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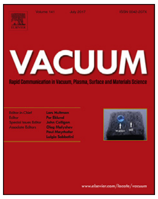

Oxidation behavior of co-deposited ZrC modified C/C composites prepared by chemical liquid-vapor infiltration process

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ABSTRACT

The oxidation behavior of C/C-ZrC composites prepared by chemical liquid-vapor infiltration (CLVI) process was studied, and the effects of co-deposited ZrC on the oxidation resistance properties were also discussed. Results indicate that an excellent oxidation resistance of C/C-ZrC composites has been obtained due to introduction of co-deposited ZrC. After 240 min oxidation at 900 °C, the mass loss of C/C-ZrC composites reaches to 11.77%, which decreases remarkably compared with C/C composites (90.74%). ZrC ceramics co-deposited on carbon fibers can improve the anti-oxidation properties of the fiber/matrix interfaces and the matrix to decrease the amounts of oxidation defects. Moreover, ZrO_2 layers are produced by the oxidation of ZrC, which can form a protective film to reduce the erosive attack. A schematic was proposed to further illustrate the oxidation behavior of C/C-ZrC composites. Additionally, co-deposition of ZrC leads to high graphitization degree of C/C composites, thus increasing the activation energy of the composites, which also improves oxidation resistance properties.

1. Introduction

Carbon fiber reinforced carbon based composites (C/C) are widely applied in advanced structural materials fields due to their high thermal conductivity, excellent thermal shock resistance, highlighted mechanical properties at high temperature and light weight [1–4]. Unfortunately, the widespread utilization of C/C composites has been greatly restricted because the composites are prone to be oxidized at temperatures above 500 °C in oxygen atmosphere [5–7]. After oxidation, the matrix and carbon fibers are damaged severely, resulting in degradation of their properties. Therefore, the oxidation of C/C composites has become one of the main factors limiting their development, and the improvement of oxidation resistance of C/C composites confronts a tough challenge.

Up to now, an effective solution is introduction of ultrahigh temperature ceramics (UHTCs) into C/C composites, which can combine the advantages of UHTCs and C/C composites. UHTCs are the refractory metal carbides and borides, which are regarded as the most promising materials according to their unique comprehensive properties. Thus there are lots of investigations about UHTCs in the fields of modified C/C composites [8–14]. In particular, zirconium carbide (ZrC) ceramic is a candidate for ultrahigh temperature application because of its excellent chemical stability, absence of phase changes in the solid state and high melting point. Moreover, ZrC ceramics convert into ZrO_2 phase after oxidation, which can provide isolation layers to reduce the corrosion of fibers and matrix [15–17]. At present, there are many approaches to be applied in fabrication of C/C-ZrC composites, such as precursor infiltration and pyrolysis (PIP), slurry infiltration by hot pressing, and chemical vapor infiltration (CVI) [15–17]. However, there are many disadvantages in these preparation methods, such as time-consuming, expensive cost and damage to carbon fibers.

In recent years, CLVI process has received wide attention due to its characteristics of high efficiency, simple and short period. Meanwhile, the densification rate of CLVI process is about one or two orders of magnitude larger than that of isothermal CVI [18]. Therefore, a lot of researches have been implemented on CLVI process. Sun et al. [19] investigated the microstructure and morphologies of the pyrocarbon and analyzed the nucleation and growth mechanism in CLVI process. Wang et al. [20] used a double heat source to prepare a large C/C composite disc and proposed a schematic model of densification process. Li et al. [21] prepared C/C composites reinforced with in situ carbon nanofibers/nanotubes by introducing catalyst and studied their microstructure and mechanical properties.

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Nevertheless, these above investigations are only performed in the researches of C/C composites, especially in revealing the complex chemical reactive mechanism and improvement in CLVI technology. Almost few reports are available to apply CLVI process in the fields of C/C-UHTCs composites. In our initial work, we produced C/C-ZrC composites by using CLVI process and found that this method could reduce the preparation period significantly, and the preparation technology, mechanical performance and ablation properties of the modified C/C composites were preliminarily studied [22]. But less information could be used to deeply analyze the oxidation behavior and mechanism of the composites. For this purpose, the oxidation behavior and mechanism of C/C-ZrC composites was investigated in the present study. The microstructure of the composites and the effects of co-deposited ZrC on the oxidation resistance properties were further explored. In addition, for better understanding the role of co-deposited ZrC, the graphitization degree of as-produced composites was studied to discuss the relationship between the graphitization degree and anti-oxidation properties.

