectively protect the C/C composites from oxidation at 1600°C for 120 h, and the corresponding weight loss was only 2.62%.

Keywords

Carbon-Carbon Composites, Spark Plasma Sintering, Anti-Oxidation, Coating

1. Introduction

Carbon/carbon (C/C) composites are promising materials used in aircraft and aerospace fields due to their excellent properties, such as high temperature strength, high thermal conductivity, low thermal expansion coefficient, good thermal shock and ablation resistance [1]. However, the oxidation of C/C composites above 723 K limits their applications in an oxygen-containing environment [2] [3].

A silicon carbide (SiC) coating, which possesses an excellent oxidation resistance and good compatibility with C/C substrates, has attracted extensive attention [4] [5] [6]. But, due to thermal expansion mismatch between SiC and C/C

composites, cracks are easily formed in the SiC coating, which could offer the path for oxygen to diffuse into the composites. Consequently, various multilayer coatings are explored, such as SiC/SiC [7] [8], mullite/SiC [9] [10], MoSi₂/SiC [11], AlPO₄/SiC [12], SiC-MoSi₂-ZrB₂/SiC [13]. Among them, double SiC coating is considered as a good choice to protect C/C composites from oxidation because of no thermal expansion mismatch between the outer layer and the inner layer.

Up to now, three methods, namely pack cementation, chemical vapor deposition and slurry method, are mainly used to prepare coatings on C/C composites. Among them, pack cementation, which is usually used to offer a strong interface bonding between SiC coating and C/C composites, is needed to heat at 2173 - 2373 K for 2 - 4 h [13] [14] [15] [16]. Cracks will be formed inevitably in the coatings due to the mismatch of thermal expansion between the coatings and the composites. CVD can prepare the coatings at a lower preparation temperature but need to be provided a very long preparation time [17] [18] [19]. The drawback of time-consumption also exists in slurry method [20] [21] [22]. In addition, double coatings are needed to be prepared by two-step methods [7]-[22].

In this paper, we use a one-step technique, spark plasma sintering (SPS), to prepare rapidly a double SiC coating on C/C composites at 1350°C for 1 min. To our knowledge, no literature has been published about using SPS technology to prepare multi-layer coatings on C/C composites. The microstructures and oxidation resistant of double SiC coating on C/C composites are investigated.

2. Experimental Procedure

C/C composites (Jiangnan Graphite Co., Ltd., Hunan, China) with a density of 1.70 g/cm³ were used as substrates, which were cut into small cylinder specimens (Φ 20 mm \times 6 mm). The substrates were hand-grinded with 400, 600 and 1000 grit SiC paper, sequentially. Then they were cleaned ultrasonically in ethanol and dried at 100°C for 1 h.

Raw materials used for inner SiC coating were Si (200 mesh, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) and graphite (200 mesh, Jiangnan Graphite Co., Ltd., Hunan, China) powders. Considering volatilization of Si and high melting point of SiC, the mole ratio of Si to C for inner coating was 1.11 and powders for outer SiC coating was composed of 90 wt% β -SiC (2.5 μ m, 99.9%, Enomaterial Co., Ltd, Qinhuangdao, China) and 10 wt% Si. Prior to SPS, the above powders were dried at 100°C for 2 h and well mixed in a ball mill for 24 h. Then, as shown in **Figure 1**, C/C composite was placed into a cylindrical graphite die of 20 mm in diameter and covered with the powders for the inner and outer coating, sequentially. Sintering experiment was carried out using a spark plasma sintering system (SPS-3.20MK-IV) in a vacuum (6×10^{-3} Pa) atmosphere. The heating and cooling rate were controlled at 200°C/min. Temperature, holding time and pressure was set as 1350°C, 1 min and 30 MPa, respectively. For comparison, SiC-coated C/C composites, that is C/C composites only with a SiC inner coating, under the same preparation conditions were also pre-

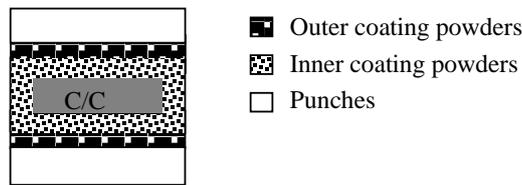


Figure 1. Schematic diagram of SPS for SiC/SiC coated C/C composites.

pared using Si and C powders. For comparison, C/C composites coated a single SiC layer with Si and graphic were prepared under the same conditions.

