Journal of the European Ceramic Society xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of the European Ceramic Society

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

Original Article

Degradation mechanisms of a self-healing $SiC_{(f)}/BN_{(i)}/[SiC\text{-}B_4C]_{(m)}$ composite at high temperature under different oxidizing atmospheres

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ARTICLE INFO

Keywords:
$SiC_{(f)}/BN_{(i)}/[SiC\text{-}B_4C]_{(m)}$
Self-healing
Oxidation behavior
Degradation mechanism

ABSTRACT

Chemical vapor-infiltrated self-healing $SiC_{(f)}/BN_{(i)}/[SiC\text{-}B_4C]_{(m)}$ composite specimens were exposed at 1300 °C for 300 h at atmospheric pressure under two different oxidizing atmospheres (i.e., wet (12%H_2O:8%O_2:80%Ar) and dry (0.01%O_2:99.99%Ar)) representative of rich and poor oxidizing conditions, respectively. Mechanical testing, microstructural observations, and element analyses were performed on the treated specimens. The flexural strength retentions of the specimens were 47.9 and 39.4% under wet and dry oxygen conditions, respectively. The SiC and B_4C matrices were severely oxidized under wet oxygen conditions, whereas the BN interphase remained intact. The BN interphase and the B_4C layered phase were both partially oxidized under dry oxygen conditions. Thus, the $SiC_{(f)}/BN_{(i)}/[SiC\text{-}B_4C]_{(m)}$ composites exhibited improved oxidation resistance under wet oxygen atmospheres as compared to dry oxygen conditions as a result of the formation of borosilicate glasses. In addition, two different degradation mechanisms for the composites during the oxidation process were discussed.

1. Introduction

Silicon carbide (SiC) fiber-reinforced SiC matrix (SiC/SiC) composites have been extensively studied for a variety of long-term applications (e.g., aeronautical and space domains and nuclear reactors) owing to their low density, good high-temperature stability, excellent thermomechanical properties, and their resistance to corrosive atmospheres [1–4]. The utilization of SiC/SiC composite components in aeronautic and space fields can potentially lead to engines with lower NO_x and CO emissions [4] and improved efficiency [5]. However, the cracks produced in the matrix during the fabrication process (as a result of the different coefficients of thermal expansion (CTE) of the fiber and the matrix components and/or mechanical loadings) provide pathways for oxidant diffusion to the interphase and fibers [6–8]. In addition, SiC/SiC composites are likely to undergo severe corrosive interactions under combustion environments containing oxygen and water vapor at high temperatures, leading to the degradation of the mechanical performances of these materials [9–11].

An oxidation-resistant fiber coating or interphase is therefore required for ceramic matrix composites (CMCs) under combustion environments. This component plays a significant role in transferring loads and deflecting the matrix microcracks, leading to graceful failure and high ultimate tensile strength via fiber-pullout mechanisms [1,12]. Pyrocarbon (PyC) and boron nitride (BN) have been mostly used as interphase materials owing to their layered microstructures. Rebillat et al. comprehensively studied the degradation mechanisms and oxidation behaviors of $SiC_{(f)}/PyC_{(i)}/[SiBC]_{(m)}$ composites [6,10,11,13]. However, a PyC interphase is easily to be actively oxidized because carbon in any form will react with oxygen and burning away rapidly at temperatures as low as 500 °C [14]. Although BN also reacts with oxygen at 500 °C, its oxidation product is liquid boria (B_2O_3), which can decrease the oxidation rate of BN at intermediate temperatures. The primary oxidation reaction is generally written as follows [15]:

$$2BN(s) + 3/2O_2(g) = B_2O_3(l) + N_2(g) \quad (1)$$

Boron oxide, with an unusually low melting point of 450 °C [16,17], can volatilize by three reactions:

$$B_2O_3(s,l) = B_2O_3(g) \quad (2)$$

$$B_2O_3(s,l) + 1/2O_2(g) = 2BO_2(g) \quad (3)$$

$$B_2O_3(s,l) + H_2O(g) = 2HBO_2(g) \quad (4)$$

While reaction (2) occurs rapidly at temperatures above 1000 °C [6], reaction (3) prevails in environments containing sufficient oxygen

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https://doi.org/10.1016/j.jeurceramsoc.2018.05.001
Received 11 January 2018; Received in revised form 3 May 2018; Accepted 3 May 2018

and reaction (4) takes place in the presence of water vapor even at concentrations as low as ppm [15]. These active reactions result in weight loss and degradation of the oxidation resistance of boron-containing materials.

