FABRICATION AND PROPERTIES OF SiO_2/ZIRCONIUM PHOSPHATE–B_2O_3–SiO_2 ANTI-OXIDATION COATINGS FOR Cf/SiC COMPOSITES

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This paper reports the fabrication of a novel SiO_2/zirconium phosphate (ZrP)–B_2O_3–SiO_2 double-layer coating on Cf/SiC composites via brushing and sol-gel routes for achieving better anti-oxidation performance. The composition of raw materials and sintering temperature were studied to explore the possibility of development of ZrP coatings to meet the demand for oxidation resistance at high temperature. It was attempted to improve the self-healing ability of coatings via an additional SiO_2 layer. Such double-layer coatings developed were characterized by Scanning Electron Microscopy (SEM), Energy Dispersive Spectrometer (EDS), X-ray Diffraction (XRD). The results showed that such coating was composed of a ZrP–B_2O_3–SiO_2 multi-phase inner layer and a SiO_2 outer layer. Better oxidation resistance was observed for coatings with higher contents of ZrP powders. After static oxidation at 1500°C for 20 min, the flexural strength of specimens containing 80 wt. % ZrP was up to 314.6 MPa, retaining 89.1 % of the original value of Cf/SiC composites.

INTRODUCTION

In hypersonic aircrafts and reentry vehicles, thermal structural components are required to prevent equipment from damages. C_f/SiC composites having low density ($1.7 \sim 2.5$ g·cm^{-3}), high modulus (>100 GPa), high strength (tensile strength >350 MPa, bending strength >500 MPa), low expansion coefficient ($1.8 \sim 4.1 \times 10^{-6}$·°C^{-1} (20 ~ 1000°C)) and good chemical resistance are attractive candidates for thermal structural components [1, 2, 3]. However, C_f/SiC composites are easy to oxidize above 400°C in oxygen atmosphere and the oxidation is prone to be severer with increasing temperature [4, 5]. Therefore, the improvement of oxidation resistance is essential for the application of C_f/SiC composites at high temperatures [6].

One efficient way to prevent C_f/SiC composites from oxidation is to fabricate protective coatings on their surface [7, 8]. According to the application temperature, the materials of coatings can be divided into three categories, including low temperature materials (B and Boride [9]), medium temperature materials (SiC [10, 11] and Si_3N_4 [12, 13]) and high temperature materials ($MoSi_2$ [14], HfO_2 [15], Y_2SiO_5 [16], $ZrSiO_4$ [17]). Among them, metal phosphate, such as $AlPO_4$–$Zn_3(PO_4)_2$–$Mn_3(PO_4)_2$, is generally used to fabricate protective coatings applied at low and medium temperatures (500 ~ 1200°C) [18, 19]. Ge et al. [20] prepared phosphate-coating for C/C composite by using liquid-impregnation. Their results showed that the specimens with fast cooling rate only lost 0.98 % of mass after oxidation at 700°C for 20 h. Hou et al. [21] fabricated phosphate-based coatings on C/C composites via pasting. After oxidation at temperatures between 600°C and 700°C for 100 h, the weight loss of samples was less than 1 % while over 1 % after oxidation at 750°C and 800°C for 50 h. At high temperatures from 1300°C to 1630°C, although zirconium phosphate, can withstand severe environment over 2900°C [22], only few papers reported ZrP coatings applied in C_f/SiC composites. This is because the sintering temperature of pure ZrP is higher than 1600°C and dense ZrP coatings are easy to crack during the sintering process due to the coefficient of thermal expansion (CTE) mismatch between the substrate and ZrP [23].

In this paper, we focus on the fabrication of zirconium phosphate coatings at relatively low temperature to achieve a good oxidation resistance at high temperature. A ZrP-B_2O_3-SiO_2 multi-phase inner layer was firstly applied on the surface of C_f/SiC composites with Al_2O_3 and MgO adopted as sintering additives. Then an outer SiO_2 layer was deposited via sol-gel process on the surface of ZrP coatings to further promote the densification of coatings. After that, the microstructure and anti-oxidation performance of the coated C_f/SiC composites were investigated.

