Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 41 (2015) 7381–7386

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Fatigue behavior and oxidation resistance of carbon/ceramic composites reinforced with continuous carbon fibers

Teresa Gumula[a,b,*], Arkadiusz Rudawski[a], Jerzy Michalowski[c], Stanislaw Blazewicz[a]

[a]AGH-University of Science and Technology, Faculty of Materials Science and Ceramics, Al. Mickiewicza 30, 30-059 Krakow, Poland
[b]Centro Universitario de la Defensa, Academia General del Aire, Calle Coronel López Peña, s/n, Santiago de la Ribera, 30720 Murcia, Spain
[c]IFJ – Institute of Nuclear Physics, Polish Academy of Sciences, ul. Radzikowskiego 152, Krakow, Poland

Received 26 January 2015; received in revised form 6 February 2015; accepted 9 February 2015
Available online 16 February 2015

Abstract

The aim of this work was to compare fatigue behavior and oxidation resistance of pitch-derived CC (carbon) composite with CC/ceramic (carbon/ceramic) composites obtained by impregnation of CC composite with polysiloxane-based preceram and their subsequent heat treatment. Two types of CC/ceramic composites were studied; CC/SiCO composite obtained at 1000 °C, and CC/SiC composite obtained at 1700 °C. Both types of composites show much better fatigue mechanical performance in comparison to pure CC composite. CC/SiCO composite had 3 times better fatigue properties, and CC/SiC composite 4.5 times better fatigue properties than the reference CC composite. After a fatigue test composites partially retain their mechanical properties, and normalized residual modulus in the direction perpendicular to laminates exceeds 50% for CC and CC/SiCO composites. In the other directions normalized residual modulus is higher than 80% for all composites. Oxidative tests led at 600 °C in air atmosphere indicated oxidation resistance of CC/SiC composites.

Keywords: B. Composites; C. Fatigue; E. Structural applications; Carbon/ceramic composites

1. Introduction

The development of advanced structures requires new low cost materials, which could work under dynamic load at elevated temperature in air.

Silicon carbide matrix composites reinforced with carbon fibers (C_f/SiC composites) represent an advantageous combination of thermal and mechanical properties and are lightweight and chemically resistant as compared to metals and metal alloys [1]. In addition, C_f/SiC composites exhibit oxidation resistance. Nevertheless, industrial application of C_f/SiC composites is still limited by mechanical and physical property retention of the fibers and matrix at elevated temperature, processing problems related to reproducibility of the materials properties and high manufacturing costs [1].

Carbon fibers-reinforced carbon composites (CC composites) are candidates for high temperature applications [2,3]. They retain their high strength and stiffness at high temperatures (even at 2000 °C), and due to low values of coefficient of thermal expansion (CTE) and high sublimation heat they exhibit a good ablation resistance. Their other advantages include thermal shock resistance and chemical resistance in non-oxidizing atmosphere. However, the main disadvantage of carbon-based materials is their low oxidation resistance [2,3]. For this reason, chemical vapor deposition (CVD) coatings or multilayer coatings have been progressively applied in order to protect CC composites against the environment. Nevertheless, brittleness, lack of thermomechanical compatibility of coating on the CC sample and its weak adhesion to the composite surface cause its cracking and spallation, resulting in decreasing the composite lifetime, especially when the composite is subjected to a dynamic fatigue load [2–5]. Moreover, dynamic load of carbon/carbon composites with SiC layers at elevated temperature in an oxidative atmosphere results in their

*Corresponding author. Tel.: +48 12 617 52 06.
E-mail address: tgumula@agh.edu.pl (T. Gumula).

http://dx.doi.org/10.1016/j.ceramint.2015.02.046
0272-8842/

superficial oxidation, whereas in the inferior regions, which are not oxidized, debonding of fiber from the matrix occurs [4]. After fatigue-stressed oxidation test, more cracks on the coating appears, thus the oxidizing gaseous species diffuse faster into the CC substrate [5].

Therefore, the aim of the work is to compare fatigue mechanical behavior of pitch-derived CC composites with CC/ceramic composites obtained by impregnation of CC composite with commercially available polysiloxane-based solutions of preceram and their subsequent heat treatment. Those polymers are valuable precursors of ceramic materials, as their controlled thermal conversion may lead to a formation of various ceramic phases [6,7]. Pyrolysis of crosslinked organic polymers from 400 to 1000 °C in an inert atmosphere leads to formation of silicon oxycarbide glass-like material (containing various ratios of Si:C:O), while at higher temperatures SiC is formed [6,7]. Our previous study indicates that depending on the structure of polysiloxane resins there is possible to obtain ceramics with a high ceramic yield, i.e., from 82 to 86 wt % at 1000 °C and 61 to 70 wt% at 1700 °C [7]. The main advantage of our approach is to avoid problems occurring in case of the use of ceramic coatings [2,3]. Due to impregnation with polysiloxane-based precerams the ceramic phase is formed in composite pores and on its surface. Moreover, both pitch and polysiloxane substrates used for the manufacture of CC/ceramic composite are inexpensive.

