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Structure and Oxidation Behavior of a Plasma Sprayed Yttrium Silicates Coated SiC-C/C with a Glass Outer Sealant from 1 573K to 1 873K

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Abstract: Different compositions of yttrium silicates coatings were deposited on SiC-C/C by plasma spraying and an outer borosilicate glass was applied on the yttrium silicates coatings surfaces. The structure of the multi-layer coatings was characterized by XRD and SEM analyses. High temperature oxidation behavior of the multi-layer coatings coated C/C composites was investigated. Results show that SiC/2SiO_2•Y_2O_3/1.5SiO_2•Y_2O_3/ SiO_2•Y_2O_3/glass multi-layer coating has better high temperature oxidation resistance, protecting carbon/carbon composites from oxidation at 1 773 K in air for 164 h with the weight loss of 1.65%. The oxidation weight loss of the coated C/C with time accorded with parabolic rule in the temperature range 1 573 K-1 873 K; and the corresponding oxidation activation energy of the coated carbon/carbon composites is 132.2 kJ/mol.

Key words: carbon/carbon composites; plasma spraying; coating; oxidation behavior

1 Introduction

Carbon/carbon composites are ideal candidates for a number of aerospace applications including structural materials for advanced vehicles, the best brake material, leading edges, structures of re-entry and hypersonic vehicles and propulsion systems[1]. Many of these applications involve oxidizing environments at high temperatures, requiring the composites to be suitably protected. Coatings are the logical choice for protection at high temperatures and should meet several requirements such as being mechanical and chemical stable at extremely thermal and oxidative environments, good thermal shock resistance and low oxygen permeability[2]. Multi-layer coating was considered to be one of the best coatings that meet the above requirements. In the research of multi-layer coating, SiC was usually used as the bonding layer; and high temperature ceramics materials were used as the outer layer because of the good physical and chemical adaptability of SiC to high temperature ceramics materials. Therefore, some new kinds of multi-later coating such as the SiC/$MoSi_2$, SiC-Al_2O_3-mullite, SiC-Al_2O_3-Mullite-Al_4SiC_4, SiC/SiO_2-ZrO_2 and SiC/yttrium silicate/glass were explored[3-8]. According to the investigation results from Aparicio and Webster, yttrium silicate coating had good oxidation resistance due to its equivalent thermal expansion coefficient to SiC, low evaporation rate and oxygen permeation constant[9,10].

The aim of the investigation reported here was to improve the oxidation resistance of C/C composites by produce some kinds of SiC/yttrium silicate/glass multi-layer coatings. The structures, properties and oxidation behaviors of the coatings were primarily investigated.

2 Experimental

Small specimens (10×10×10 mm^3) as substrates were cut from bulk 2D-C/C composites (plane disk brakes made in Xi'an) with a density of 1.72 g/cm^3. SiC coating was prepared by a pack cementation process with Si, C and Al_2O_3 powders in an argon atmosphere at 2 073 K for 2 h. The preparing details were reported in reference[5]. The SiO_2-Y_2O_3 powders for plasma spray in different mol compositions (SiO_2•Y_2O_3, 1.5SiO_2•Y_2O_3 and 2SiO_2•Y_2O_3) were synthesized at 1 873 K for 3 hours at ambient atmosphere in an electric furnace. The SiO_2 and Y_2O_3 commercially available

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powders were analytically grade with the particle size from 5 to 25 μm. SiO_2•Y_2O_3, 1.5SiO_2•Y_2O_3, 1.5SiO_2•Y_2O_3/SiO_2•Y_2O_3 and 2SiO_2•Y_2O_3/1.5SiO_2•Y_2O_3/SiO_2•Y_2O_3 yttrium silicate coatings were deposited through the Plasmagyne SG-100 torch. The preparation details were reported in reference[8]. After the preparation of yttrium silicate coating, a borosilicate glass was applied directly to the surface of yttrium silicates coating. The preparation details were also reported in reference[8].