EXPERIMENTAL

Two dimensional (2D) C_f/SiC composites of dimensions 35 × 35 × 4 mm used as the substrate materials for the double-layer coatings were produced by National University of Defense Technology via Precusor Infiltration Pyrolysis (PIP). They were hand-abraded with a series of SiC papers up to 800 grits, and then degreased with ethyl alcohol and dried at 100°C. The zirconium phosphate powders (2 - 3 μm, 99 % purity) were purchased from Wuhan Huanyu Chemical Co. Ltd., China. SiO_2 (AR) and B_2O_3 (1 - 3 μm, 99.3 % purity) were produced by Hunan Geology Research Institute, China and Beijing Jia'anheng Technology Co. Ltd., China respectively. Phenolic resin was provided by Xi'an Taihang polymer research Institute, China. The commercial silica sol has a concentration of 25 wt. %.

To gain the inner coatings, ZrP (containing 5 wt. % Al_2O_3 and 2 wt. % MgO), B_2O_3 and SiO_2 were weighted to a desired composition and then added to a premix phenolic resin/ethanol solution. The solid loadings of ceramics was 40 wt. % and the weight ratio of B_2O_3 and SiO_2 was constant at 1:1. The slurry obtained was mixed by magnetic stirring for 2 h and brushed directly on the whole surfaces of substrate materials. Then the coated specimens were dried at 80°C for 10 min and cured at 120°C (1 h) and 160°C (30 min) in turn in an electric furnace. Subsequently, the specimens prepared were sintered at 1200°C in nitrogen for 1 h. After that, the sintered coatings were infiltrated with silica sol in vacuum and heat treated at 100°C. This process was repeated for 4 times and eventually a double-layer coating was obtained.

The oxidation resistance of the coated C_f/SiC composites was determined in a muffle furnace (KBF1700) at 1500°C for 20 min in air. After oxi-dation, specimens were taken out directly and cooled in nature. Then the samples were weighted by an analytical balance with a sensitivity of ± 0.001 g to calculate the weight losses of the coated composites. The coatings' morphology was examined by a scanning electron microscope (SEM) JSM-6360LV (JEOL) and the chemical composition was investigated by EDS. The phase composition was characterized by X-ray diffraction (XRD) using Bruker Advanced D8 diffractometer at a wavelength of 1.5418 Å (Cu K_α radiation). The mechanical properties were measured in a three-point test machine (WDW-100) with a span of 30 mm and crosshead speed of 0.5 mm·min^{-1} carried out at a test piece of 35 × 4 × 3 mm.

RESULTS AND DISCUSSION

Design of SiO_2/ZrP-B_2O_3–SiO_2 coatings

In this study, phenolic resin was chosen as adhesive material to improve the bond strength of the green coatings. Its effect on brushing process was investigated by adjusting the mass ratio of phenolic resin and ceramic powders. The results showed that when the ratio was about 1:3, the slurry was easy to brush and the thickness of coatings can also be controlled.

As mentioned above, ZrP can withstand high temperature, so it was chosen as main skeleton of anti-oxidation coatings. B_2O_3 with a low melting point of 450°C has excellent oxidation protection in a temperature range of 600 to 1100°C [24]. It was attempted to increase the adhesive strength of coatings by introducing B_2O_3 into the inner layer to form a liquid phase at high temperature. Meanwhile, according to the phase diagrams, SiO_2 can partially dissolve into boron-oxygen network and it can retard the evaporation of B_2O_3 [25]. Thus, B_2O_3 and SiO_2 were combined with ZrP powders to form a dense and uniform inner coating. The outer layer should also be dense for the requirement of oxidation resistance, and it would be better to have the ability to flow into and seal cracks in the ZrP inner layer. In this paper, the SiO_2 layer fabricated by sol-gel process can meet this demand and the reaction between ZrP and SiO_2 was also hoped to further improve the densification of such protective coatings.

