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Yttrium silicate oxidation protective coating for SiC coated carbon/carbon composites

Jian-Feng Huang [a,b,*], He-Jun Li [a], Xie-Rong Zeng [c], Ke-Zhi Li [a]

[a] *C/C Composites Technology Research Center, Northwestern Polytechnical University, Xi'an, Shannxi 710072, PR China*
[b] *School of Materials Science and Engineering, Shaanxi University of Science and Technology, Shaanxi 712081, PR China*
[c] *Department of Materials Science, Shenzhen University, Shenzhen 518060, PR China*

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Abstract

Four kinds of yttrium silicate oxidation protective coatings $SiO_2 \cdot Y_2O_3$, $1.5SiO_2 \cdot Y_2O_3$, $1.5SiO_2 \cdot Y_2O_3/SiO_2 \cdot Y_2O_3$ and $2SiO_2 \cdot Y_2O_3/1.5SiO_2 \cdot Y_2O_3/SiO_2 \cdot Y_2O_3$ were prepared by plasma spray on the surface of SiC pre-coated carbon/carbon composites. The structures of the coatings were characterized by XRD, SEM and EDS analyses. It was shown that the gradied $2SiO_2 \cdot Y_2O_3/1.5SiO_2 \cdot Y_2O_3/SiO_2 \cdot Y_2O_3$ multi-layer coating had better high-temperature oxidation resistance. It could protect carbon/carbon composites from oxidation at 1773 K in air for 73 h with a weight loss of less than 2%. The oxidation activation energy of the coated carbon/carbon composites is 87.3 kJ/mol, and the oxidation process in C/C substrates with a multi-layer coating was controlled by the rate of oxygen diffusion through the holes in the coating.

Keywords: B. Composites; D. Carbon; Thermal spray coatings; Oxidation

1. Introduction

Carbon/carbon composites (C/C) exhibit excellent properties in many aspects, and are considered as an advanced thermal protection material, the best brake material and the most promising candidate materials for high-temperature structural applications [1]. But the oxidation of these composites limits their use in oxygen containing atmosphere [2], which has led to research on improving their oxidation resistance.

An oxidation-resistant coating is considered to be a reasonable choice for high-temperature protection of C/C composites. SiC coating is considered as one of the best bonding layers between C/C composites and the ceramic outer layer because of its good physical and chemical adaptability of coating-to-matrix and bonding layer-to-outer layer [3]. Therefore, the choice of the outer layer materials becomes important. In our research, we have prepared ceramic outer layers such as $MoSi_2$, Al_2O_3-mullite, zircon and yttrium silicate [4–6]. The yttrium silicates exhibit better bonding to SiC internal coating and better oxidation resistance due to their equivalent thermal expansion coefficient to SiC, low evaporation rate and oxygen permeation constant [7]. But to the investigation results of some researchers, the bonding of yttrium silicates coating to SiC is not only relies on the match of thermal expansion coefficient, but also relies on the preparing technology to a great extend. The yttrium silicates coating for C/SiC composites produced by Webster et al. [8] by a slurry dipping process showed a spallation of the outer coating after oxidized in air at 1873 K for approximately 50 h due to the oxidation of the SiC internal layer.

The scope of the investigation reported here was to improve the oxidation resistance of SiC–C/C composites by producing novel yttrium silicate coatings. The structures, properties and oxidation behaviors of the yttrium silicate coatings are reported.

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* Corresponding author. Tel.: +86 910 3579720; fax: +86 910 3579723.
E-mail addresses: hjfnpu@163.com, huangjf@sust.edu.cn (J.-F. Huang).

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2. Experimental

Small specimens (10 mm × 10 mm × 10 mm) as substrates were cut from bulk 2D-C/C composites (airplane disk brakes made in Xi'an, China) with a density of 1.72 g/cm^3. Before pack cementation procedure, the specimens were hand-polished using 340 grit SiC paper, cleaned with distilled water and dried at 373 K for 2 h. The SiC coating was prepared by a pack cementation process with Si, C and Al_2O_3 powders in an argon atmosphere at 2073 K for 2 h. The preparation details were reported in [5].

