Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Oxidation protection and mechanism of the HfB_2-SiC-Si/SiC coatings modified by in-situ strengthening of SiC whiskers for C/C composites

Tianying Wang, Ruiying Luo*

School of Physics and Nuclear Energy Engineering, Beihang University, Beijing 100191, PR China

ARTICLE INFO

Keywords:
Carbon/carbon composites
SiC whisker
HfB_2-SiC-Si
Oxidation resistance
Thermal shock resistance

ABSTRACT

To improve the oxidation resistance and alleviate the thermal stress of the HfB_2-SiC-Si/SiC coatings for C/C composites, in-situ formed SiC whiskers (SiC_w) were introduced into the HfB_2-SiC-Si/SiC coatings via chemical vapor deposition (CVD). Effects of SiC_w on isothermal oxidation and thermal shock resistance for the HfB_2-SiC-Si/SiC coatings were investigated. Results showed that the SiC_w-HfB_2-SiC-Si/SiC coatings exhibited excellent oxidation resistance for C/C composites with only 0.88% weight loss after oxidation for 468 h at 1500 °C, which was markedly superior to 4.86% weight loss for coatings without SiC_w. Meanwhile, after 50 times thermal cycling, the weight loss of the SiC_w-HfB_2-SiC-Si/SiC coated samples was 4.48%, which showed an obvious decrease compared with that of the HfB_2-SiC-Si/SiC coated samples. The SiC_w-HfB_2-SiC-Si/SiC coatings exhibited excellent adhesion to the C/C substrate and had no penetrating cracks after oxidation. The improved performance of the SiC_w-HfB_2-SiC-Si/SiC coatings could be ascribed to the SiC_w, which effectively relieved CTE mismatch and remarkably suppressed the cracks through toughening mechanisms including whiskers pull-out and bridging strengthening. The above results were confirmed by thermal analysis based on the finite element method, which demonstrated that SiC_w could effectively alleviate thermal stress generated by temperature variation. Furthermore, the SiC_w-HfB_2-SiC-Si/SiC coating can provide a promising fail-safe mechanism during the high temperature oxidation by the formation of $HfSiO_4$ and SiO_2, which can deflect cracks and heal imperfections.

1. Introduction

Carbon materials are promising candidates for aeronautical and aerospace components. In particular, carbon fibre-reinforced carbon matrix composites (C/C) possess excellent high-temperature mechanical behavior and thermal physical properties, and are appropriate for high-temperature structural components [1,2]. Unfortunately, C/C composites will be oxidized rapidly and have some significant detrimental effects on their mechanical properties when exposed to high-temperature oxidative environments above 500 °C, and the poor oxidation resistance severely reduces their service life and restricts their applications. Therefore, oxidation-resistant coatings are used as an effective technical solution to prevent the oxidation of C/C composites and extend their service life as much as possible. In particular, ceramic coating systems are considered as a promising way to avoid C/C composites becoming oxidized [3].

Silicon carbide (SiC) is a common ceramic coating as it has outstanding chemical compatibility and oxidation resistance and is considered the most ideal bonding layer for C/C composites [4,5]. During high-temperature oxidization, SiC can form a continuous silicon oxide (SiO_2) glass with a self-healing function which will close some cracks. However, the gradual volatilization of SiO_2 above 1500 °C will weaken the SiC coating and its oxidation protection performance, thereby shortening its service life [6]. HfB_2 is an ultra-high temperature ceramic material (UHTC), and is considered as a potential candidate to improve the stability of the SiC layer by the formation of a new thermally stable phase $HfSiO_4$ [7–9]. $HfSiO_4$ is helpful to deflect/terminate cracks and to effectively improve the coating's oxidation resistance [10]. Monteverde et al. studied the oxidation resistance of HfB_2-SiC composites, which, as their research showed, was limited below 1300 °C, but markedly improved at temperatures higher than 1400 °C [11]. Ren et al. studied the isothermal oxidation performance of HfB_2-SiC/SiC coatings, and found that coated samples could withstand 265 h of oxidation at 1500 °C, with a weight loss of 0.41×10^{-2} g/cm^2 [10]. Wang et al. fabricated an HfB_2-SiC-$MoSi_2$/SiC coating through the pack cementation method, and obtained a mass loss of the coated samples of 0.76% after 408 h of oxidation at 1500 °C [6]. From the above results, HfB_2-SiC ceramic coatings have excellent high-temperature oxidation resistance for

