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Oxidation protection of carbon/carbon composites with SiC/indialite coating for intermediate temperatures

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Abstract

In order to improve the oxidation resistance of carbon/carbon composites at intermediate temperatures, a novel double-layer SiC/indialite coating was prepared by a simple and low-cost method. The internal SiC transition layer was prepared by pack cementation and the external indialite glass–ceramic coating was produced by in situ crystallization of ternary $MgO–Al_2O_3–SiO_2$ glass. The microstructures and morphologies of coating were determined by scanning electron microscopy (SEM), X-ray diffraction (XRD) and energy dispersive spectroscopy (EDS). Oxidation resistance of the as-coated C/C composites was evaluated in ambient air at temperature from 800 °C to 1200 °C. Nearly neglectable mass loss was measured after 100 h isothermal oxidation test, indicating that SiC/indialite coating possesses excellent oxidation protection ability. The as-coated samples have a good thermal shock resistance and no obvious damage was found in the coating even after suffered more than 11 thermal cycles between test temperature and room temperature. The oxidation protection mechanism of this coating was also discussed.

Keywords: Sintering; Interfaces; Corrosion; Glass ceramics; Engine components

1. Introduction

Carbon/carbon (C/C) composites are attractive thermostructural materials for high-temperature application due to their low density, low coefficient of thermal expansion (CTE), high thermal conductivity, excellent thermal shock resistance and mechanical properties.[1] However, C/C composites have an inherent defect, that is, rapid oxidation in oxidizing environment above 400 °C, which restricts wide application of these materials.[2]

Multilayer coatings were proved to be an effective way to improve the oxidation resistance of these composites[3] and the choice of coating systems was highly dependent on the application temperature. Generally, SiC coating has been considered as one of the best bonding layer due to its good physical and chemical adaptability with C/C substrates.[4,5] Several coating systems, such as SiC/Y_2SiO_5,[6] SiC/Si–W–Mo[7] and SiC/mullite,[8] can effectively protect C/C composites over 1400 °C for a long time. However, some serious problems existing in the coating systems include inherent brittleness of ceramic coating and large mismatch of CTE between C/C substrates and coating. As a result, these coatings are prone to cracking under thermal cycles and the stress-induced cracks fail to self-seal below 1200 °C, which lead to the severe oxidation of C/C composites at intermediate temperatures. To solve this problem, some researchers proposed a feasible way to reduce the interface thermal stress by preparing a low CTE external coating.[9]

Some glass–ceramic materials possess unique combination of properties, such as good mechanical strength and high-temperature stability, especially, the low CTE.[10] In this work, a double-layer SiC/indialite glass–ceramic coating was prepared for protection of C/C composites at intermediate temperatures and the microstructures and oxidation resistance of the coating system were fully investigated.

2. Experimental

Small samples (10 mm × 10 mm × 10 mm) used in this work were cut from bulk felt C/C composites with a density of $1.75\ g/cm^3$. After being polished with 500 grits SiC paper,

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samples were ultrasonically cleaned in acetone and dried at 100 °C for 30 min. The composition for preparing SiC internal coating by pack cementation was: 65–80 wt.% Si, 10–25 wt.% graphite and 5–10 wt.% Al_2O_3. C/C samples and pack mixtures were put in a graphite crucible and heat-treated at 1800–2000 °C for 1–2 h in argon to form the internal SiC coating.

External glass–ceramic coating was prepared by slurry spraying. Glass chosen in this study fell into primary phase field of cordierite and the compositions of glass were composed of 50–75 wt.% SiO_2, 2–10 wt.% Al_2O_3, 10–20 wt.% MgO and a few amounts of CaO and TiO_2. The mixtures were ball-milled in polyurethane container for 30 min, melted in Al_2O_3 crucible at 1500 °C for 2 h to form homogenous glass, and then quenched in distilled water immediately. Followed by gas-free piece was ground to 30 μm, the fine powders were mixed with carboxymethyl cellulose to form homogeneous slurry and sprayed onto the surface of SiC coating. Finally, the samples were heated to 1400 °C for 10 min to form the glass coating and dwelled at 1000 °C for 2 h for further crystallization to form glass–ceramic coating. During cooling step, slow cooling rate was set at 3–5 K/min to minimize thermal shock.