SiO_2–Y_2O_3 powders for plasma spray in different mol compositions ($SiO_2 \cdot Y_2O_3$, $1.5SiO_2 \cdot Y_2O_3$ and $2SiO_2 \cdot Y_2O_3$) were synthesized at 1873 K for 3 h at ambient atmosphere in an electric furnace. The SiO_2 and Y_2O_3 commercially available powders are analytically grade, with particle sizes from 5 to 25 μm. $SiO_2 \cdot Y_2O_3$, $1.5SiO_2 \cdot Y_2O_3$, $1.5SiO_2 \cdot Y_2O_3/SiO_2 \cdot Y_2O_3$ and $2SiO_2 \cdot Y_2O_3/1.5SiO_2 \cdot Y_2O_3/SiO_2 \cdot Y_2O_3$ yttrium silicate coatings were deposited using a Plasmagyne SG-100 torch; operating conditions are shown in Table 1.

The as-coated specimens were heated at 1573–1873 K in air in an electrical furnace to investigate the isothermal and thermal cycling oxidation behavior. Cumulative weight change of the samples after every thermal cycle from high temperature to room temperature was measured by a precision balance and were recorded as a function of time. The % mass loss was calculated using Eq. (1).

$$\% \text{mass loss} = \frac{m_1 - m_0}{m_0} \times 100\% \tag{1}$$

m_0 is the original mass of the coated C/C composites; m_1 is the mass of the coated C/C composites after oxide at high temperature for some time.

The crystalline structure of the yttrium silicate coating was measured with a Rigaku D/max-3C X-ray diffractometer (XRD). The morphology element distribution of the as-prepared multi-layer coatings was analyzed using JSM-5800 scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS).

3. Results and discussion

Fig. 1 showed the surface XRD pattern of the as-sprayed $2SiO_2 \cdot Y_2O_3/1.5SiO_2 \cdot Y_2O_3/SiO_2 \cdot Y_2O_3$ coating. It revealed that the phase composition of the outer layer was Y_2SiO_5. The weak peak between 18 and 23° of 2θ in Fig. 1 also verified the existence of some SiO_2 phase.

Table 1
Plasma spray conditions

Spray torch	Plasmadyne SG-100
Plasma arc power	35 kW
Primary gas pressure (Ar)	0.42 MPa
Secondary gas pressure (He)	0.63 MPa
Spray distance	100 mm

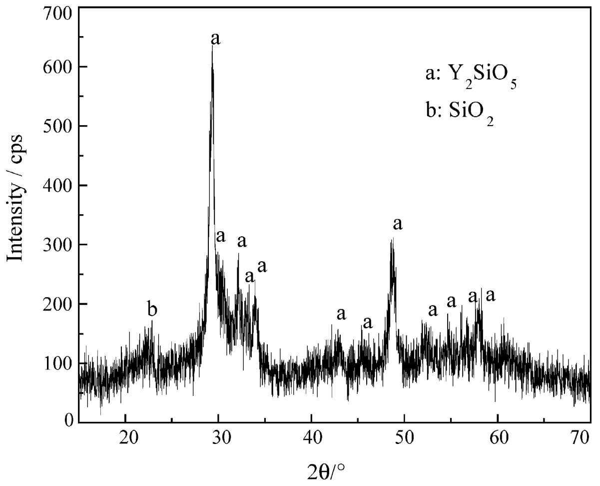

Fig. 1. Surface XRD patterns of the as-sprayed yttrium silicate coating.

Fig. 2 showed the cross-section SEM images of the four kinds of yttrium silicates coatings on SiC–C/C. The yttrium silicate outer layer and the SiC bonding layer were obviously distinguished by their colors white and gray, respectively. There were some visible defects such as holes and cracks in the monolayer yttrium silicate outer layer of $SiO_2 \cdot Y_2O_3$ (Fig. 2a) and $1.5SiO_2 \cdot Y_2O_3$ (Fig. 2b) coatings, which led to the loose structure of the coatings. When the gradient composition layers were deposited, the density of the coating was improved (Fig. 2c and d) though small holes were not eliminated completely. The cross section of SiC/$2SiO_2 \cdot Y_2O_3/1.5SiO_2 \cdot Y_2O_3/SiO_2 \cdot Y_2O_3$ coating (Fig. 2d) also displayed a dense structure with the thickness of around 90 μm and a SiC bonding layer with 50 μm in thickness. No obvious interfaces between the three different compositions of the graded yttrium silicate coatings were observed; no cross-coating cracks appeared due to the good match in coefficients of thermal expansion between the SiC layer and yttrium silicate outer coating. In addition, some Si infiltrates into the C/C substrate to form a gradient SiC coating as seen in Fig. 2, which may promote excellent thermal shock resistance of the coating.