Composition and microstructure of SiO_2/ZrP–B_2O_3–SiO_2 coatings

Figure 1 shows the XRD patterns of raw ZrP powders after heat treatment at various temperatures. At room temperature, there are no characteristic peaks, and it reveals that ZrP remains amorphous. When the temperature is increased up to 1200°C, $Zr_2P_2O_9$ and ZrO_2 are detected resulting from the decomposition of ZrP. It can also be observed that $Zr_2P_2O_9$ transfers into $Zr_2O(PO_4)_2$ and yields ZrO_2 when it comes to 1500°C. Similar phenomenon has been reported by Fei Chen *et al.*

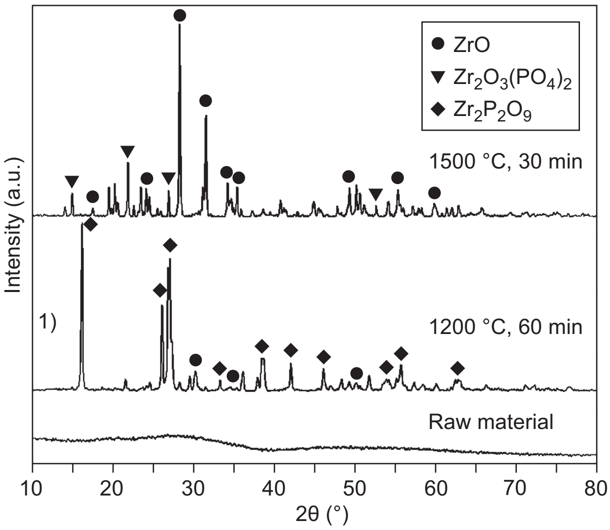


Figure 1. XRD patterns of raw zirconium phosphate after heat treatment at different temperatures.

[26], but the decomposition of ZrP is more serious even at temperature in excess of 1200°C in this study. Therefore, we choose the sintering temperature at 1200°C to ensure less decomposition of ZrP.

The XRD patterns of the coatings with different amount of ZrP (mass ratio of SiO_2 and B_2O_3 kept at 1:1) after oxidation at 1500°C for 20 min in atmosphere is presented in Figure 2. As denoted in the patterns, the $ZrSiO_4$ phase (melting point: 2500°C) is obtained and it indicates the reaction between ZrP and SiO_2 occurs after oxidation. The diffraction peaks for the main planes in the structure of $ZrSiO_4$ (JCPDS card number 83-1374) exhibiting at 20.1(1 0 1), 27.1(2 0 0), 33.9(2 1 1), 35.7(1 1 2), 38.6(2 2 0), 40.8(2 0 2), 43.9(3 0 1), 47.7(1 0 3), 52.3(3 2 1), 53.6(3 1 2), 55.7(2 1 3), etc., are obvious, which indicates a relatively good crystallization of $ZrSiO_4$ [27]. Meanwhile, though not significantly, the intensity of $ZrSiO_4$ peaks (e.g. 35.7(1 1 2)) gradually increase with increasing content of ZrP in ceramic powders.

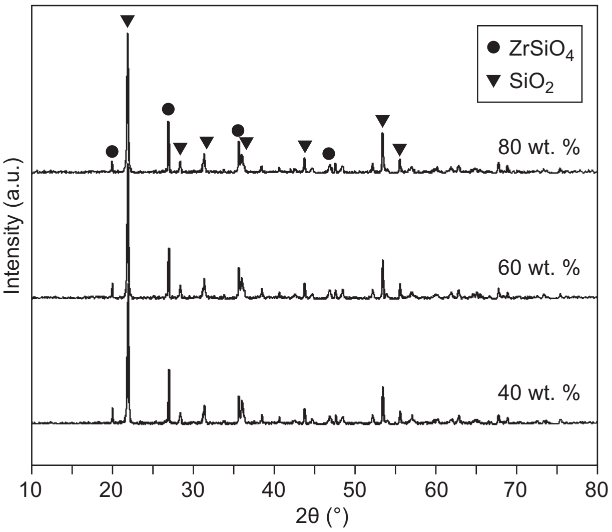


Figure 2. XRD patterns of SiO_2/ZrP–B_2O_3–SiO_2 coatings after oxidation at 1500°C for 20 min with different contents of ZrP.

