Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 39 (2013) 6769–6776

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Mechanical and thermophysical properties of carbon/carbon composites with hafnium carbide

Cuiyan Li, Kezhi Li*, Hejun Li, Haibo Ouyang, Yulei Zhang, Lingjun Guo

The State Key Laboratory of Solidification Processing, Northwestern Polytechnical University, 127# Youyi Road, Xi'an 710072, Shaanxi, PR China

Received 18 December 2012; received in revised form 3 January 2013; accepted 3 February 2013
Available online 11 February 2013

Abstract

Carbon/carbon (C/C) composites with addition of hafnium carbide (HfC) were prepared by immersing the carbon felt in a hafnium oxychloride aqueous solution, followed by densification and graphitization. Mechanical properties, coefficients of thermal expansion (CTE), and thermal conductivity of the composites were investigated. Results show that mechanical properties of the composites decrease dramatically when the HfC content is greater than 6.5 wt%. CTE of the composites increases with the increase of HfC contents. The composites with addition of 6.5 wt% HfC show the highest thermal conductivity. The high thermal conductivity results from the thermal motion of CO in the gaps and pores, which can improve phonon–defect interaction of the C/C composites. Thermal conductivities of the composites decrease when the HfC content is greater than 6.5 wt%, which is due to formation of a large number of cracks in the composites. Cracks increase the phonon scattering and hence restrain heat transport, which results in the decrease of thermal conductivity of the composites.

Keywords: B. C/C composites; C. Mechanical properties; D. Carbides; Thermophysical properties

1. Introduction

Carbon/carbon (C/C) composites are one of the most promising high temperature structure materials due to their excellent high temperature strength, high thermal conductivity, low coefficient of thermal expansion (CTE), and good ablation resistance [1,2]. However, the poor oxidation resistance of carbon limits its high temperature applications. To improve the ablation resistance of C/C composites in the severe ablative environment, introducing refractory metal carbides into the composites has been employed. Researches on the C/C composites with addition of refractory carbide (such as zirconium carbide, tantalum carbide, and hafnium carbide) have been reported [3–6], which focus on the effect of carbides content, distribution and particle dimension on the ablation resistance of the C/C composites.

Ablation is an erosive phenomenon with removal of material by a combination of thermomechanical, thermochemical, and thermophysical mechanisms in a severe high temperature environment [7]. Recently, researches focus on thermophysical properties of ultra-high temperature ceramics (such as ZrC, HfC, ZrB_2–ZrC–SiC, and ZrB_2–ZrC–SiC–Si_3N_4) and refractory metal with addition of carbide (such as ZrC–Mo, and ZrC–W) in the ablation application [8–12]. It is found that thermophysical properties play an important role in the oxidation and ablation of ultra-high temperature ceramics. The materials with low CTE and high thermal conductivity tend to have impressive thermal shock resistance, as the thermal gradients are minimized by increasing heat conduction of heated zone and increasing the thermal stresses in the materials. However, few researches focus on thermophysical properties of the C/C composites with addition of carbides.

In this paper, the C/C composites with addition of HfC were prepared by immersing the carbon felt in a hafnium compound aqueous solution, followed by densification and graphitization. Thermophysical and mechanical properties of the composites were studied. The heat conduction mechanism of the composites was investigated.

*Corresponding author. Tel./fax: +86 29 88495764.
E-mail address: likezhi@nwpu.edu.cn (K. Li).

0272-8842/$ - see front matter © 2013 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2013.02.006

2. Experimental

2.1. Preparation of the composites

Integral needle punching carbon fiber felts with a density of 0.20 g/cm^3 were used as the preforms for fabrication of the composites. The felts were formed by alternatively stacking the carbon fabric, short cut fiber web as 0°/90°/0°/90° (X–Y direction) pierced with carbon fiber bundles in the Z direction. Hafnium oxychloride octahydrate ($HfOCl_2 \cdot 8H_2O$, analytical grade, made by Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) was used as HfC precursor.

The C/C composites with addition of HfC were prepared by the following process. Firstly, carbon fiber felts were impregnated in a hafnium oxychloride ($HfOCl_2$) aqueous solution with the assistance of ultrasonic. The content of HfC was controlled by the impregnation time and cycles. The impregnated felts were dried at 150 °C and treated at 600 °C in a nitrogen atmosphere to convert the $HfOCl_2$ into HfO_2. Secondly, the carbon fiber preform was put into a thermal gradient chemical vapor infiltration (TCVI) furnace. Pyrolytic carbon was deposited in the carbon fiber preform. Methane was used as carbon source in densification. Finally, the composites were graphitized at 2500 °C for 2 h in an argon atmosphere. Pure C/C composites were prepared with the same TCVI and graphitization history.