The cross-section EDS element line scan analyses of SiC/$2SiO_2 \cdot Y_2O_3/1.5SiO_2 \cdot Y_2O_3/SiO_2 \cdot Y_2O_3$ coating is shown in Fig. 3. It revealed the concentration distributions of C, O, Si and Y in the coating cross direction. According to the element line scan analyses, the multi-layer coating could be divided into five zones, designated a, b, c, d and e (Fig. 3). Zone e is carbon/carbon composites matrix infiltrated by Si to about 10 μm. Its formation should be attributed to the pack cementation technology [5]. Zone d is the SiC bonding layer. But it also contains small concentration of Y and O, which infers that the yttrium silicate penetrated into the porous SiC coating during the plasma spray process. It was found that the concentration of Y increased while that of Si decreased with the distance from the interface of

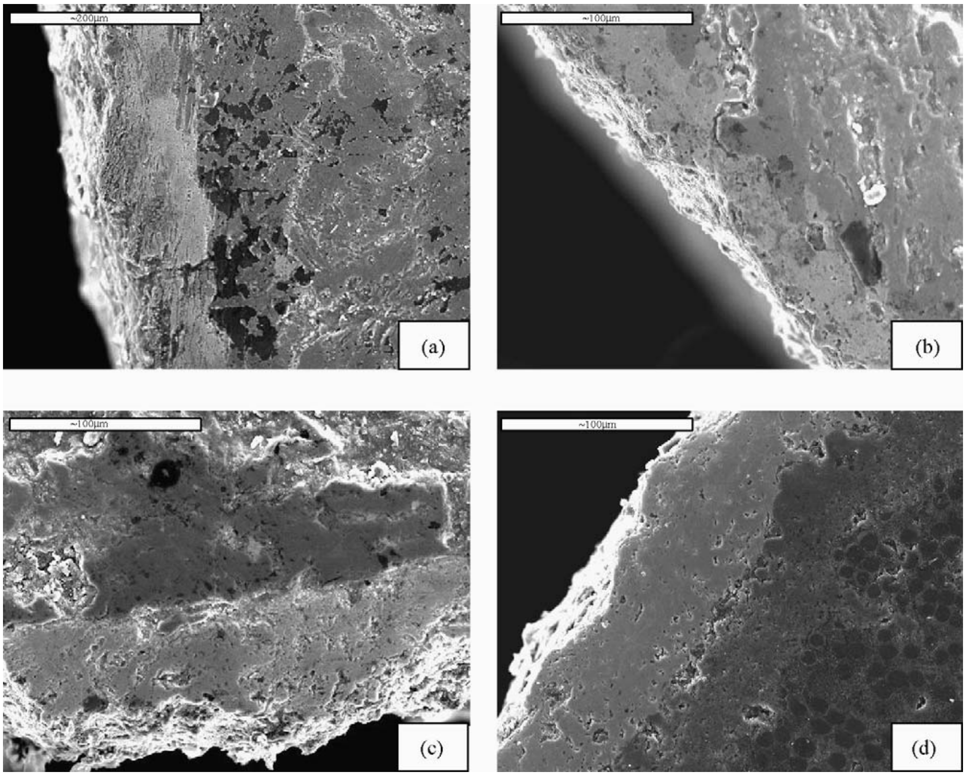

Fig. 2. Cross-section SEM pictures of yttrium silicate coating. (a) SiC/$SiO_2 \cdot Y_2O_3$ (b) SiC/$1.5SiO_2 \cdot Y_2O_3$ (c) SiC/$1.5SiO_2 \cdot Y_2O_3$/$SiO_2 \cdot Y_2O_3$ (d) SiC/$2SiO_2 \cdot Y_2O_3$/$1.5SiO_2 \cdot Y_2O_3$/$SiO_2 \cdot Y_2O_3$.

SiC–yttrium silicate surface to yttrium silicate coating surface, which accorded with our experimental design. It verified that zones a, b and c are composed of $2SiO_2 \cdot Y_2O_3$, $1.5SiO_2 \cdot Y_2O_3$ and $SiO_2 \cdot Y_2O_3$ respectively. In addition, the composition zones a, b and c showed almost the same thickness 30 μm, each of its component of $2SiO_2 \cdot Y_2O_3$, $1.5SiO_2 \cdot Y_2O_3$ and $SiO_2 \cdot Y_2O_3$ layers.