2. Materials and methods

As a fiber reinforcement M40J carbon fibers (Torayca) in a form of roving were used. Tensile strength of the fibers is 4.41 GPa and Young's modulus 377 GPa. To prepare the unidirectional fiber prepreg tapes the M40J carbon fiber roving was impregnated with isotropic pitch with a predetermined quantity of pitch. The pitch was obtained from the Institute for Chemical Processing of Coal, Zabrze, Poland (Table 1). The tapes were cut to obtain 7 cm long laminates and unidirectionally stacking laminates were placed in a metallic mold. The stacked layup was heated up to 400 °C in air atmosphere under a pressure of 10 MPa. Then, the composite samples were heated to 1000 °C in an argon atmosphere to obtain CC composite. In order to manufacture CC/ceramic composites, CC composite was impregnated with Lukosil 901 polysiloxane resin produced by Lucebni zavody, Kolin (Czech Republic). The base characteristic of the resin can be found in our previous publication [7]. The impregnated samples were first cured at 160 °C and then subjected to heat treatment in an argon atmosphere up to two levels of final temperature, namely to 1000 °C in order to obtain (CC/SiCO) carbon/silicon oxycarbide composite, and to 1700 °C in order to obtain (CC/SiC) carbon/silicon carbide composite. Fiber volume fractions in composite matrices were determined from micrographs of polished section of the composite samples. Open porosity of composite samples was determined by the standardized method of a mercury porosimeter PoreMaster 60 of the Quantachrome Instruments Company. The characteristics of the obtained composites are collected in Table 2.

Static mechanical properties of CC and CC/ceramic composite samples in the form of bars (2 mm × 4 mm × 70 mm) were determined in 3-point bending mode using an universal testing machine Zwick (model 1435) PC controlled by TestXpert (v.8.1) software, with the deflection rate of 2 [mm/min]. Tests were performed using a span-to-thickness ratio of 20. Interlaminar shear strengths (ILSS) were determined in 3-points bending test using a constant span-to-thickness ratio of 5, according to the ISO 14130 standard. For each type of the composite samples 5 individual measurements were made. The results are presented as mean ± SD.

On the basis of results obtained in static loading conditions, parameters of dynamic test were set up. Deflection in fatigue three point bending test was 50% of elastic deflection measured in the static three point bending test. Composite samples were placed in testing machine and subjected to dynamic bending load with the frequency of 11.7 Hz. After every 10,000 cycles, ultrasonic wave velocity in three directions of a sample was measured (Fig. 1). The ultrasonic measurements were conducted until wave velocity changes were not observed, i.e., during dynamic bending test a permanent sample deformation (sample fracture) corresponding to its deflection was reached. Three samples for each type of composite were evaluated in this experiment. When the constant velocity of ultrasonic wave was achieved, normalized residual Young's modulus was calculated from the following:

$$E_R = \left[1-(E_F/E_I)\right] \times 100[\%] \quad (1)$$

E_R—normalized residual modulus
E_F—modulus calculated according to ASTM C747, when the constant ultrasonic velocity in fatigue test was reached
E_I—modulus calculated according to ASTM C747, before fatigue test

Oxidation resistance of the samples was determined by mass losses of composites heated in an air atmosphere at 600 °C, for 2 h. Carbon–carbon composites without impregnation were used as a reference.

Table 1
Properties of isotropic pitch.

Name	Metter softening point [°C]	Coking number [%]	Fraction insoluble in toluene [%]	Fraction insoluble in chinoline [%]	Ashes [%]
Isotropic carbon pitch	131.6	52.6	43.5	16.5	0.19

Table 2
Characteristics of composites.

Sample	Fiber volume fraction	Apparent density [g/cm^3]	Porosity [%]
CC (reference)	0.67 ± 0.02	1.33 ± 0.01	21 ± 1
CC/SiCO	0.68 ± 0.02	1.52 ± 0.01	11 ± 1
CC/SiC	0.68 ± 0.02	1.52 ± 0.01	20 ± 1