The as-coated specimens were heated at 1 573-1 873 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 was reported as a function of time. The crystalline structure of the yttrium silicate coating was measured with the Rigaku D/max-3C X-ray diffractormeter (XRD). The morphology of the as-prepared multi-layer coatings was analyzed using JSM-5800 scanning electron microscope (SEM).

3 Results and Discussion

Fig.1 shows the XRD spectra of the as-synthesized yttrium silicate powders. It reveals that different phase compositions of the powders were obtained when using different SiO_2/Y_2O_3 mol ratio. The major phase of Y_2SiO_5 and the minor one of $Y_2Si_2O_7$ and Y_2O_3 were observed when SiO_2/Y_2O_3 (mol ratio) is 1/1. With the increase of SiO_2 content in the powder, the peak intensity of Y_2SiO_5 phase decrease, while that of $Y_2Si_2O_7$ phase increase. When SiO_2/Y_2O_3 is 2:1, the phase of the synthesized powder is $Y_2Si_2O_7$. After depositing the synthesized yttrium silicate powders on the surface of the SiC-C/C, the surface phase composition is changed in a way. The phase composition of the coating is not the same as the powder but is composed by Y_2SiO_5 and a little SiO_2 (Fig.2). It may be caused by the decomposition of $Y_2Si_2O_7$ during the plasma spraying process at high temperature, which results in the formation of Y_2SiO_5 and SiO_2.

Fig.3 displays the morphology of the yttrium silicate coating (SiO_2•Y_2O_3) surface. It is clear that the coating surface is composed of some small molten spherical particles. The coating possesses a dense microstructure though some small holes are also visible on the coating surface. The cross section of the SiC/2SiO_2•Y_2O_3/1.5SiO_2•Y_2O_3/SiO_2•Y_2O_3/glass multi-coating is shown in Fig.4. An obvious three-layer structure is found. It is clear that the thickness of the SiC bonding layer, yttrium silicates coating and glass outer layer are around 100 μm, 50 μm and 60 μm respectively. Some pin-pores are visible in the cross-section of yttrium silicate layer, indicating that it is difficult to achieve an entirely dense yttrium silicates layer by plasma spray technique. Therefore, a dense glass sealant is necessary to seal the defects of the yttrium silicates coating. From Fig. 4, it can be seen that no pores and penetrated cracks were detected in the glass layer after sintering process, which infers that the glass layer can provide effective protection for the coated C/C. In addition, no obvious gaps between the three layers and no obvious interfaces between 2SiO_2•Y_2O_3, 1.5SiO_2•Y_2O_3 and SiO_2•Y_2O_3 coatings were observed, which indicates that they have good compatibility and bonding with each other.

Fig.5 shows the isothermal oxidation curves of the SiC/yttrium silicates/glass at 1 773 K. The multi-layer coatings coated C/C exhibit the similar oxidation behavior at high temperature. The weight loss of SiC/SiO_2•Y_2O_3/glass coated C/C increase parabolicly with time. After 117 h oxidation at 1 773 K, the weight