The isothermal oxidation test was carried out in air in an electric furnace. Weight change of the samples were measured by a precision balance and recorded as a function of time. Cumulative weight change percentages of the samples were calculated using the following equation:

$$\Delta W\% = \frac{m_0 - m_1}{m_0} 100\%$$

where m_0 and m_1 were the weight of the samples before oxidation and after oxidation, respectively.

The crystalline phase of the as-coated C/C was identified with Rigaku D/max-3C X-ray diffraction (XRD). The surface and cross-section morphologies of the as-coated samples were determined by JSM-6460 scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). CTE values of glass–ceramic and C/C material were performed on DIL-402 high-temperature thermal expansion apparatus. The specimens (20 mm × 4 mm × 4 mm) of indialite glass–ceramic were obtained by the same process as external coating preparation.

3. Results and discussion

3.1. Microstructures of the coatings

Fig. 1 shows the surface and cross-section SEM images of the internal coating prepared by pack cementation. From Fig. 1a, it can be seen that internal coating exhibits a dense and homogeneous structure. However, a few microcracks can be observed in the coating, which resulted from the great resid-

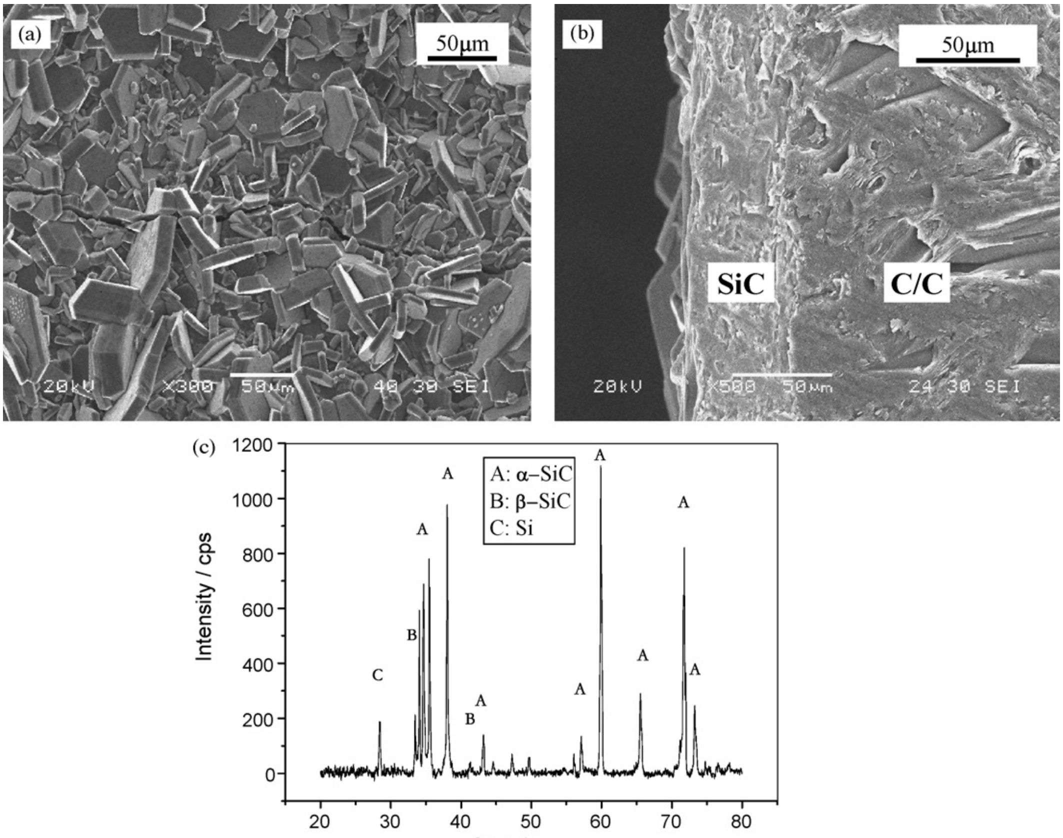

Fig. 1. Morphologies and phase analysis of SiC transition coating prepared by pack-cementation (a) surface SEM image, (b) cross-section SEM image and (c) XRD patterns.

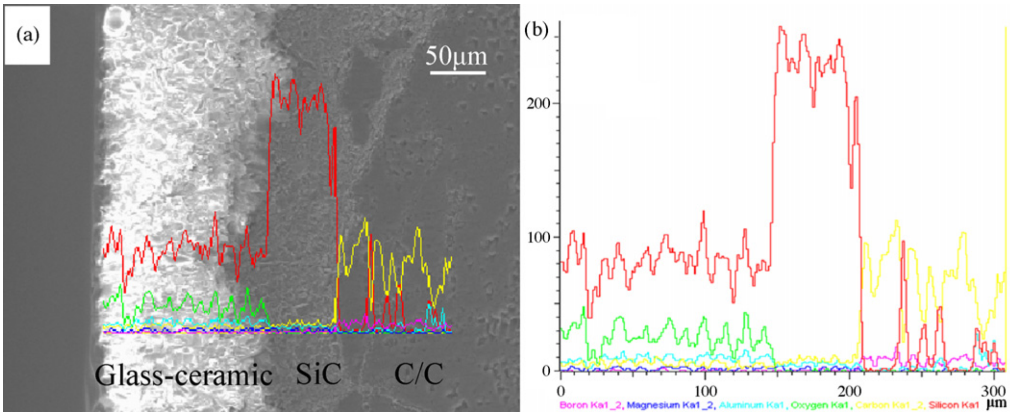

Fig. 2. Cross-section SEM image and EDS profile of the glass–ceramic coating prepared by slurry spraying.