* Corresponding author.
E-mail address: ryluo@buaa.edu.cn (R. Luo).

https://doi.org/10.1016/j.ceramint.2018.04.025
Received 7 March 2018; Received in revised form 1 April 2018; Accepted 4 April 2018

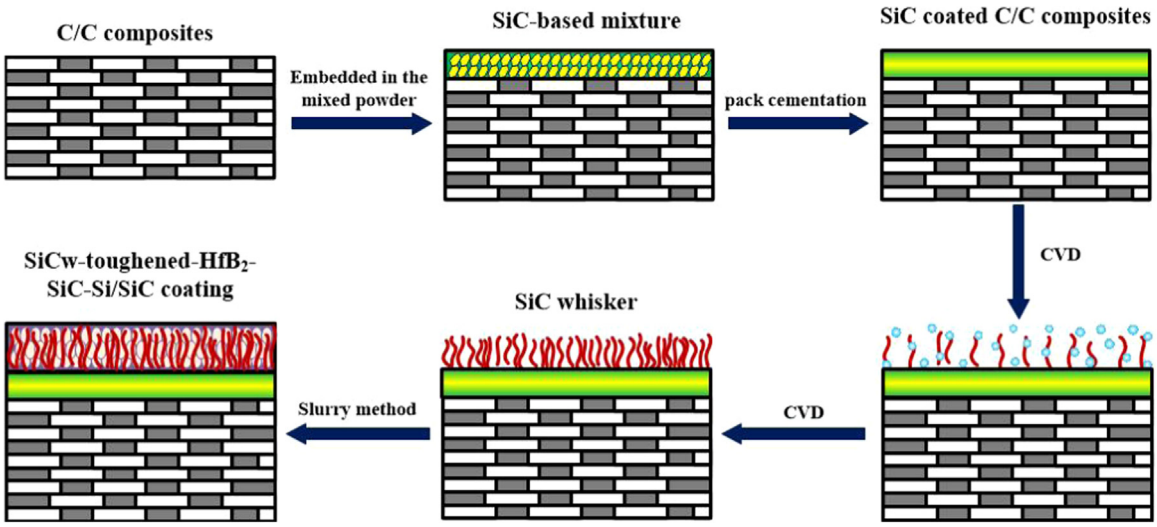

Fig. 1. Schematic of the preparation of SiC_w-toughened-HfB_2-SiC-Si/SiC coating.

carbon materials at high temperatures [12]. Nevertheless, due to the mismatch of the coefficient of thermal expansion (CTE) between the HfB_2-SiC coating and the substrate ($\alpha C/C = 1 \times 10^{-6}$/K, $\alpha SiC = 4.7 \times 10^{-6}$/K, $\alpha HfB_2 = 6.36 \times 10^{-6}$/K, $\alpha Si = 4.1 \times 10^{-6}$/K), a huge thermal stress will instantly be generated during isothermal oxidation and thermal cycling process. This will lead to peeling, cracking, or catastrophic failure of the coating. Consequently, oxygen invades the C/C substrate through cracks and causes the protective effect of the coating to fail [13,14].