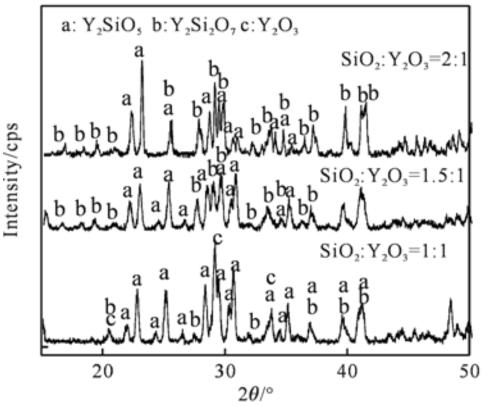


Fig.1 XRD patterns of the as-synthesized yttrium silicate powders

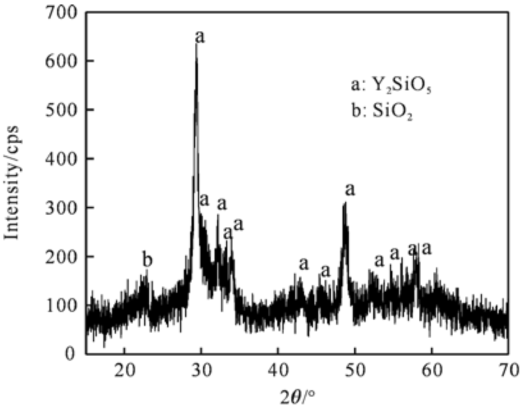


Fig.2 Surface XRD patterns of the as-sprayed SiC/2SiO_2 • Y_2O_3/1.5SiO_2 • Y_2O_3/SiO_2 • Y_2O_3 coating

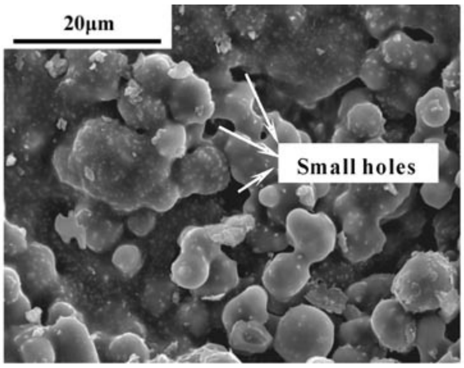


Fig.3 Surface morphology of the yttrium silicate coating

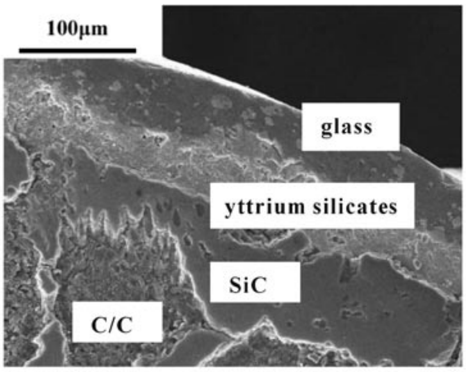


Fig.4 Cross section SEM micrograph of the as-prepared $SiC/2SiO_2 \cdot Y_2O_3/1.5SiO_2 \cdot Y_2O_3/SiO_2 \cdot Y_2O_3$/glass multi-layer coating

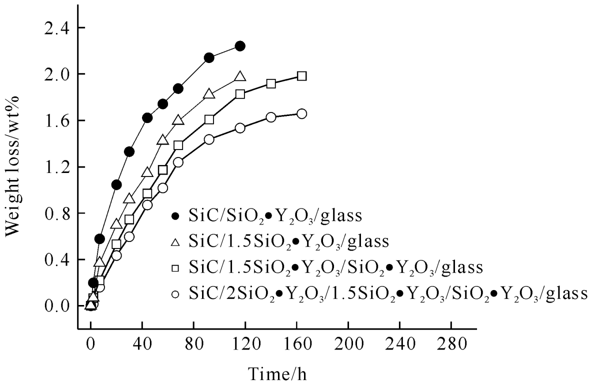


Fig.5 The isothermal oxidation curves of the SiC/yttrium silicate/glass at 1 773 K

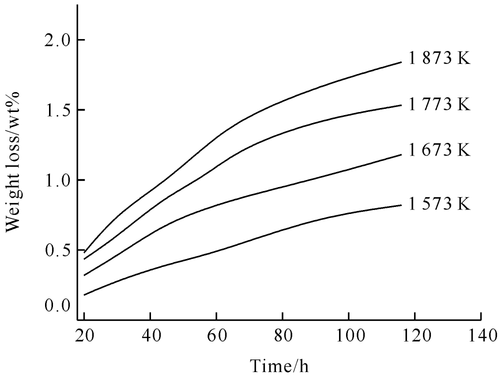


Fig.6 The isothermal oxidation curves of $C/C-SiC/2SiO_2 \cdot Y_2O_3/1.5SiO_2 \cdot Y_2O_3/SiO_2 \cdot Y_2O_3$/glass in the steady oxidizing stage at different temperature