ual thermal stress during cooling. The average thickness of SiC coating is about 50 µm. From XRD patterns, strong diffraction peaks corresponding to α-SiC, β-SiC and Si phase were detected. The main crystalline is α-SiC which can be deduced from the peak intensity and diffraction angle. The occurrence of Si peak indicates that internal coating is a Si-riched SiC coating.

Fig. 2 shows the cross-section SEM micrographs of SiC/glass–ceramic coating. From Fig. 2a, it is clear that a dense and crack-free external coating was obtained by slurry spraying. The thickness of double-layer coating adds up to 200 µm. Furthermore, no discontinuous area or microcracks can be observed at the interface zone between internal and external coating, indicating that glass–ceramic coating is physically compatible with SiC coating. Or else, if poor wetting exists between them, some pores or discontinuities would be inevitably present at the interface zone.[11]

Fig. 3 shows the XRD patterns of the external glass–ceramic coating before and after crystallization treatment. It is clear to see that no crystalline peak was detected before crystallization and the diffraction pattern is well consistent with typical glass material. In contrast, after 90 min heat-treatment at 1000 °C, the transparent external coating became translucent and some strong crystalline peaks appeared in diffraction patterns. XRD analysis result reveals that only the indialite ($Mg_2(Al_4Si_5O_{18})$) phase formed in the external coating.

3.2. Oxidation protective ability of the coating

Fig. 4 illustrates the isothermal oxidation curves of the as-coated C/C composites at different temperatures. It can be seen that single SiC coated C/C composites exhibits rapid mass loss at 900 °C in air. After oxidation only for 5 h, the mass loss of sample almost up to 4.7%. Microcracks in the SiC coating provide the entrance channels for oxygen to diffusion into C/C matrix and lead to the final failure of internal coating.