To relieve thermal stress in high-temperature coatings, adding SiC_w is a feasible method to relieve the CTE mismatch of coatings, owing to the low elastic modulus and the good compatibility of SiC_w [15,16]. However, due to the uneven dispersion of SiC_w and its poor connectivity with the ceramic coating, the stress transfer capability of SiC_w is limited enormously. It has been found that preparing SiC_w by chemical vapor deposition (CVD) is a credible way to improve the uniform decentralization of reinforcements in the ceramic coating [17]. In view of the above, this study seeks to improve the coating toughness, thermal shock performance, and oxidation resistance via integrating SiC_w, SiC, Si, and HfB_2. To reduce crack sizes and improve the connectivity between SiC_w and the coating, the SiC_w in-situ- modified HfB_2-SiC-Si/SiC coating was fabricated by CVD and the slurry method. The SiC_w porous structure could provide a permeable inlet passage for the slurry, helping the SiC_w to homogeneously disperse in the outer layer of the coating, and enhance the bonding strength between SiC_w and coating. A self-healing coating that can work as a thermally stable system at high temperatures was therefore developed. Moreover, we precisely illustrate the effectiveness of SiC_w-HfB_2-SiC-Si/SiC at easing thermal stress and extending service life. A theoretical approach with finite-element analysis was adopted, in which we calculated and analyzed the temperature gradient and stress state of the double-layer coating. On this basis, isothermal oxidation and thermal shock experimental results were presented to confirm our theoretical inference and analysis.

In the current work, a SiC_w-toughened-HfB_2-SiC-Si/SiC coating was developed to improve the high-temperature oxidation resistance of the C/C composite. The inner SiC layer of the coating was prepared by the pack cementation method, and the SiC_w-toughened-HfB_2-SiC-Si outer layer employed CVD coupled with the slurry method. The temperature field and stress distribution of the coating during thermal shock were studied using finite-element analysis. Furthermore, the isothermal oxidation and thermal shock resistance of the fabricated coating were investigated. The oxidation mechanism and coating microstructure were also studied.

2. Experimental

2.1. Specimen preparation

The two-dimensional C/C composite specimens used as substrates with density 1.70 g/cm^3 were obtained using rapid directional diffused (RDD) chemical vapor infiltration technology [18]. The C/C composites were machined to small cubes with dimensions 10 mm × 10 mm × 10 mm. All samples were polished with 400 mesh silicon carbide sandpaper and ultrasonically cleaned with anhydrous alcohol before being dried at 120 °C for 2 h in an oven.

2.2. Preparation of coating

The SiC inner layer was prepared by the pack cementation method as follows: the raw materials were 80–85 wt% Si powder (325 mesh) and 15–20 wt% graphite (425 mesh). All powders were ground in a ball mill for 5 h to mix them evenly. The samples were embedded in the well-mixed powder and then heated at 1700 °C for 1 h before being heated at 1800 °C for 2 h. Both heating processes were carried out under an inert atmosphere. After cooling to room temperature, the pre-treated samples were cleaned with an ultrasonic cleaning instrument. This process was followed by the preparation of the SiC_w-HfB_2-SiC-Si outer layer by CVD combined with the slurry method. The SiC-coated C/C composites were subjected to CVD to deposit SiC_w on the inner layer to toughen the outer layer (HfB_2-SiC-Si). Trichloromethylsilane (CH_3SiCl_3, MTS) as a precursor was deposited on SiC-coated samples at 1100 °C for 4 h to obtain SiC_w, using H_2 as the carrier gas and the diluent gas. Ar was also used as a diluting gas. The deposition of SiC_w was carried out in a tube furnace with the flow rates of H_2 and Ar were 500 ml/min and 300 ml/min, respectively. And the gas ration of H_2 to MTS was kept at 24. The previously processed samples were then immersed into the HfB_2-SiC-Si slurry, which was composed of 70–80 wt% HfB_2 (425 mesh), 20–30 wt% Si (325 mesh), and polycarbosilane solution, after then dried at 120 °C for 2 h, and were heated at 1300 °C for 1 h under an Ar atmosphere subsequently. The preparation procedures for the coatings are illustrated in Fig. 1.

2.3. Oxidation tests

Isothermal oxidation tests were completed in static air at 1500 °C and the experimental equipment was a tube furnace. The samples were loaded directly into the tube furnace when the temperature reached 1500 °C. After a certain period of oxidation, the samples were removed