Fig. 4 reveals the results of isothermal oxidation testing at 1773 K. It was found that the yttrium silicate coated SiC–C/C exhibited similar oxidation behavior. The weight loss of $SiO_2 \cdot Y_2O_3$ coated SiC–C/C increased linearly with time. After 37 h oxidation, the weight loss reached almost 2%. Above 37 h, the weight loss rate increased more rapidly with time. We found that the yttrium silicate coating reacted with the Al_2O_3 support, which could be confirmed by observing the color and shape changes of the Al_2O_3 support. After reacting with the support for some time, the yttrium silicate became thinner and large defects that could not be self-cured

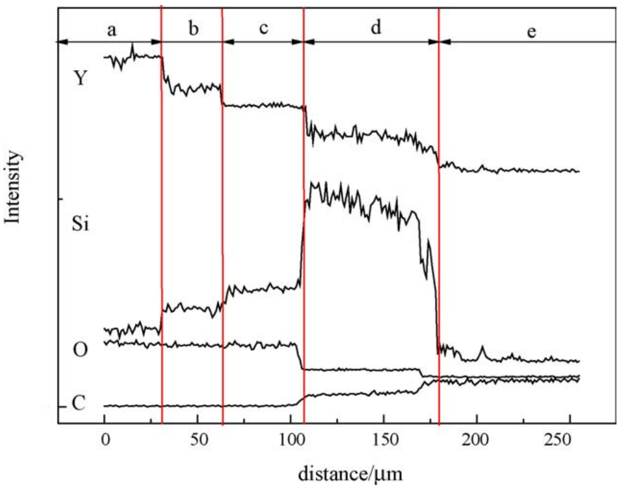

Fig. 3. Cross-section EDS element line scan analysis of SiC/$2SiO_2 \cdot Y_2O_3$/$1.5SiO_2 \cdot Y_2O_3$/$SiO_2 \cdot Y_2O_3$ coating.

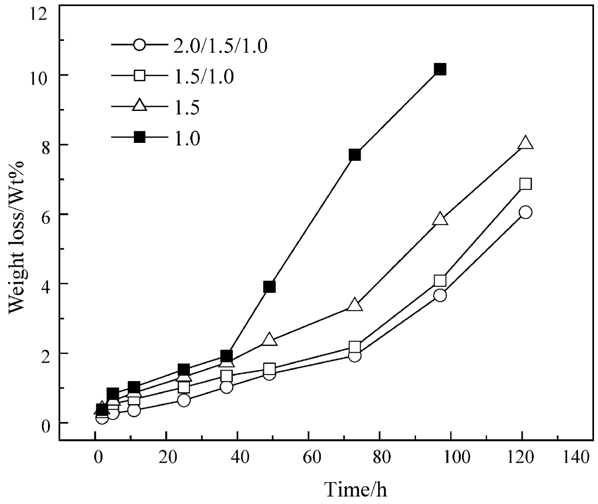

Fig. 4. Isothermal oxidation curves of C/C–SiC/yttrium silicate at 1773 K.

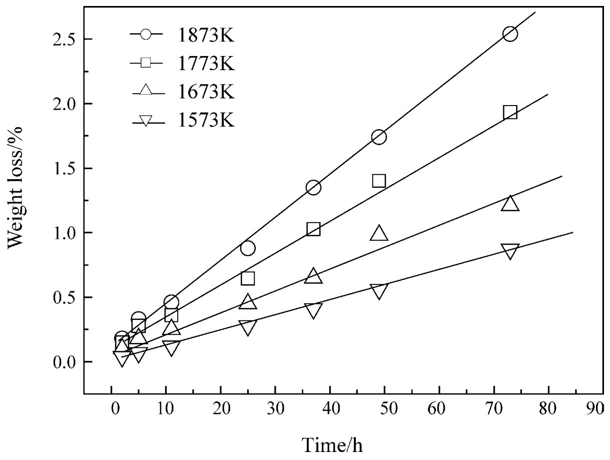

Fig. 5. Isothermal oxidation curves of the C/C–SiC/$2SiO_2 \cdot Y_2O_3$/$1.5SiO_2 \cdot Y_2O_3$/$SiO_2 \cdot Y_2O_3$ at different temperature.