The microstructures for the sintered coatings containing 60 wt. % ZrP before and after heat treatment at 1500°C in air for 20 min are shown in Figure 3. It can be seen from Figure 3a that obvious crack and white particles (SiO_2) exist on the surface of the sintered coatings, resulting from the mismatch of CTE between different coating layers. As seen in Figure 3b, the coating has a layered structure including a ZrP layer (interior, about 26 um) and a SiO_2 layer (exterior, about 47 µm), and there is a particular boundary between these two layers. After heat treatment, from the surface of the coatings (shown in Figures 3c and e), crack is self-healed and white particles disappeared. There only exists little micro-cracking showing the promotion of densification by liquid phase of SiO_2 and B_2O_3. It is also interesting to note that, as observed in Figure 3d, the boundary between two layers disappeared, and the average breadth of coatings has not changed keeping at around 75 µm. This indicates the diffusion of atoms in the two layers occurs which makes the reaction between ZrP and SiO_2 possible to produce $ZrSiO_4$ as found in the XRD patterns. By comparing Figure 3b with Figure 3d, C_f /SiC composites have not been destroyed after oxidation and there is not obvious fiber oxidation phenomenon. It proves that such coatings has excellent anti-oxidation performance at high temperature up to 1500°C.

As can be seen from Figure 4, the Energy Dispersive Spectrometer (EDS) was used to study the element composition of the double-layer coatings as shown in Figure 3b. Figure 4a reveals that the exterior coating layer mainly contains Si and O elements, while the interior coating layer (shown in Figure 4b) mainly contains Zr, P, Si, O, Al and Mg elements. As to the light B element, it is beyond the detection range for this technology. Despite the specific content of each element, the results indicate that the target coatings, SiO_2 and ZrP-B_2O_3-SiO_2 layers, are obtained.

Anti-oxidation performance of SiO_2/ZrP–B_2O_3–SiO_2 coatings

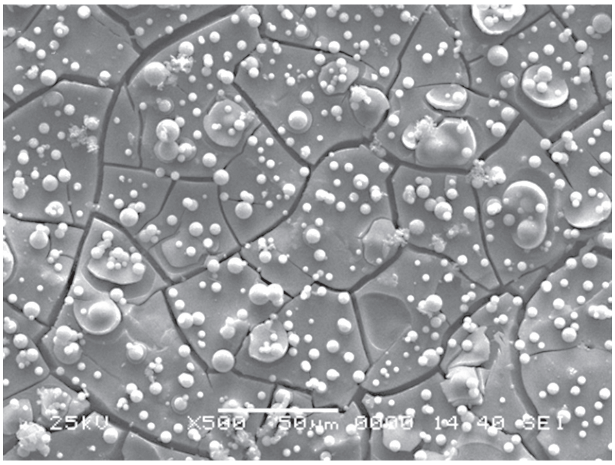
To prevent C_f/SiC composites from oxidation, high bonding strength, high densification, well self-sealing ability and low evaporation during application are necessary for protective coatings [28]. The general properties of such sintered samples after oxidation are listed in Table 1. Time at 1500°C is held constant for 20 min for all specimens. For coatings sintered at 1200°C, it is clear that the flexural strength increases by increasing the ZrP mass fraction of ceramic powders,

Table 1. General properties of Cf/SiC composites with SiO_2/ZrP–B_2O_3–SiO_2 coatings after static oxidation at 1500°C for 20 min.