Surface and cross-section morphology of the coated composites were observed by scanning electron microscopy (SEM) using a KYKY2800 digital scanning electron microscope (Beijing, China). Crystalline structure of the coatings was measured by means of X-ray diffraction (XRD) using a D/Max-2500pc diffractometer (Japan) equipped with a standard *Cu-K α* radiation source employing a step size of 0.02° in 2θ .

Thermal behavior of double SiC coatings was analyzed using differential scanning calorimeter test and thermogravimetry (DSC-TG) complex thermal analysis with a NETZSCH differential scanning calorimeter (Model STA449C, Germany). The coatings were heated at $20^\circ\text{C}/\text{min}$ up to 1500°C in flowing air.

To study the protection effects of double SiC coatings, the coated samples were placed in a furnace and oxidized at 1600°C for different time with a heating rate of $10^\circ\text{C}/\text{min}$. The weight of the coated samples was measured before and after the oxidation test, and the weight changes rate was determined according to Equation (1):

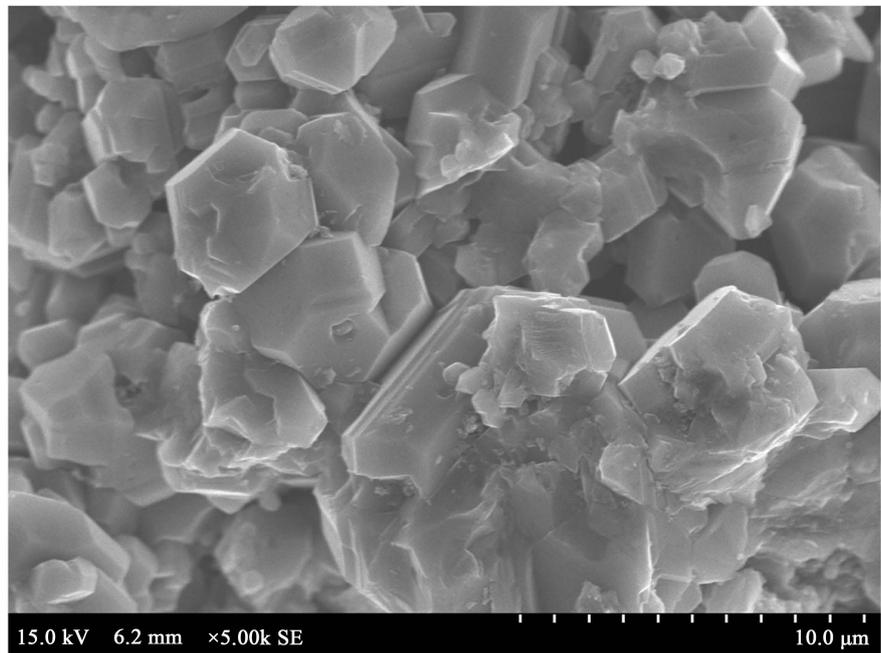
$$\Delta M = \frac{m_f - m_i}{m_i} \times 100 \quad (1)$$

where m_i is the initial weight (before the oxidation test) and m_f is the final weight (after the oxidation test). The morphologies and phase structures of the coated composites after the oxidation test were also examined by means of SEM and XRD, respectively.