loss reaches almost 2.4%. In comparison with $SiC/SiO_2 \cdot Y_2O_3$/glass coated C/C, $SiC/1.5SiO_2 \cdot Y_2O_3$/glass coated C/C exhibits better oxidation resistance at high temperature (around 1.98% in weight loss after 117 h oxidation at 1 773 K). Obviously, when the interlayer yttrium silicates coatings were deposited in gradient composition, the oxidation resistance of the coated C/C was improved; and the more the gradient layer was prepared, the better oxidation resistance of the multi-coating. The $SiC/2SiO_2 \cdot Y_2O_3/1.5SiO_2 \cdot Y_2O_3/SiO_2 \cdot Y_2O_3$/galss coating has the best oxidation protective property in all the prepared coatings. Its effective oxidation protective time for C/C can be extended to 164 h with only 1.65% weight loss.

In order to make clear the oxidation behavior of $SiC/2SiO_2 \cdot Y_2O_3/1.5SiO_2 \cdot Y_2O_3/SiO_2 \cdot Y_2O_3$/glass coated C/C composites, the isothermal oxidation tests at different temperature (from 1 573 K to 1 873 K) were conducted. Results are displayed in Fig.6. It was found that the oxidation weight loss of the as-prepared sample increase parabolicly with time at the temperature range 1 573-1 873 K, which is similar to the result at 1 773 K (Fig.5). According to the high temperature oxidation theory, it is non-protective and protective coating if the weight loss of the coated sample as a function of time accords with linear and parabolic rules, respectively[11]. Therefore, the prepared $SiC/2SiO_2 \cdot Y_2O_3/1.5SiO_2 \cdot Y_2O_3/SiO_2 \cdot Y_2O_3$/glass multi-layer coating is an effective protection coating.

The oxidation weight loss of the multi-layer coating coated C/C is controlled by the following three processes. (a) Oxygen diffuses through the dense borosilicate glass layer and diffuses to the interface between glass layer and yttrium silicates layer. (b) Oxygen diffuses along the dense yttrium silicates layer and the defects (pores, holes and micro-cracks) of the yttrium silicate layer and diffuses to the interface between SiC layer and yttrium silicate layer. (c) Oxygen diffuses along the defects (pores, holes and micro-cracks) of the SiC coating and diffuses to carbon matrix, and reacts with carbon resulting in weight loss.

If the oxidation process is controlled by process (a), the oxidation weight loss is determined by the oxygen diffusion rate through the borosilicate glass, and the coating could achieve the optimum protection for C/C composites. When the oxidation process is controlled by process (b), the oxidation rate of the coated composites would be controlled by the oxygen

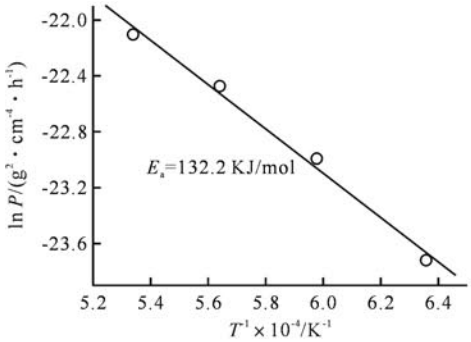
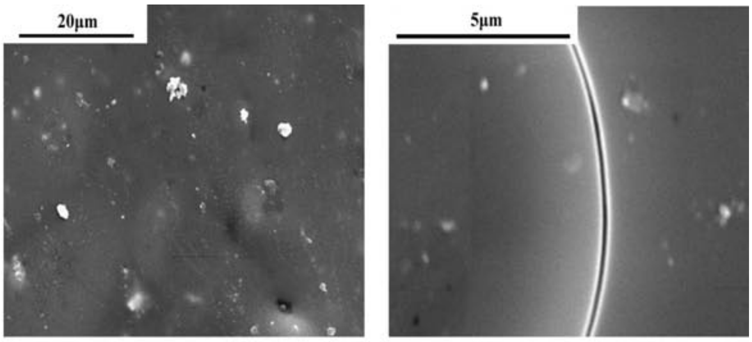