Oxidation resistance of the samples was clearly improved by adding indialite external coating. The test results show that SiC/indialite glass–ceramic coating possess excellent protection ability and can effectively protect C/C composites from oxidation. Nearly zero mass loss was measured when isothermal oxidized at 800 °C in air for 100 h. With the increasing test temperature, mass loss of the coated samples increased from 0.27% at 900 °C, 0.34% at 1000 °C to 0.45% at 1200 °C. After oxidation at 1200 °C for 75 h, the mass loss of sample increased abruptly, which due to the mechanical damage on the surface of sample during the experiment.

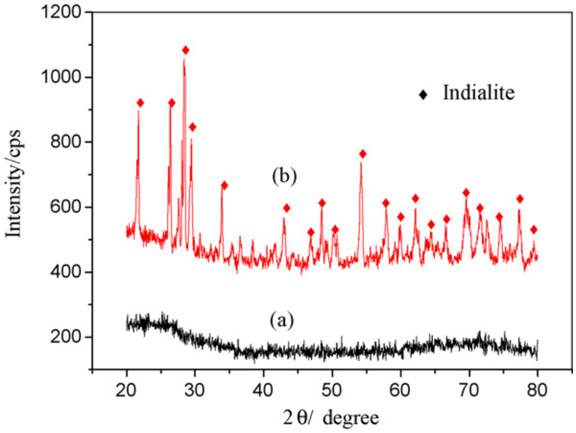

Fig. 3. XRD patterns of the glass–ceramic coating (a) before and (b) after crystallization.

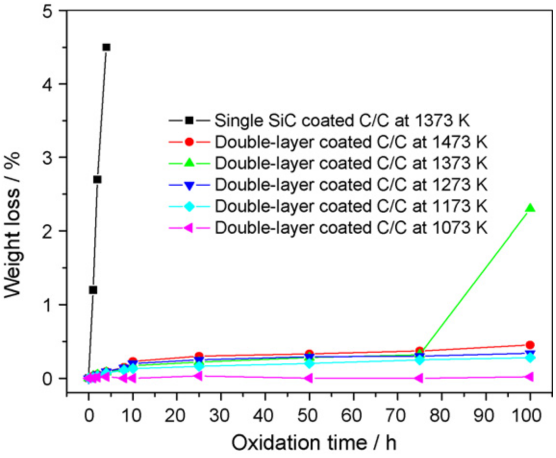

Fig. 4. Isothermal oxidation curves of as-coated samples at different temperature in air.

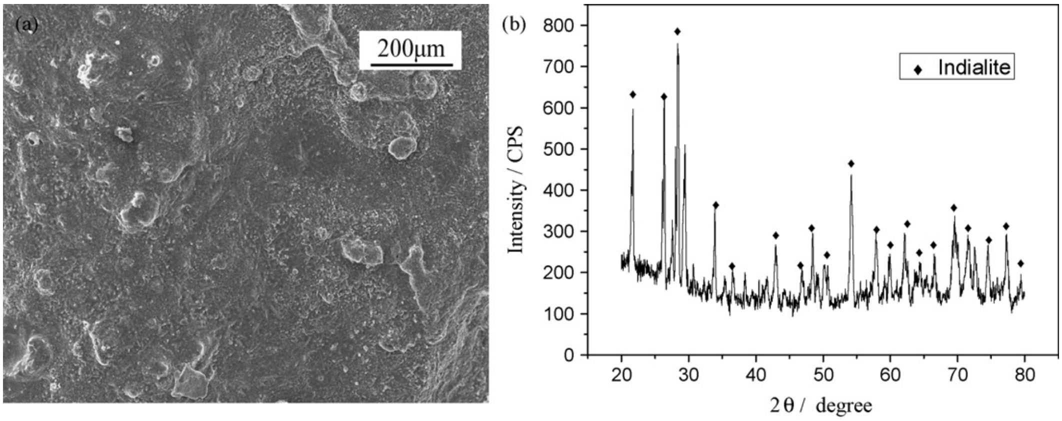

Fig. 5. Surface SEM image and XRD patterns of the glass–ceramic coating after isothermal oxidation.