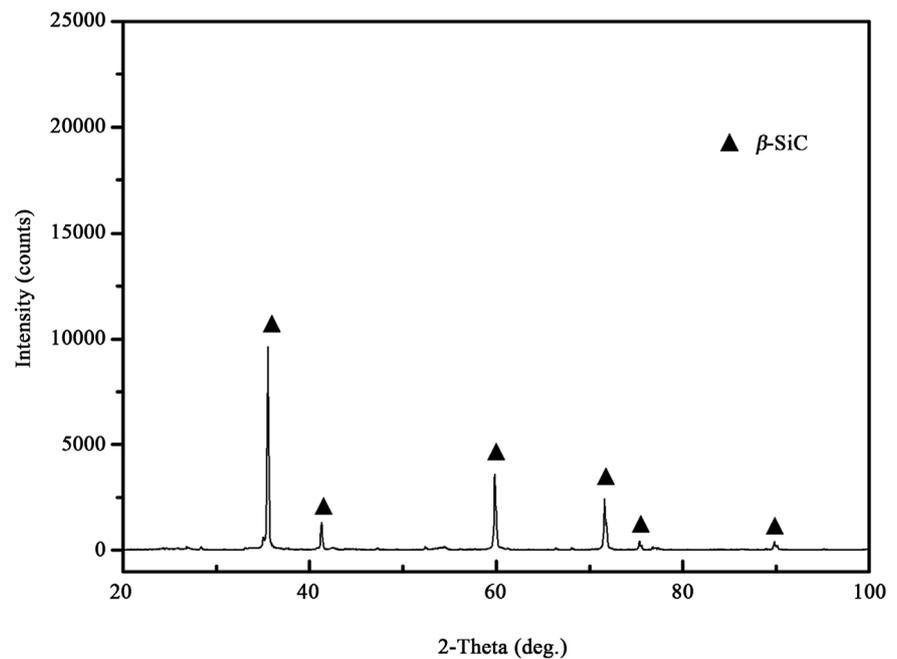
3. Results and Discussions

The surface SEM image and XRD pattern of SiC inner coating are shown in **Figure 2(a)** and **Figure 2(b)**, respectively. As shown in **Figure 2(a)**, SiC inner coating is dense with many good crystalline particles ranged from 3 to 6 μm . No visible holes and cracks are found in the coating. Moreover, as shown in **Figure 2(b)**, only β -SiC could be detected in the inner coating, indicating that Si and C have reacted with each other at 1350°C to form a SiC coating on the substrate. In addition, no Si and C are detected, meaning that they have been consumed completely during SPS.

The surface SEM image and XRD pattern of SiC outer coating are shown in **Figure 3(a)** and **Figure 3(b)**, respectively. The coating is dense and crack-free. From **Figure 3(b)**, it can be found that the coating is composed of β -SiC and a



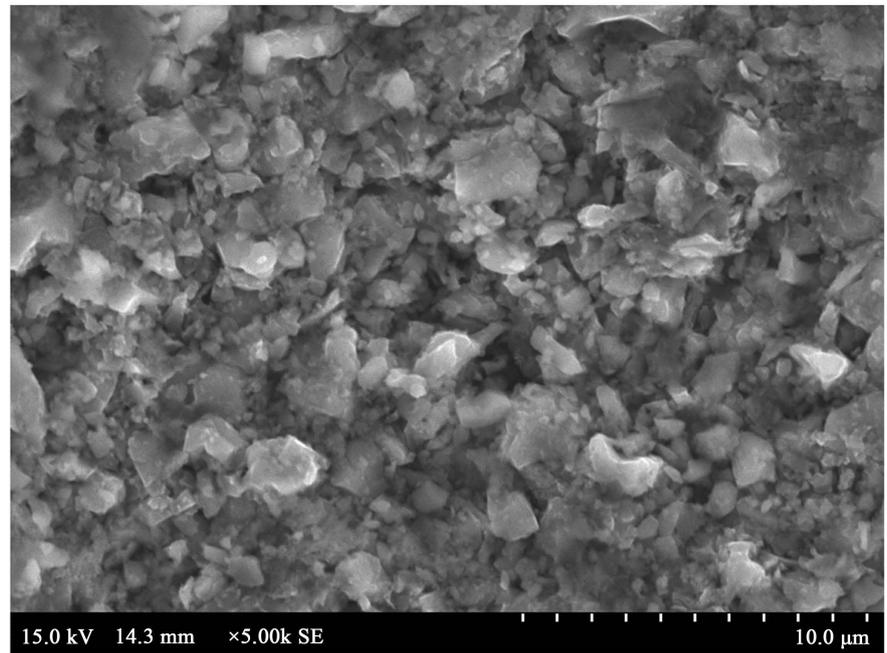
(a)