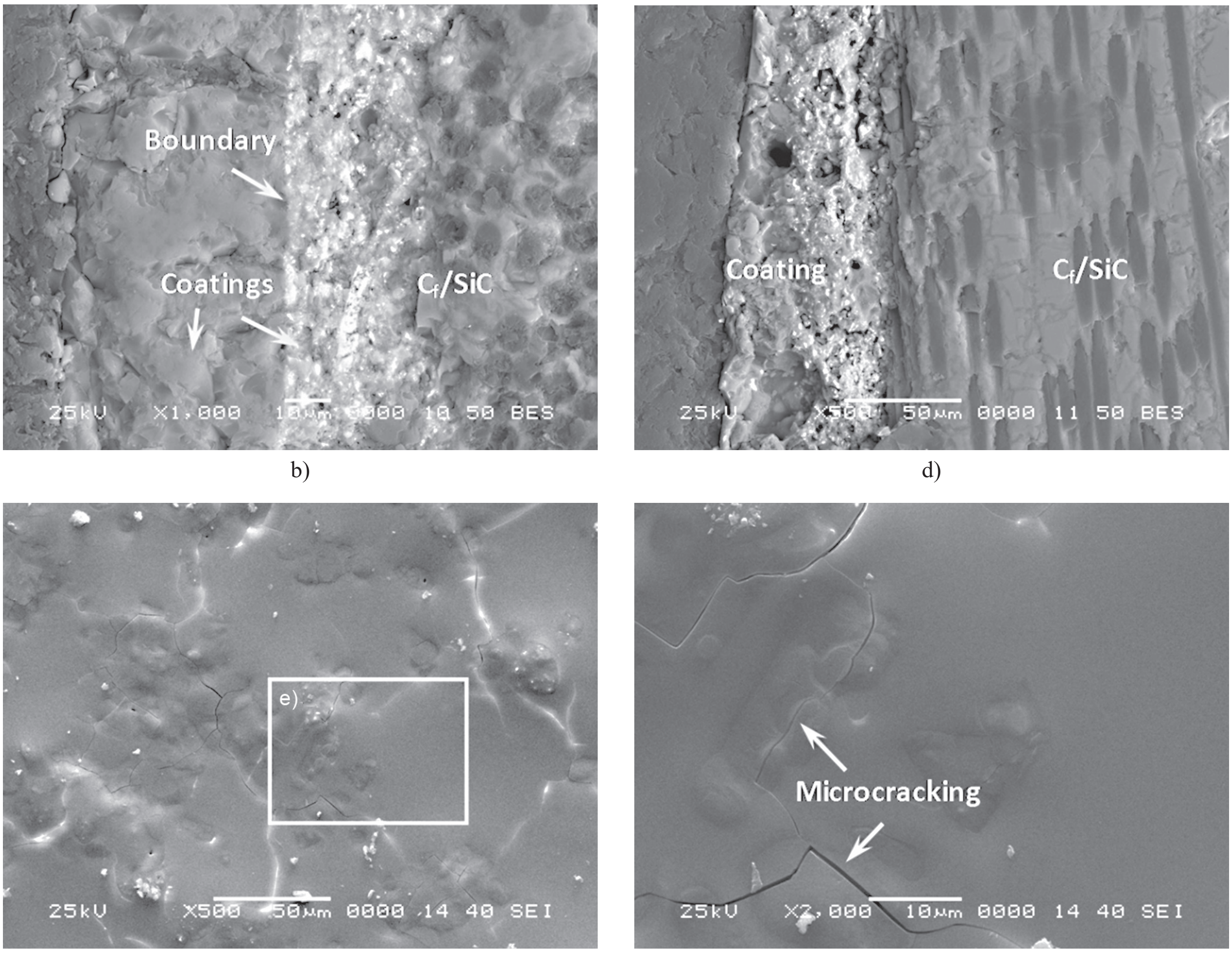
Content of ZrP (wt. %)	Sintering temperature (°C)	Flexural strength (MPa)	Mass retention percentage (%)	Strength retention percentage (%)
40	1200	285.3	97.1	80.7
60	1200	303.9	98.6	86.0
80	1200	314.6	98.2	89.1
60	1500	292.9	97.8	82.9

from 285.3 MPa (40 wt. %) to 314.6 MPa (80 wt. %). Also, the strength retention percentage of 80 wt. % ZrP samples reaches the highest level at 89.1 %. Note that the mass retention percentage of 60 wt. % ZrP_2O_7 samples is higher than that of 80 wt. % ZrP samples, reaching up to 98.6 %. For comparison, coatings containing 60 wt. % ZrP were also sintered at 1500°C and the flexural strength retention rate decreases by nearly 3 % compared with that of specimens sintered at 1200°C. However, the property of such samples is better than that of 40 wt. % ZrP samples sintered at 1200°C, indicating that the ZrP content has a significant influence on anti-oxidation performance.