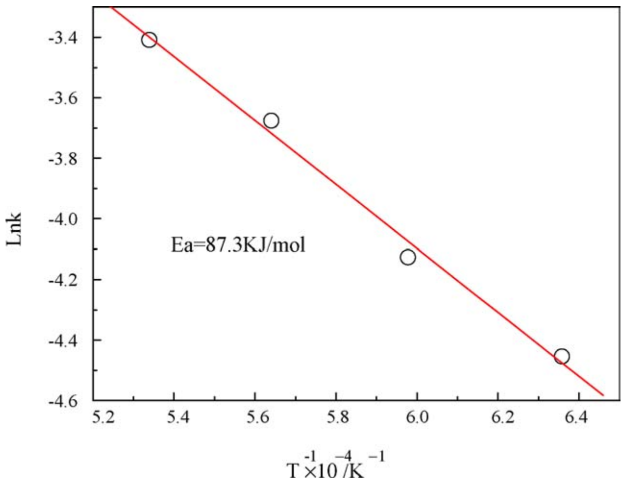

Fig. 6. Arrhenius curve of C/C–SiC/$2SiO_2 \cdot Y_2O_3$/$1.5SiO_2 \cdot Y_2O_3$/$SiO_2 \cdot Y_2O_3$ sample.

were generated, which may lead to the failure of the coating. This explained why the weight loss rate shown in Fig. 4 increased rapidly after about 37 h. From Fig. 4, we also concluded that $1.5SiO_2 \cdot Y_2O_3$, $1.5SiO_2 \cdot Y_2O_3$/$SiO_2 \cdot Y_2O_3$ and $2SiO_2 \cdot Y_2O_3$/$1.5SiO_2 \cdot Y_2O_3$/$SiO_2 \cdot Y_2O_3$ coatings had better oxidation resistance than a $SiO_2 \cdot Y_2O_3$ coating; the effective oxidation protection time of SiC–C/C was extended to ~73 h. It inferred that the improvement of the oxidation resistance was due to formation of a gradient composition in the yttrium silicate outer coating.

Additionally, the thermal shock resistant property of the multi-coating was also investigated in the oxidation test. In the test the samples, placed upon a corundum support, were put in or taken out of the furnace directly to air in about 10 s. During the oxidation test, the sample had endured thermal cycling between 1773 K and room temperature nine times without visible cracking and spallation, from which it could be inferred that the coating had excellent thermal shock resistance. This was because of the formation of SiC gradient bonding layer and the good match of thermal