2.2. Tests and characterization

The calculation of mass content of HfC in the C/C composites was based on

$$C_{HfC} = \frac{M_{HfC}(m_1 - m_0)}{M_{HfO_2}} \Big/ m \quad (1)$$

where C_{HfC} is the mass content of HfC in the composites, m_0 is the mass of carbon felt before impregnation, m_1 is the mass of carbon felt after impregnation and heat treatment, m is the final mass of the composites after graphitization, $(m_1 - m_0)$ refers to the mass of HfO_2 remaining in the carbon fiber felt. M_{HfC} is the molecular weight of HfC, and M_{HfO_2} is the molecular weight of HfO_2.

Compressive tests were performed on a universal testing machine using cylindrical specimen (Φ6 mm × 9 mm). The tests were carried out with a constant speed of 0.2 mm/min at room temperature. Three-point bending test was carried out on the electron universal testing machine (CSS-1110). Specimens dimension was 55 × 10 × 4 mm^3. The support span was 40 mm and the span-to-thickness ratio was 10:1. Specimens were tested with a speed of 0.5 mm/min. Flexural strength and flexural modulus was calculated by the following equations:

$$\sigma_f = \frac{3PL}{2bh^2} \quad (2)$$

$$E_f = \frac{\Delta P L^3}{4bh^3 \Delta f} \quad (3)$$

where L is the span of bend test, h is the thickness, and b is the width of specimen. $\Delta P/\Delta f$ is the slope of the straight line of the load–displacement curve.

CTE of the composites was measured by a thermomechanical analyzer (DIL402C) ranging from 30 to 1300 °C. The sample dimension was 3.5 × 3.5 × 20 mm^3. Thermal diffusivity and specific heat capacity of the composites were measured by a TC-3000 thermal properties analyzer. The sample dimension was Φ10 × 2.5 mm^2. Thermal conductivity of the composites was calculated by

$$\lambda = \alpha C_p \rho \quad (4)$$

where α is thermal diffusivity, C_p is specific heat capacity at constant pressure, and ρ is density of the composite.

A polarized light microscope (PLM, Leica DMLP) was used for the characterization of microstructure of the composites. The phase composition and morphology of the composites were investigated by X-ray diffraction (XRD, Cu-Kα, X'Pert HighScore) and scanning electron microscopy (SEM, JSM6460).

3. Results and discussion

3.1. Phase analysis

Fig. 1 shows XRD patterns of the composites. The composites are composed of carbon and HfC. It is indicated that the impregnated HfO_2 is converted into HfC after graphitization. With the increase of HfC content, the

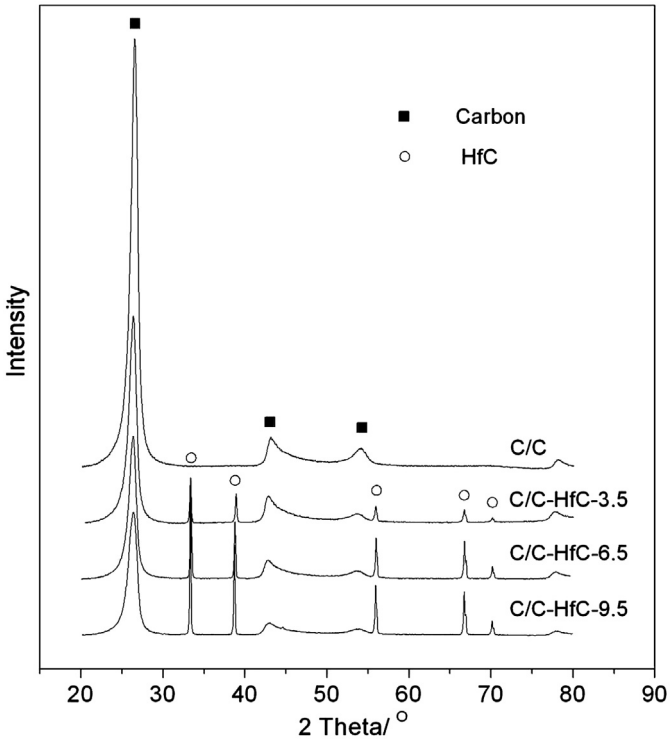

Fig. 1. XRD patterns of the C/C composites with addition of HfC.