Fig.7 Arrhenius curve of C/C-SiC/$Y_4Si_3O_{12}$/$Y_2Si_2O_7$/Y_2SiO_5/glass in the steady oxidizing stage (P: parabolic coefficient)



(a) (b)

Fig.8 Surface morphologies of the glass coating surface (a) before oxidation (b) after oxidation at 1 773 K for 164 h

diffusion rate along the pores, holes and micro-cracks of the yttrium silicate layer because it is quicker than that through the dense yttrium silicate layer that possess low oxygen permeation constant. It has been verified that there are some defects really existing in the yttrium silicates coatings prepared by plasma spray from Fig. 3 and Fig.4. Therefore, the oxidation rate would mainly be decided by the oxygen diffusion along the defects in this case. If the oxidation process is controlled by process (c), the oxidation weight loss is determined by the oxygen diffusion rate along the defects of SiC coating, which would result in quick weight loss rate[12]. In general, the oxidation process of the multi-layer coating is controlled by process that has the slowest oxygen diffusion rate. From the above analyses, it is reasonable that the oxidation process of the prepared multi-layer coating coated C/C is controlled by process (a).

In another point, according to the investigation results of Wu[13], the oxidation activation energy is 112 kJ/mol when the oxidation process of the coated C/C is controlled by the rate of oxygen diffusion along the SiO_2 glass film; it is 80 kJ/mol when the oxidation process is controlled by the oxygen diffusion along the defects of the coating. It was found that the relationship between oxidation weight loss rate and oxidation temperature of SiC/$2SiO_2 \bullet Y_2O_3$/$1.5SiO_2 \bullet Y_2O_3$/$SiO_2 \bullet Y_2O_3$/glass coated C/C at 1 573-1 873 K accords well with Arrhenius relation. By curve fitting and calculation, the oxidation activation energy of SiC/$2SiO_2 \bullet Y_2O_3$/$1.5SiO_2 \bullet Y_2O_3$/$SiO_2 \bullet Y_2O_3$/glass coated sample was determined to be 132.2 kJ/mol (Fig.7), which is near to 112 kJ/mol, inferring that the oxidation process of the coated C/C is controlled by the rate of oxygen diffusion through the dense borosilicate glass, which verifies the above analyses result.

Fig.8 shows the surface morphologies of the glass coating before and after oxidation at 1 773 K for 164 h. Before oxidation, a dense surface was acquired (Fig.8(a)). After oxidation at 1 773 K for 164 h, no obvious changes were found except the formation of some micro-cracks, which may be generated during the quickly cooling from 1 773 K to room temperature during the isothermal oxidation test, and they could self-seal when the coating is heated to 1 773 K again. From Fig.8, some pinpoint sealed holes were also found, which may be generated by the escape of the oxidation gases. Because the holes and the cracks could be self-cured quickly by the borosilicate glass at high temperature, the oxidation rate of the coated C/C is controlled by the oxygen diffusion through the dense borosilicate glass within 164 h and no failure behaviors are observed during the oxidation process.

4 Conclusions

In conclusion, the SiC/yttrium silicates/glass coatings are good oxidation protective coating for C/C composites. With the increase of the composition gradient yttrium silicates interlayer, the oxidation resistant property was obviously improved. The SiC/$2SiO_2 \bullet Y_2O_3$/$1.5SiO_2 \bullet Y_2O_3$/ $SiO_2 \bullet Y_2O_3$/glass coated C/C exhibits the best oxidation resistance; and it could protect the C/C composites from oxidation perfectly in air condition at 1 773 K for 164 h with the weight loss of 1.65% and at 1 873 K for 117 h with the weight loss of 1.77%. The oxidation process in C/C substrates with SiC/$2SiO_2 \bullet Y_2O_3$/$1.5SiO_2 \bullet Y_2O_3$/$SiO_2 \bullet Y_2O_3$/ glass multi-layer coating is controlled by the diffusion rate of oxygen along the dense borosilicate glass coating; and the corresponding oxidation activation energy of the multi-layer coated C/C is 132.2 kJ/mol.

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