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Journal of the European Ceramic Society 35 (2015) 2555–2562

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Effect of boron doping on the thermal properties of carbon fibers reinforced lithium aluminosilicate matrix composites

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Received 28 November 2014; received in revised form 7 March 2015; accepted 9 March 2015
Available online 26 March 2015

Abstract

Boron doped carbon fibers reinforced lithium aluminosilicate matrix composites (Cf/LAS) were prepared via slurry infiltration following by hot pressing procedure, and characterized by TG-DTA, XRD analysis and TEM. Their thermal expansion behavior and thermal conductivity properties were investigated across various temperatures. Dense composites samples (>99%) were sintered at 1350 °C for 0.5 h. The XRD data revealed an occurrence of single-phase β-spodumene in boron doped Cf/LAS composites. Boron doping increased the thermal stability of Cf/LAS composites in oxidizing condition, where the weight loss of Cf/LAS composites decreased with increasing boron content. Boron doped Cf/LAS composites exhibited nearly zero thermal expansion at the temperature range from room temperature to 720 °C. The thermal conductivity of boron doped Cf/LAS composites was also higher than that of boron free Cf/LAS composites. These properties were correlated with the interfacial microstructure between the fiber and the matrix as determined by TEM results.

Keywords: Carbon fibers; Ceramic-matrix composites (CMCs); Thermal properties; Electron microscopy

1. Introduction

Materials with very low thermal expansion coefficient (CTE) have been investigated extensively due to their widely application in very different fields, from the microelectronic industry to precision optics, especially in the applications requiring dimensional stability and size precision, where the materials with low CTE are required urgently [1–5].

Lithium aluminosilicate glass ceramics is an important kind of materials in the low CTE material family. The dominant crystalline phases in the Li_2O–Al_2O_3–SiO_2 (LAS) system are β-eucryptite (Li_2O–Al_2O_3–$2SiO_2$) and β-spodumene (Li_2O–Al_2O_3–$4SiO_2$). The β-eucryptite phase has the hexagonal quartz structure in which half of the Si^{4+} ions are replaced by Al^{3+} ions. The charge is balanced by the incorporation of Li^+ ions in the (Si, Al)O_4 framework [6].

LAS materials with eucryptite or spodumene as main phase often exhibit low fracture strength due to the strong anisotropy between the different crystallographic orientations, where it is common to find the negative behavior in one direction and positive in the others [7–9]. This anisotropy results in microcracks which lower the mechanical performance of these materials.

Numerous attempts have been made to improve the toughness of these materials by incorporating fibers or whiskers [10–14]. Carbon fiber reinforced glass matrix composites have demonstrated a wide range of attributes including high strength, high stiffness, low density, unique wear resistance, and environmental stability for structural application [15–18]. The oxidation of the carbon fiber in Cf/LAS composites may happen at as low as 500 °C when placed in oxidizing environments. The pores and

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http://dx.doi.org/10.1016/j.jeurceramsoc.2015.03.010
0955-2219/

Table 1
Typical properties of carbon fiber.

Diameter (μm)	Density (g/cm^3)	Young modulus (GPa)	Tensile strength (MPa)	Thermal conductivity (W/m K)		CTE (10^{-6} K^{-1})	
				Axial	Transverse	Axial	Transverse
6–8	1.76	200–220	2930	320	5	−1.0	12

cracks in the composites originating from fabrication process and thermal mismatch between carbon fiber and LAS matrix, provide fast access for oxygen.

Introduction of boron-containing phases can effectively weaken the oxidation reaction of carbon fiber, due to the formation of boric oxides. Boric oxides have low viscosity at temperature above 500 °C, which can fill pores and cracks in the composites, rendering the whole composites "self-healing" [19]. The concept of self-healing is mainly achieved by introduction of boron species at relatively low temperature. Efforts to assess the boron addition in carbon fiber reinforced ceramics composites have been focused mainly on the room and high temperature mechanical properties. However, there has been comparatively little research on thermal properties of carbon fiber reinforced glass–ceramics matrix composites, which are the crucial aspects for their application.