From the result of anti-oxidation experiment, it can be also concluded that the effect of the introduction of SiO_2 is inspiring. Firstly, SiO_2 in ZrP powders partially dissolves into B_2O_3 network and it can help to decrease the viscosity of liquid phase so that less B_2O_3 would vaporize, which is expected to benefit the densification of coatings to some extent. Secondly, despite obvious crack on the surface after sol-gel process, SiO_2 reacts with ZrP and yields a more stable and dense $ZrSiO_4$ phase after oxidation, which can also ensure the high strength of the composite materials. Consequently, the introduction of SiO_2 plays an important role in further increasing the mechanical and anti-oxidation performance of ZrP coatings.



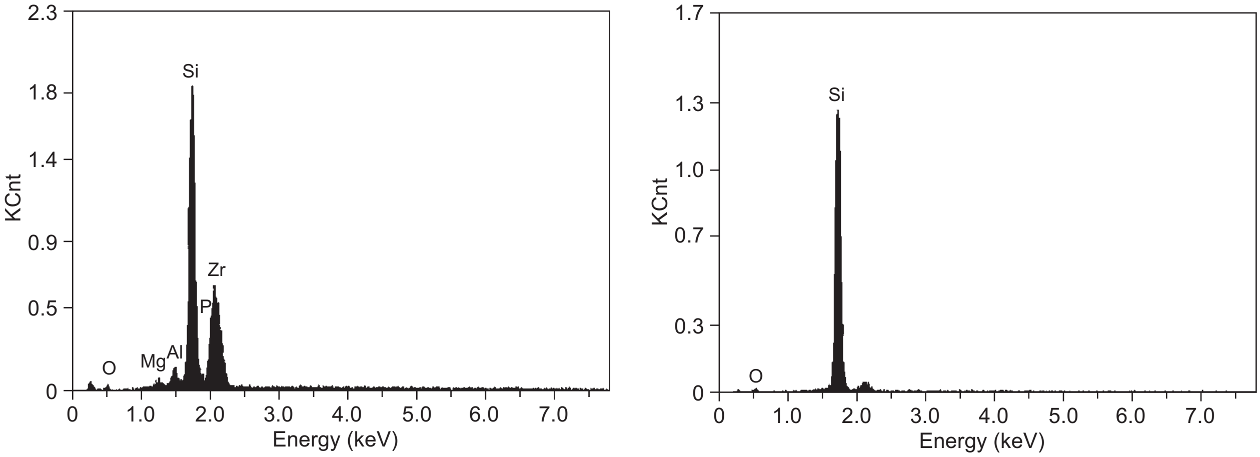
a)



b) d)

c) e)

Figure 3. SEM images of SiO_2/ZrP–B_2O_3–SiO_2 coatings containing 60 wt. % ZrP before (a, b) and after oxidation (c, d, e); (e) is the highlight morphology of (c).



a) exterior layer

b) interior layer

Figure 4. EDS images of a) exterior and b) interior layer of SiO_2/ZrP–B_2O_3–SiO_2 coatings as shown in Figure 3b.

CONCLUSIONS

We have fabricated a novel SiO_2/ZrP–B_2O_3–SiO_2 double-layer coating for C_f/SiC Composites through brushing and sol-gel routes for the application at high temperature up to 1500°C, and the structures, compositions, anti-oxidation performance were investigated. The main conclusions are summarized as follows:

- The crystal form of zirconium phosphate is sensitive to the temperature and the decomposition of zirconium phosphate begins at temperature up to 1200°C.
- Such novel double-layer coatings with an inner ZrP layer synthesized from mixed ceramic powders and an outer SiO_2 layer fabricated by sol-gel process show excellent high temperature oxidation resistance and well self-sealing ability.
- For coatings containing 60 wt. % ZrP, C_f/SiC composites show no obvious oxidation phenomenon after oxidation at 1500°C for 20 min and the mass retention percentage peaks at 98.6 %, while the highest flexural strength of the composites belongs to the 80 wt. % ZrP_2O_7 samples, reaching 303.9 MPa.

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