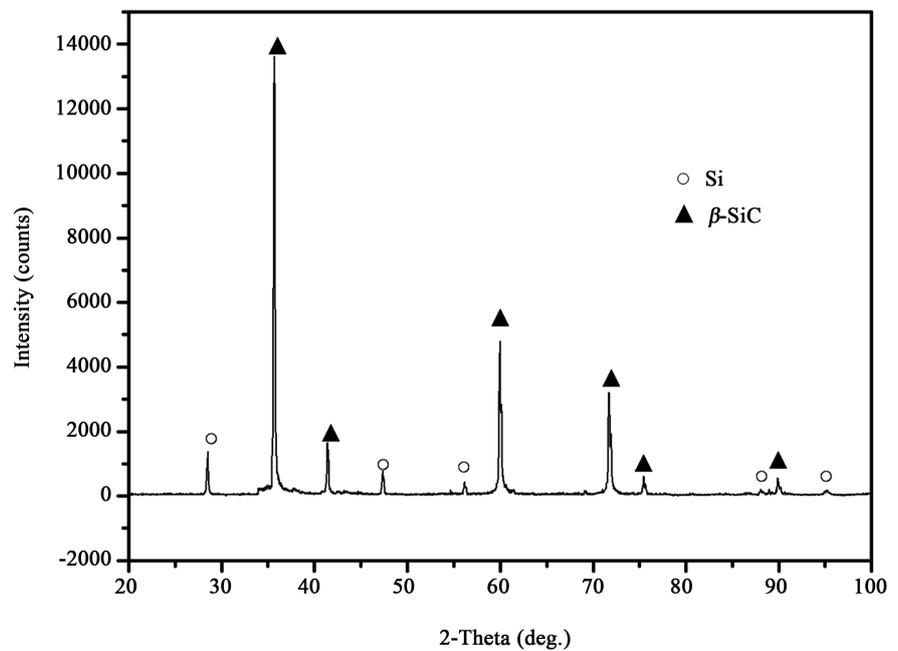
(b)

Figure 2. SEM image (a) and XRD pattern (b) of SiC inner coating prepared at 1350°C for 1 min.

small quantity of Si. The size of the particles in the coating is found to be less than 2 μm, which indicates that original SiC particles remain, and while large Si particles have melted. The liquid Si could fill in the gaps among SiC particles and act as a binder to bond SiC particles together, which is advantageous to form a dense coating and inhibit oxygen diffusion inwards C/C composite.



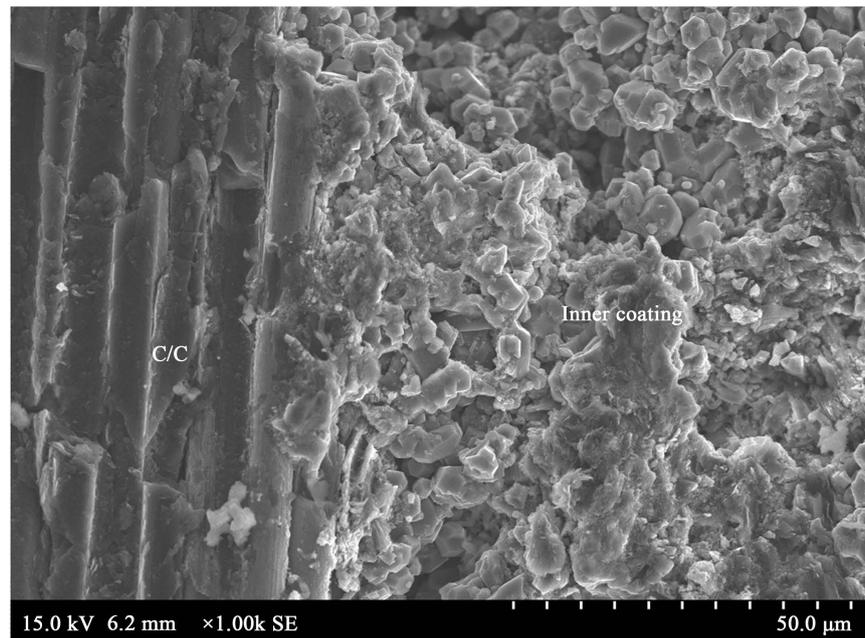
(a)