The oxidation behavior of SiC has been studied extensively [18–22]. The degradation mechanism of SiC under combustion environments has been identified. Thus, oxygen and water vapor present in the ambient environment oxidize SiC to silica (SiO_2), which is simultaneously volatilized by water vapor via $Si(OH)_4$, leading to undesired surface recession [23,24]. These reactions can be written as follows:

$$SiC + 3/2O_2(g) = SiO_2 + CO(g) \quad (5)$$

$$SiC + 3H_2O(g) = SiO_2 + 3H_2(g) + CO(g) \quad (6)$$

$$SiO_2 + 2H_2O(g) = Si(OH)_4(g) \quad (7)$$

Opila et al. have conducted a large number of investigations on the oxidation behaviors of $SiC_{(f)}/BN_{(i)}/SiC_{(m)}$ composites [25,26]. The formation of a protective silica layer in sufficient amounts and with enough flowability to seal matrix cracks via oxidation of the SiC matrix only takes place at temperatures higher than 1000 °C, which favors comsumption of the BN interface [27]. Thus, it is necessary to introduce in the matrix boron-containing ceramic materials such as B_4C, which can form protective oxides at lower temperatures [28]. In addition, the oxidation product of these boron-containing materials (B_2O_3) enhances the oxidation of SiC to form borosilicate glasses with better crack-sealing properties [28,29]. Thus, several studies have reported SiC-based CMCs containing B_4C or SiBC multilayer matrices or coatings [6,13,30–34]. Under dry air, B_4C undergoes the following oxidation reaction:

$$B_4C + 4O_2(g) = 2B_2O_3 + CO_2(g) \quad (8)$$

As a result, CMCs having a self-healing matrix are expected to have high oxidation resistance at elevated temperatures. Thus, a $SiC_{(f)}/BN_{(i)}/SiC_{(m)}$ composite with several B_4C layers in the matrix ($SiC_{(f)}/BN_{(i)}/[SiC\text{-}B_4C]_{(m)}$) was used in this work.

In addition, the concentration of oxidant in the oxidizing environment is crucial to the passive-to-active transition during the oxidation of SiC [35]. Thus, two oxidizing atmospheres (i.e., wet oxygen containing sufficient oxidant concentrations and dry oxygen with insufficient oxidant concentrations) were chosen to study the oxidation behaviors of $SiC_{(f)}/BN_{(i)}/[SiC\text{-}B_4C]_{(m)}$ composites. For the sake of comparison, the composites were heated at 1300 °C under pure helium (99.999% He) for 300 h to verify the in-situ stability of the SiC fiber in the composites. Moreover, although the role of the B_4C component of the SiC matrix in favoring matrix cracks healing has been widely studied, the detailed mechanisms responsible for the degradation of the composites via oxidation of B_4C under different oxidizing environments are not yet understood.

In this study, the oxidation behaviors of $SiC_{(f)}/BN_{(i)}/[SiC\text{-}B_4C]_{(m)}$ composites under wet and the dry oxygen conditions were compared. The fracture behaviors and microstructure evolution during the oxidation process were investigated. Moreover, two different degradation mechanisms of the composites under these oxidizing environments were discussed.