2. Experimental

2.1. Materials preparation

A T300 PAN-based carbon felt (density: 0.43 g/cm^3, Φ80 mm × 10 mm) was used as a preform, which was fabricated by alternate lamination of long fiber layers and short-chopped fiber layers with a needing punching. The long fiber layers were interlaced in the orientation of 0°/90°. Liquid xylene (C_8H_{10}) was chosen as precursor of carbon, and the purity and boiling point were 99.0% and 138.4–144.4 °C, respectively. Zirconium-containing polymer (PZC) (Institute of Process Engineering, Chinese Academy of Science, China) was dissolved in liquid xylene, which was chosen as the ZrC precursor. The experimental device was shown in Ref. [22], and the operation procedures are somewhat same. The CLVI process was performed at the temperature of 1100–1200 °C, and followed by a heat-treatment of 1500 °C for 2 h under an argon atmosphere. The final density of the C/C-ZrC was 1.84 g/cm^3. For comparison, a pure C/C composite with 1.76 g/cm^3 was prepared with the similar processing history.

2.2. Oxidation test

The oxidation behavior of the composites was studied by isothermal cyclic tests. The specimens were weighed by using an electronic balance, and the test samples were cut off to be the same dimension. The isothermal oxidation tests were performed at temperatures of 600, 700, 800 and 900 °C in air flowing. Once the required temperature was obtained, the specimens were directly put into electrical furnace and maintained at the fixed temperature for 30 min. At the designated time, the samples were taken out of the electrical furnace and then weighed again. After weighing, the samples were pushed into the furnace for the next cycle. At each oxidation temperature, this process was repeated for 8 times, and the total oxidation time was 240 min. The mass loss (θ) of samples was calculated by the following Eq. (1)

$$\theta = \frac{m_0 - m_1}{m_0} \times 100\% \qquad (1)$$

where m_0 and m_1 are the weight of the composites before and after oxidation, respectively. For each temperature, three samples were tested, and the final mass loss values were obtained by the average values.

2.3. Characterization

The crystalline phase of samples before and after oxidation was identified by X-ray diffraction (XRD, X'pert PROMPD). The microstructure morphology was characterized by scanning electron microscopy (SEM) with an energy-dispersive spectroscopy (EDS) system. Raman spectroscopy was used to characterize the graphitization degree of the composites. Three points (A: fiber, B: fiber/matrix interface, C: matrix) were detected by Raman spectra to investigate the influence of ZrC ceramics on the graphitization degree (shown in Fig. 1).

3. Results and discussion

3.1. Microstructure

Fig. 2 shows the XRD patterns of C/C-ZrC sample before and after oxidation, from which it can be seen the composites consists of pyrocarbon and ZrC before oxidation. After oxidation, there is a new phase of ZrO_2 existing in the composites, which is produced by the oxidation of ZrC in the air. From the SEM images of C/C-ZrC composites, it can be seen that lots of white components disperse homogeneously in gray matrix (Fig. 3 (a)). Combined with EDS analyses (Fig. 3 (b)), the white and grey phases can be identified as ZrC and carbon phases, respectively. The carbon fibers in non-woven layers are wrapped around with ZrC grains and pyrolytic carbon (Fig. 3 (c)), indicating that PyC and ZrC ceramics are co-deposited in CLVI process and a strong interface bonding exists between ZrC grains and PyC. Similarly, it also can be seen that pyrocarbon and ZrC are embedded mutually in fiber webs (Fig. 3 (d)), and there is no obvious aggregation of two phases, which means that the composites possess a uniform microstructure after CLVI process.

Raman spectrum is a sufficient method to identify the integrality of carbon crystallite and the existence of defects in carbon

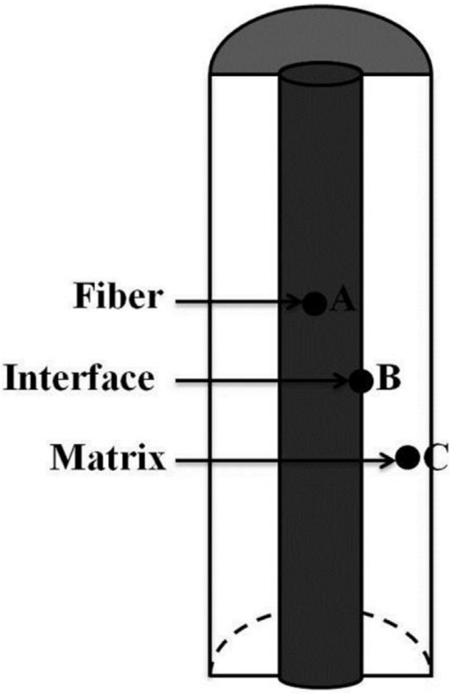

Fig. 1. The configuration of Raman spectrum analysis (A: fiber, B: fiber/matrix interface, C: matrix).