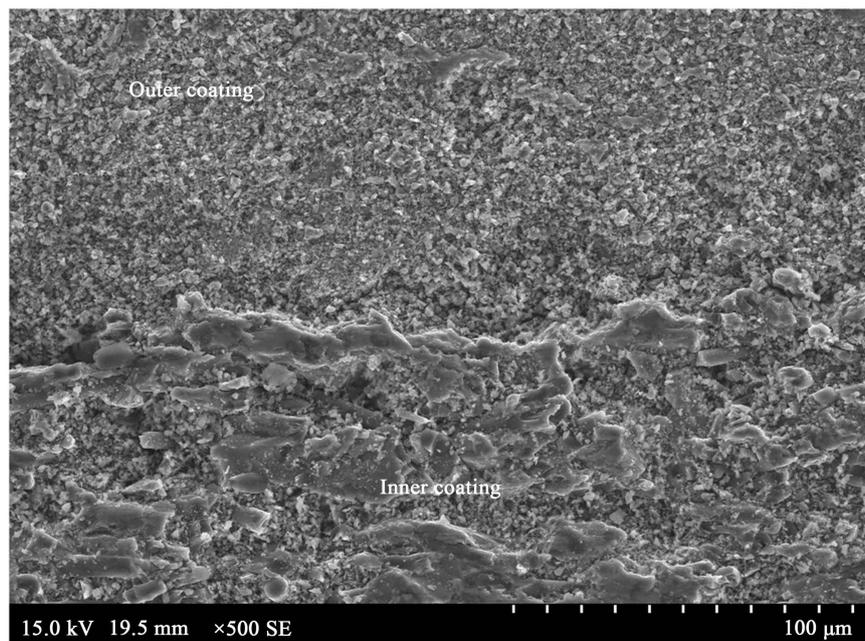
(b)

Figure 3. SEM image (a) and XRD pattern (b) of SiC outer coating prepared at 1350°C for 1 min.

Cross-section images of SiC/SiC coated composite are shown in **Figure 4**. A good adhesion between the inner coating and the substrate is found due to reaction between Si powder and C/C substrate. The outer coating is well bonded with the inner coating due to no thermal mismatch between them, as shown in **Figure 4(b)**.



(a)



(b)

Figure 4. Cross-section SEM images of double SiC coating prepared at 1350°C for 1 min: (a) between inner coating and substrate (b) between outer and inner coating.

The thermal behavior of the SiC/SiC coating under air has been measured by TG-DSC. The corresponding TG-DSC curves are shown in **Figure 5(a)** and **Figure 5(b)**, respectively. A gradual weight gain is observed on heating to 1181°C due to the ambient SiO₂ layer on the surface of SiC/Si, which reduces the oxidation rate of SiC/Si to a very low speed. Above this temperature, the diffusion rate of oxygen from air to SiC/Si promotes and an obvious weight gain is