Fig. 5a shows the surface SEM image of the double-layer coating after oxidation at 900 °C for 100 h. As shown in Fig. 5a, no microcracks were observed on the surface of double-layer SiC/indialite coating and the coating is dense as before. It is noted that the translucent external coating gradually became white. Fig. 5b shows XRD pattern of external coating after isothermal oxidation. No obvious difference in XRD pattern was observed before and after oxidation, besides a little change in intensity of indialite diffraction peak. There is no new phase detected in external coating which indicates that the coating system is chemically steady enough at intermediate temperatures. Increment of diffraction intensity may be mainly attributable to the increasing crystallization degree of indialite glass–ceramic.

3.3. Oxidation protective mechanism

Commonly, glass–ceramic cannot provide oxidation protection for C/C composites, which based on the fact that most glass–ceramic material fail to wet the surface of C/C composites and would react with C/C substrates at high temperature. Despite of single SiC coated C/C composites can only provide limited protection ability, in fact, SiC coating plays an important role in double-layer coating. As a transition layer, SiC coating not only completely inhibits the reaction between both of them, but also can effectively improve the wetting ability of glass–ceramic on C/C substrate, which was studied in our previous research.[12]

The SiC/indialite coating exhibits excellent oxidation resistance at intermediate temperatures, owing to no cracks can be detected in the double-layer coating during isothermal oxidation, which mainly profits from the good match of CTE between C/C composites and coatings. Table 1 lists the CTE value of C/C substrates and coating materials. These data measured range from 20 °C to 800 °C with heating rate of 5 K/min. It can be seen clearly that CTE of SiC-coated sample is only a few higher than pure C/C composites, while much lower than sintering SiC. This result can be explained as the SiC coating is too thin to influence the integral CTE value of the coated samples. The most interesting matter is that CTE of indialite glass–ceramic is lower than that of SiC coated C/C sample in full temperature range of 30–600 °C. Consequently, external glass–ceramic coating ordinarily bears compressive stress during the cooling process. This compressive effect actually reduced the cracking tendency of external coating. The slight mass loss of the as-coated samples utmost probable came from the volatilization of the glass phase in the glass–ceramic. Another possible reason is the oxygen diffused into the double-layer coating and resulted in oxidation of C/C matrix.

Table 1
The CTE values of C/C substrates and coating material.

Materials	CTE ($\times 10^{-6}$ K^{-1}) (30–300 °C)	CTE ($\times 10^{-6}$ K^{-1}) (30–600 °C)
Pure C/C composites	1.5	2.4
SiC-coated C/C composites	1.7	2.7
Sintering SiC	–	4.7
Indialite glass–ceramic	1.3	2.5

The SiC/indialite glass–ceramic coating not only provides good oxidation protection ability for C/C composites, but also possesses excellent thermal shock resistance. As shown in Fig. 5a, after 11 thermal cycles from 900 °C to room temperature, the glass–ceramic coating is still dense and intact, without any cracks or defects occurred on its surface, which also benefits from the low CTE of external coating.

4. Conclusions

Low CTE glass–ceramic coating for C/C composites was successfully prepared by a simple and cost-effective method. A good wettability of the glass on the C/C composites was obtained through composites' surface modified by SiC coating. The SiC/indialite coating system exhibits excellent oxidation resistance which can effectively protect C/C composites from oxidation in air at 900–1100 °C. In addition, the coated samples can withstand thermal cycles between test temperature and room temperature for more than 11 times. The excellent oxidation resistance ability is attributed to its dense, defect-free coating structure and good match of CTE. A little amount of mass loss of as-coated C/C composites resulted form the volatilization of the external coating.

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