In this work, the lithium aluminosilicate matrix is fabricated using sol-gel method. The Cf/LAS composites are processed using slurry infiltration techniques, followed by uniaxial hot pressing, where the slurry was fabricated by mixing LAS gel and boric acid powder. The effect of H_3BO_3 on thermal conductivity and thermal expansion properties is discussed thoroughly.

2. Experimental

2.1. Fabrication of Cf/LAS composites

The PAN-based carbon fibers used in this study (Guangwei Industries, Inc. China) have a diameter of 6–8 μm, and its properties provided by manufacturer are summarized in Table 1. LAS sol in the form of β-spodumene (Li_2O–Al_2O_3–$4SiO_2$) was synthesized using a sol–gel method by starting with mixing boehmite sol, silica sol and lithium salt, using deionized water as media [20,21]. The slurry was prepared by mixing H_3BO_3 (less than 0.05 mm) powder with the LAS sol through ball milling method. Ball milling was carried out for 2 h in a sealed agate mortar containing half the volume of agate balls. The concentrations of H_3BO_3 loading in LAS gel solids range from 0 to 4 wt%. The corresponding samples are denoted as Cf/LAS-0B, Cf/LAS-1B, Cf/LAS-2B, Cf/LAS-3B, Cf/LAS-4B.

Carbon fiber tows were carefully guided through a slurry tank containing the as-prepared slurry. The slurry impregnated carbon fiber tows were wound on to a hexagonal drum in an aligned arrangement. After the impregnation, the fiber sheets were dried and cut into the desired size. Unidirectional carbon fiber reinforced lithium aluminosilicate glass–ceramics matrix (Cf/LAS) composites were prepared by stacking the fiber sheets into a graphite mold and hot-pressing with 10 MPa at 1350 °C for 0.5 h under vacuum condition. The content of carbon fiber was approximate 35∼40 vol%.

2.2. Characterization of Cf/LAS composites

Bulk densities and open porosity of the samples were measured with deionized water as immersion medium according to the Archimedes principle. The oxidation behavior of boron free and boron doped Cf/LAS composites were characterized by differential thermal analysis (DTA) and thermogravimetry (TG) (Netzsch STA 409c) from 30 to 1000 °C in air atmosphere at the heating rate of 10 °C/min.

The microstructure observation and composition analysis were carried out in transmission electron microscope (TEM, JEM-2010, Jeol, Japan) and high resolution transmission electron microscopy (TEM and HRTEM, Philips Tecnai F30 FEG) equipped with electron energy loss spectroscopy (EELS). The phases in the samples were identified by X-ray diffractometer (XRD, D/max-γB, Rigaku, Japan).

For the determination of thermal expansion of the final sintered Cf/LAS composites, the bar specimens with the dimension of 3 mm × 3 mm × 8 mm were tested using Shimadzu dilatometry (TMA60, Kyoto, Japan) at a heating rate of 10 °C/min in ambient atmosphere.

The linear thermal strain was calculated by following formula:

$$\varepsilon = \frac{L - L_0}{L_0} \tag{1}$$

The CTE (α) is calculated by the following equation:

$$\alpha(T) = \frac{\varepsilon}{T - T_0} \tag{2}$$

where T_0 is the room temperature, T the tested temperature, l_0 the specimen length at room temperature, and l the specimen length at the tested temperature.

The thermal conductivity of the composite was evaluated using the thermal diffusivity, bulk density, and specific heat capacity. The thermal diffusivity of the composite was measured on disk-shaped samples 10 mm in diameter of 2.0 mm thick using a laser flash apparatus (LFA 427, Netzsch, Germany) at room temperature. The top and bottom surfaces of the samples were coated with carbon using a carbon spray to enhance absorption of the laser beam. In order to obtain reliable results, five measurements were conducted on each sample and the mean value of thermal diffusivity was used for further calculations throughout this paper. The specific heat of the Cf/LAS composite was calculated from the rule of mixtures. The specific heats of the carbon fiber and β-spodumene were assumed to be 0.711 and 0.831 J g^{-1} K^{-1}, respectively [22,23].