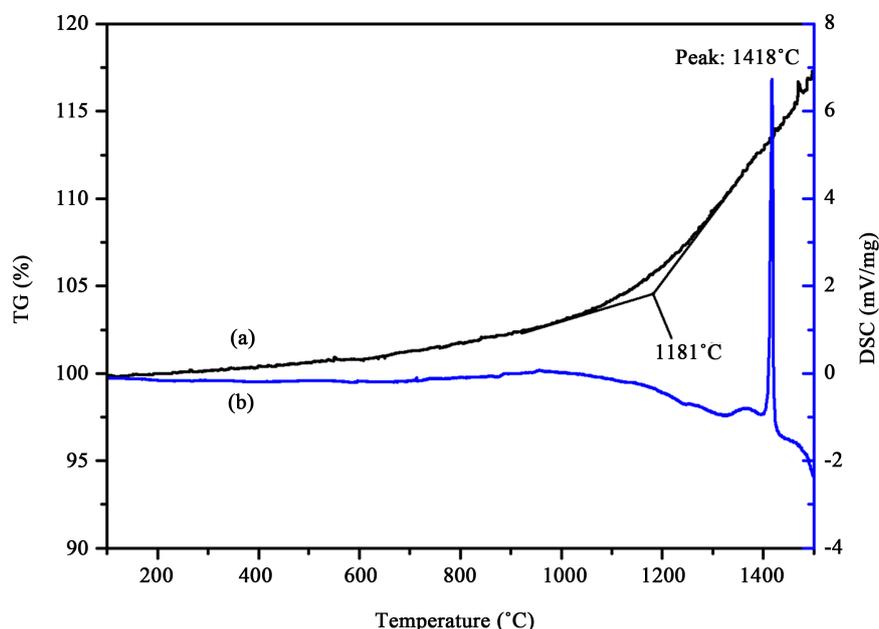


Figure 5. TG-DSC curves of double SiC coating prepared by SPS at 1350°C for 1 min: (a) TG; (b) DSC.

obtained due to the oxidation of SiC/Si. There is an endothermic reaction occurring at approximately 1418°C in DSC curve. This endothermic effect is attributed to the melt of Si powder in SiC outer coating. Around 1500°C, double SiC coating has a residual mass of 117.6 wt%.

Figure 6 shows oxidation curves of the coated C/C composite at 1600°C in air. It can be seen that from **Figure 6(a)** that the weight of SiC coated C/C composites loses rapidly with oxidation time and reaches up to -8.0 wt% after oxidation only for 36 h, which indicates that SiC inner coating cannot protect C/C composites from oxidation effectively. As shown in **Figure 6(b)**, SiC/SiC coating can effectively protect the substrate from oxidation and the oxidation process of SiC/SiC coated C/C composites can be divided into three stages. At the first 24 h, weight gains slowly due to the formation of SiO₂ phase and the low oxygen permeation constant. With the oxidation time increased, from 24 h to 72 h, weight change versus time starts to exhibit the trend of weight loss and the weight loss of 2.54% is detected after oxidation for 72 h, suggesting oxygen has passed through the double coating and eroded the substrate. Above 72 h, weight losses is almost constant, suggesting that oxidation enters a steady state, indicating the tunnel of oxygen diffusion has remedied by the vitreous SiO₂ glass. When oxidation for 120 h, the weight loss of the double SiC coated composite is only 2.62%.

Figure 7 shows the SEM images of the coated composites after oxidation at 1600°C in air for different time. For SiC coated C/C composite, when oxidation at 1600°C for 36 h, as shown in **Figure 7(a)**, the particles are invisible and covered by vitreous SiO₂ due to the oxidation of SiC. So the coating surface becomes smoother and denser. However, vitreous SiO₂ is not in sufficient quantities to seal cracks. Therefore, a long and deep crack is found in SiC coating due to

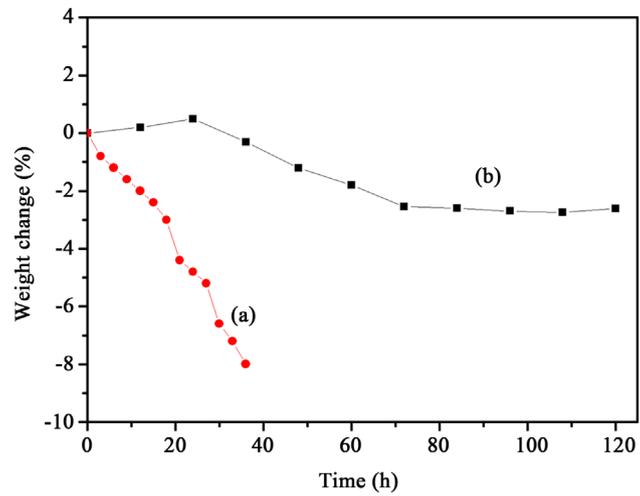


Figure 6. Oxidation curves of (a) SiC and (b) SiC/SiC coated C/C composite at 1600°C in air.

