

Oxidation behavior of silicon carbide based biomorphic ceramics prepared by chemical vapor infiltration and reaction technique

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Abstract

The oxidation behavior of biomorphic SiC based ceramics with different microstructure and composition was studied at 1450 °C in airflow for 50 h by thermal gravimetric analysis (TGA). SiC with amorphous, coarse grain, crystalline and fine grain crystalline microstructures as well as SiC–Si₃N₄ composite ceramics were processed from paper preforms by chemical vapor infiltration and reaction technique. The ceramics were characterized by X-ray diffraction and scanning electron microscopy coupled with energy dispersive spectroscopy (SEM/EDX) before and after oxidation. The results show that the crystalline SiC with fine grain structure and SiC–Si₃N₄ composite ceramics show very good oxidation resistance at a temperature of 1450 °C.

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1. Introduction

Preparation of biomorphic porous materials from natural products having various compositions and tailored microstructures such as porosity, pore size distribution and morphology have attracted a great deal of attention in the last decades due to the increased number of applications [1]. Silicon based covalent ceramics including SiC and Si₃N₄ are widely studied because of their potential as high temperature structural materials in the development of advanced heat engines, heat exchanger structural components due to their high temperature strength, low coefficient of thermal expansion and high thermal conductivity. Moreover, SiC and SiC–Si₃N₄ possess the highest oxidation resistance among the non-oxide structural ceramics [2]. These materials oxidize to form an adherent SiO₂ protective film on the surface, which shows the lowest permeability to oxygen of all the common oxides [3]. Interesting results concerning oxidation resistance have been obtained with carbon/carbon composites, on which layers of TiC and SiC were deposited. As a result, the number of cracks decreased and oxidation resistance was improved depending on

the thickness ratio of TiC to SiC layer as compared with SiC monolayer [4].

Recently, we have published several articles describing the processing of biomorphic ceramics such as SiC, Si₃N₄ and SiC–Si₃N₄ by chemical vapor infiltration and reaction technique (CVI-R) using paper preforms as template [5–7]. SiC with different microstructure like amorphous and crystalline in addition to SiC–Si₃N₄ composites with different composition were obtained. Although biomorphic porous ceramics have much attention there are almost no reports dealing with their oxidation resistance performances up to now. There are several reports in the literature about the oxidation behavior of SiC and Si₃N₄ coatings deposited by plasma spraying, physical vapor deposition, and chemical vapor deposition [8] as well as by tape casting and sintering method [9], which were used as a protective layer on C/C composites [10] and graphite [11]. However, the difficulty in developing effective SiC oxidation protective layers comes from the mismatch of the coefficient of thermal expansion (CTE) between SiC and SiO₂, which leads to crack formation and even debonding under severe oxidation conditions. Some authors tried to solve this problem applying functionally graded coatings [12] or multi-layer coatings [13]. Our approach, studied in this work was to introduce a second phase such as Si₃N₄ in addition to SiC to form SiC–Si₃N₄ composites in order to improve the oxidation resistance minimizing the thermal mismatch with SiO₂

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layer formed after oxidation. The advantage of Si_3N_4 phase is its very low CTE compared to SiC resulting in a good thermal shock resistance [14].

The present work presents the experimental results on investigation of the oxidation behavior of SiC based biomorphic ceramics at temperature as high as 1450°C depending on their microstructure and chemical composition.

2. Experimental work

Biomorphic SiC based ceramics were produced by chemical vapor infiltration and reaction technique (CVI-R) using carbonized paper preform as template as well as carbon source for SiC formation in some cases. Paper consisting mainly of cellulose fibers was converted first into carbon biotemplate (C_b) by pyrolysis in inert atmosphere at 800°C [5], followed by chemical vapor infiltration step with an appropriate precursor system such as MTS/ H_2 or SiCl_4/H_2 depositing a ceramic or preceramic layer onto carbon fibers. In some cases high temperature treatment was performed as an additional step after CVI, where solid–solid and/or solid–gas chemical reactions took place. The microstructure and the composition of the resulting biomorphic ceramics could be controlled in a wide range varying the precursor system and the conditions during the CVI-R process.