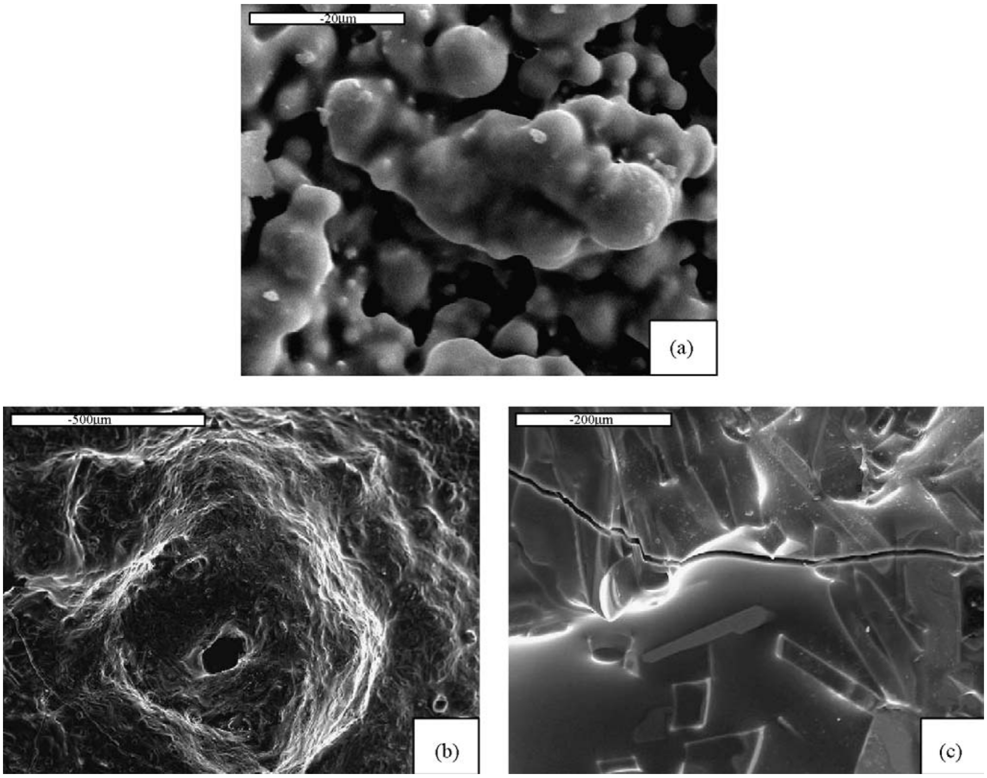

Fig. 7. Surface microstructures of C/C–SiC/$2SiO_2 \cdot Y_2O_3$/$1.5SiO_2 \cdot Y_2O_3$/$SiO_2 \cdot Y_2O_3$ before oxidation (a) and after oxidation at 1773 K for 120 h (b: hole; c: crack).

expansion coefficient between yttrium silicate coating and SiC internal layer.

Fig. 5 shows the isothermal oxidation test results of the C/C–SiC/$2SiO_2 \cdot Y_2O_3$/$1.5SiO_2 \cdot Y_2O_3$/$SiO_2 \cdot Y_2O_3$ at different temperatures in the range 1573–1873 K. It revealed a similar linear increase in weight loss with oxidation time up to 73 h. According to the high-temperature oxidation theory, it was not an effective protection for the coating when the oxidation weight loss as a function of time accorded with linear rule. The oxidation process of the coated C/C was controlled by the rate of oxygen diffusion along the defects in the coating [9]. According to Wu and Wu [10], the oxidation active energy was 112 kJ/mol when the oxidation process of the coated C/C was controlled by the rate of oxygen diffusion through the SiO_2 film, decreasing to 80 kJ/mol when the oxidation process was controlled by the oxygen diffusion through the defects of the coating. The Arrhenius curve (Fig. 6) of the C/C–SiC/$2SiO_2 \cdot Y_2O_3$/$1.5SiO_2 \cdot Y_2O_3$/$SiO_2 \cdot Y_2O_3$ sample showed that the oxidation active energy of the coated sample was 87.3 kJ/mol, inferring that the oxidation process of the gradient yttrium silicate coated SiC–C/C was controlled by the rate of oxygen diffusion along the defects in the coating. Fig. 7 displays the surface microstructures of the C/C–SiC/$2SiO_2 \cdot Y_2O_3$/$1.5SiO_2 \cdot Y_2O_3$/$SiO_2 \cdot Y_2O_3$ before oxidation (a) and after oxidation at 1773 K for 120 h (b and c). Before oxidation, it was clear that the coating surface was composed of some small molten spherical particles. Some small holes were also visible on the coating surface, while no cracks were found. After oxidation at 1773K, the SiO_2 phase in the coating is transferred to glass, apparently in Fig. 7b and c. The small hole of the coating could be self-cured by the molten SiO_2. But the molten SiO_2 film could not fill bigger holes (Fig. 7b), which provided channels for oxygen to attack the C/C substrate resulting in the oxidation weight loss of the coated C/C. Therefore, the oxidation process of the coated C/C was controlled by the oxygen diffusion along the big holes. Additionally, some microcracks were also found in the coating surface (Fig. 7b). We considered that these microcracks may be generated during quick cooling from 1773 K to the room temperature during the isothermal oxidation test, and they could self-seal when the coating was reheated to 1773 K. Therefore, the microcracks were not the main cause of the efficiency loss of the coating at 1773 K, which was due to the formation of big holes in the coating, though the convincing reasons for the formation of these big holes needed further research.

4. Conclusions

In conclusion, the yttrium silicate coating produced by plasma spray presenting excellent thermal shock resistance is a good oxidation protective coating for C/C composites. With the increase of the composition gradient layer, the oxidation resistant property is obviously improved. $2SiO_2 \cdot Y_2O_3$/$1.5SiO_2 \cdot Y_2O_3$/$SiO_2 \cdot Y_2O_3$ coated C/C–SiC exhibit better oxidation resistance; it could protect the C/C composites from oxidation in air flowing by natural convection condition at 1773 K for 73 h. The oxidation activation energy of $2SiO_2 \cdot Y_2O_3$/$1.5SiO_2 \cdot Y_2O_3$/$SiO_2 \cdot Y_2O_3$ multi-layer coated C/C–SiC is 87.3 kJ/mol. Oxidation process in C/C substrates with a gradient multi-layer coating is controlled by the rate of oxygen diffusion through the holes in the coating.

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