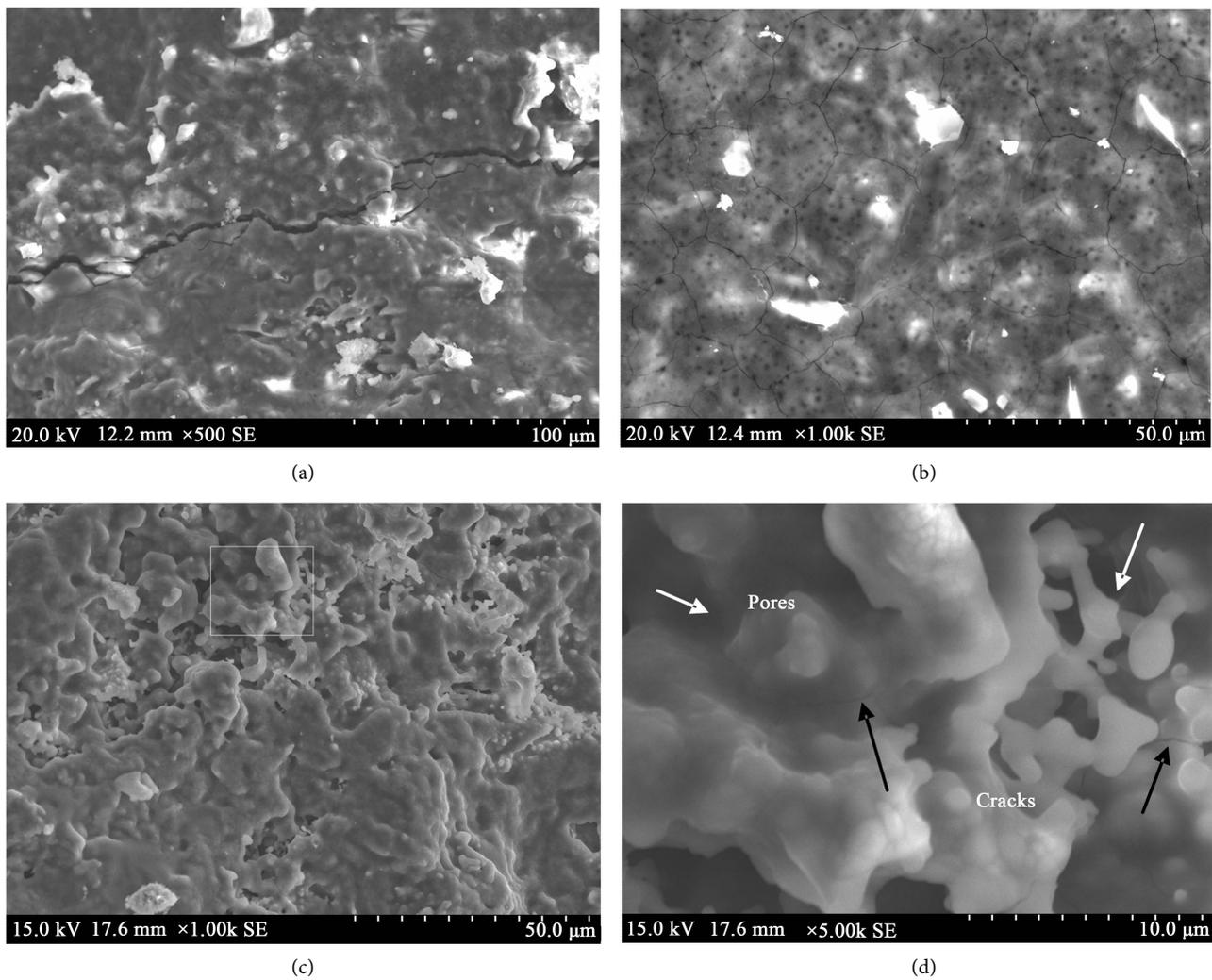


Figure 7. SEM images of (a) SiC- and (b)-(d) SiC/SiC-coated composites after oxidation at 1600°C in air for different time: (a) 36 h; (b) 72 h; (c) 120 h; (d) magnification of (b).