2. Experimental Procedure

2.1. Materials preparation

Two-dimensional (2D) SiC fiber preforms were laminated by a 10-harness plain weave [0°/90°] cloth prepared by SiC fiber tows (Xiamen Torch Group Co., Ltd., China). Properties of this kind of SiC fiber are shown in Table 1. A BN interphase with a thickness of 500 nm was deposited on the fibers via a chemical vapor infiltration (CVI) method, then SiC and B_4C were subsequently deposited layer by layer by CVI as a matrix. BCl_3 + NH_3, methyltrichlorosilane (MTS, $CH_3\text{-}SiCl_3$), and BCl_3 + CH_4 were employed for the deposition of BN, SiC and B_4C, respectively. The composite panels were subsequently machined into samples with dimensions of 40 mm × 5 mm × 3 mm. Then, the slurry-infiltrated SiC layer and the chemical vapor-deposited SiC coating were prepared to protect the fibers exposed after machining. Finally, self-healing $SiC_{(f)}/BN_{(i)}/[SiC\text{-}B_4C]_{(m)}$ composites with a density of 2.64 g/cm^3 and an open porosity of 7 vol% were obtained.

2.2. Oxidation tests and heat treatment

All oxidation tests and heat treatments were conducted in an alumina tube furnace for 300 h at 1300 °C at atmospheric pressure under flowing gas (7.0 cm/s). The furnace was heated up to the selected temperature at 5 °C/min under the selected atmosphere. Three samples were subsequently placed on a rectangular alumina crucible and pushed into the furnace slowly at elevated temperature. The samples were slowly taken out from the furnace and subsequently weighed on an analytic balance (sensitivity: 0.1 mg, Mettler Toledo, AG 204, Switzerland) at varying times (10, 20, 30, 40, 50, 100, 150, 200, 250, and 300 h). After weighing, the flexural moduli (E_b) of each sample were measured by the three-point bending method under a maximum load of 70 N using an electric loading frame (SANS CMT 4304, Sans Materials Testing Co., Ltd., Shenzhen, China). The loading rate was fixed to 0.5 mm/min, while the outer span was 30 mm. Since the loading force was very low, the measured E_b actually reflected the flexural modulus of the ceramic matrices of the composites at the elastic deformation stage. The values were calculated by the equation:

$$E_b = \frac{L^3}{4bh^3}\cdot\left(\frac{\Delta F}{\Delta f}\right) \quad (9)$$

where L, b, and h are the span of the three-point bending test (herein L = 30 mm), the width, and thickness of the sample, respectively. $\Delta F/\Delta f$ was obtained from the slope of the linear part of the load–displacement curve.

After 300 h, the flexural strength of each specimen was tested at room temperature by the three-point bending method using an electric loading frame (SANS CMT 4304, Sans Materials Testing Co., Ltd., Shenzhen, China). The loading rate was fixed 0.5 mm/min, while the outer span was 30 mm.

2.3. Characterization

The fractured surfaces and polished cross sections of the samples were observed by a scanning electron microscopy (SEM, S-4700, Hitachi, Japan) device provided with a scanning electron image (SEI) and back-scattered electron image (BSI) units. Electron probe micro-analysis (EPMA-1720, Shimadzu, Japan) was employed to identify the element species.

3. Results and discussion

3.1. Microstructure

The microstructures of the as-fabricated $SiC_{(f)}/BN_{(i)}/[SiC\text{-}B_4C]_{(m)}$ composites are shown in Fig. 1. As can be seen in Fig. 1c, the SiC fibers were first covered by a 500 nm BN layer as the interphase, and a 4-layer SiC matrix with a thickness of ca. 4 μm was deposited on it. Consequently, a 500 nm layer of B_4C (i.e., inner B_4C layer) was formed by CVI. As shown in Fig. 1b, four additional layers of CVI SiC were prepared after the inner B_4C layer, followed by another 500 nm layer of B_4C (i.e., outer B_4C layer). Finally, a porous slurry infiltrated SiC layer and a dense chemical vapor deposition (CVD) SiC coating enwrapped the specimen to protect the naked fibers formed during the sample processing from the corrosive environment. Owing to the bottle-neck