2.1. Investigated materials

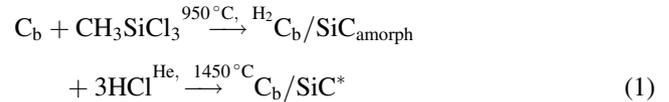
2.1.1. Biomorphic SiC ceramics

Biomorphic SiC with different microstructure such as amorphous and crystalline were produced in order to investigate the effect of the phase structure on its oxidation behavior. Methyltrichlorosilane (MTS)/hydrogen mixture was used as a precursor for the CVI to coat the carbon fibers of the template with SiC. Amorphous SiC was produced at infiltration temperature of 950°C by CVI-I route (Fig. 1) according to Eq. (1). A subsequent thermal treatment in He atmosphere at 1450°C for 1 h leads to crystallization with the formation of crystalline SiC^* with coarse grain structure as indicated by SEM analysis.

The infiltration of the carbon template with MTS/ H_2 at higher temperature of 1050°C according to CVI-II route (Fig. 1) results in deposition of crystalline SiC^{**} with fine grain structure. All CVI experiments to produce biomorphic SiC were performed for 1 h at molar fraction of MTS of 0.08 and α

(H_2/MTS) = 3. The residual carbon originated from the template was burned out by oxidation at 750°C for 5 h in airflow. Fig. 1 presents the flow chart of processing of biomorphic SiC ceramics with different phase structures.

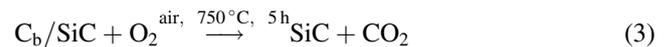
CVI-I



CVI-II



Removal of residual C_b by burning out in airflow

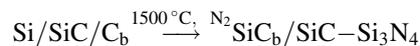


2.1.2. Biomorphic SiC– Si_3N_4 composite ceramics

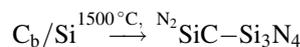
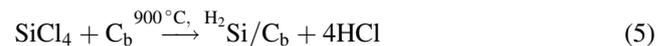
Two different CVI routes with different precursors were used to produce SiC– Si_3N_4 composites with different SiC/ Si_3N_4 ratio (Fig. 2).

CVI-III route uses MTS in excess of hydrogen ($\alpha = \text{H}_2/\text{MTS} = 11$) at temperature as low as 900°C to deposit Si rich SiC layer ($\text{Si}/\text{SiC}/\text{C}_b$) onto the carbon fibers according to Eq. (4) [6]. On the other hand, via CVI-IV route silicon coated carbon template (Si/C_b) was obtained using SiCl_4 in excess of hydrogen ($\alpha = \text{H}_2/\text{SiCl}_4 = 17$) at 900°C with SiCl_4 molar fraction of 0.065 (Eq. (5)). Then, in a second step by submitting the coated $\text{Si}/\text{SiC}/\text{C}_b$ and Si/C_b templates to N_2 atmosphere at 1500°C for 5 h, composite ceramics with different molar ratio of SiC– Si_3N_4 (9:1) and SiC– Si_3N_4 (4:1), respectively were obtained as a result of solid–solid (C_b –Si) and solid–gas (Si– N_2) reactions. High temperature above the melting point of silicon (1410°C) and long reaction time is required because of the low diffusion coefficient of the compounds in the solid phase. The residual carbon was also burned out by oxidation at 750°C in airflow (Eq. (3)).

CVI-III



CVI-IV



2.2. Experimental setup

2.2.1. Determination of the composition of the SiC– Si_3N_4 composite ceramics

The composition of SiC– Si_3N_4 ceramics was determined from the mass balance after each processing step (Fig. 2). The amount of the carbon template reacting with silicon to SiC was

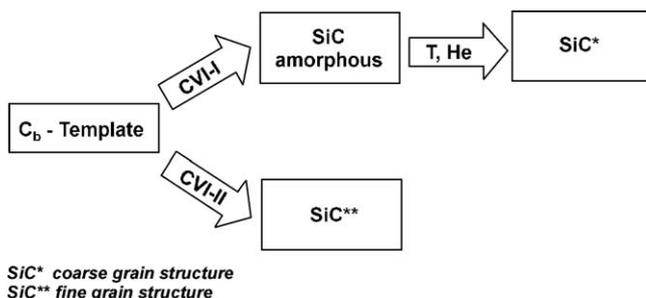


Fig. 1. Flow chart of processing of biomorphic SiC ceramics with different microstructure.

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