thermal expansion mismatch between SiC coating and the substrate, through which oxygen would diffuse into the substrate directly and cause severe oxidation. This is in good agreement with the result of **Figure 6(a)** and well explained why the protection of SiC coating was not desirable. For SiC/SiC coated C/C composite, when oxidation for 72 h, large amounts of fluid is formed because of the melted Si and the oxidation of SiC and Si, so the coating surface became much denser and smoother and the cracks are healed into narrow and shallow ones, which had little effect on the oxidation resistance of the coating, as shown in **Figure 6(b)**. After oxidation at 1600°C for 120 h, as shown in **Figure 7(c)** and **Figure 7(d)**, the cracks are less and invisible resulting in a steady anti-oxidation ability of double SiC coating. It is worth mentioning that the coating surface become microscopically very rough due to volatilization of SiO₂. The pores formed by the gas resultant remained in the coating, which greatly are disadvantageous to the oxidation resistance of the coating.

Figure 8 shows the XRD patterns of SiC/SiC coated composites after oxidation at 1600°C in air for different time. After oxidation at 1600°C for 24 h, the diffraction peaks are β -SiC, Si and SiO₂. After oxidation at 1600°C for 72 h, the diffraction peaks of Si disappeared and the intensity of SiO₂ peaks become stronger due to the oxidation of Si. With the increase of oxidation time, the intensity of SiO₂ peaks becomes stronger and stronger, while the intensity of SiC peaks gets weaker and weaker due to the oxidation of SiC. However, after oxidation at 1600°C for 120 h, the intensity of SiC peaks is still strong, which indicates that the failures of the coating are mainly caused by cracks and oxygen diffusion.

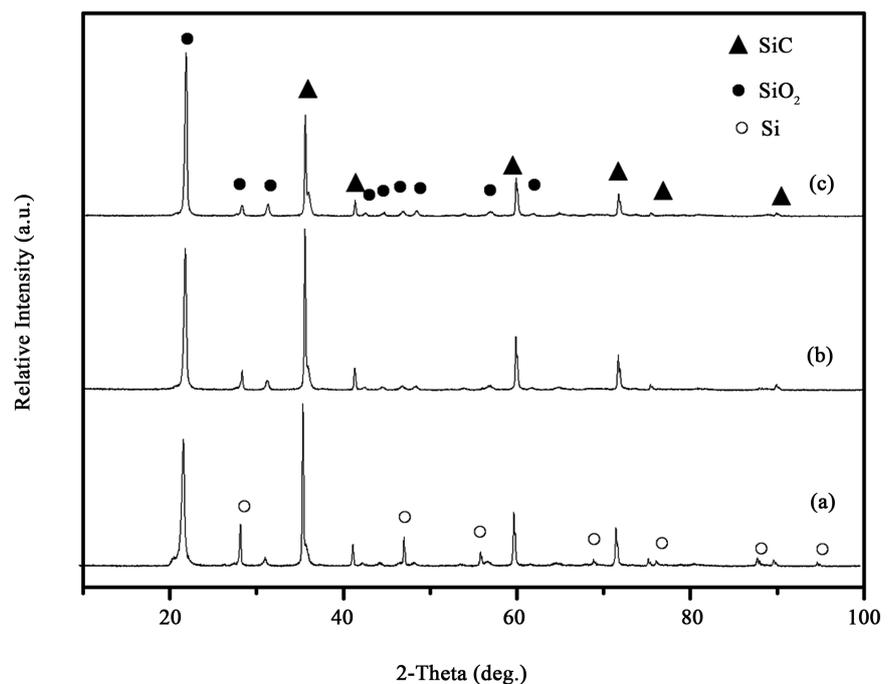


Figure 8. XRD pattern of the coated sample after oxidation at 1600°C for different time: (a) 24 h; (b) 72 h; (c) 120 h.

4. Conclusions

1) SPS is a promising method to prepare double SiC coatings on C/C composites. The double SiC coating could be obtained by SPS at 1350°C for 1 min.

2) The double coating is very dense and crack-free, composed of β -SiC and Si, and has a good bonding with the substrate.

3) The double SiC coating has good oxidation resistance and can protect C/C composites against oxidation at 1600°C for 120 h with a weight loss of 2.62%. The failures of the coating are mainly caused by cracks and oxygen diffusion.

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