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Interface engineering of fiber-reinforced all-oxide composites fabricated by the sol–gel method with fugitive pyrolytic carbon coatings

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ABSTRACT

This paper describes the interface engineering of three–dimensional (3D) Nextel™440 fiber-reinforced aluminosilicate composites fabricated by the sol–gel method with fugitive pyrolytic carbon (PyC) coatings. The coating thickness on the fiber strength, interfacial characteristics and there corresponding effects on mechanical properties of the composites were investigated. The study shows that the fiber strength was influenced by the coating thickness and optimized with the thickness of 0.15 μm. The composites with uncoated fibers showed brittle fracture behavior without fiber pullout because of strong interactions between the fiber and the matrix. However, higher strengths and pseudo-ductile fracture behaviors were obtained in the composites with PyC interphases, where different deflections and branches of propagating cracks and fiber pullout patterns were observed. Moreover, induced fugitive PyC interface conditions have great effects on the density, microstructure and mechanical properties of the resultant composites.

1. Introduction

Advanced applications, such as aircraft turbine engine components, land-based turbines, hypersonic missiles and fighting vehicles, and most recently, spacecraft re-entry thermal protection systems, require structural materials that exhibit superior long-term mechanical properties under high temperatures, high pressures and various environmental factors, such as moisture [1]. Continuous fiber-reinforced ceramic matrix composites (CFRCMCs) are the most attractive material concept that can meet such needs. Oxide/oxide CMCs, in particular, provide high strength, toughness, notch insensitivity, refractoriness and environmental stability at high application temperatures, where metals are usually limited by their melting temperature and monolithic ceramics are limited by their low damage tolerance [2,3].

Conventional processing methods for oxide/oxide composites, such as reaction-sintering and hot-pressing, normally require high temperatures and high pressures to provide adequate consolidation of the ceramic body [4]. Fiber degradation and interface reactions, which contribute to brittle fractures, will inevitably occur under such conditions [5]. Several new fabrication processes, including slurry infiltration and hot-pressing (SI–HP) [6], electrophoretic deposition (EPD) [7], precursor infiltration and pyrolysis (PIP) [8] and the sol–gel method [9], have been introduced to address these issues. Among these techniques, the sol–gel method is the most feasible one for fabricating three-dimensional (3D) composites because of its low densification temperature (<1300 °C), low shrinkage, reduced drying stress and near-stoichiometric matrix composition. The sol–gel method is also a near-net-shape technique that can be used to prepare large products with complex shapes directly [10]. General properties and issues for advanced oxide/oxide composites are summarized in Table 1.

Interfaces between the fibers and the matrix in oxide/oxide composites are extremely important considerations for structural applications. An optimized interface can bring the deflection of cracks at the interface, fiber pullout during the fracture, excellent interfacial shear strength and ductility between the fiber and matrix, which contribute to high-energy consumption and excellent mechanical properties [11–13]. Among the interface concepts suggested recently [14–17], fugitive carbon is recognized as one of the most potential one. It can be readily deposited onto tows or woven fabrics by chemical vapor deposition (CVD) or pyrolysis of organic precursors, and be readily oxidized at moderately high temperature.

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Table 1
List of developmental oxide/oxide composites for structural materials and corresponding issues.

Category	SI–HP	EPD	PIP	Sol–gel
Fiber	Nextel™720	Nextel™720	Nextel™720	Nextel™480
Interphase	None	$NdPO_4$	None	BN
Matrix	Mullite + alumina	Mullite	Alumina	Mullite
Porosity (%)	~32	~20	~20	~10
General issues				
Interlaminar shear strength	Low	Low	Moderate-high	Moderate-high
Hermeticity	Poor	Poor	Good	Good
Near-net-shape technique	No	No	Yes	Yes

Weaver and Keller et al. [18,19] investigated the effects of fugitive carbon coating thickness on mechanical properties of one or two-dimensional oxide/oxide composites fabricated by SI–HP process. Results showed that fugitive carbon coatings can remarkably reduce the interfacial sliding resistance and enhance the damage tolerance of the composites, even after exposure at 1000 °C for 500 h. However, fugitive carbon coatings have rarely been used in 3D oxide/oxide composites. The present study focuses on the influence of fugitive pyrolytic carbon (PyC) coating thickness on the density, microstructure and mechanical properties of 3D Nextel™440 fiber-reinforced aluminosilicate (N440/AS) composites fabricated by the sol–gel method.

2. Material and methods

2.1. Raw materials

Nextel™440 fibers (3M, USA) were used as reinforcements. The fibers were composed of 70 wt% Al_2O_3, 28 wt% SiO_2 and 2 wt% B_2O_3. The tensile strength and Young's modulus announced by the manufacture were 2070 MPa and 186 GPa, respectively. Diphasic Al_2O_3–SiO_2 sols (Suzhou Nanodispersions Ltd., China) were used as precursors of the aluminosilicate matrix. The weight ratio of Al_2O_3 and SiO_2 particles in the sols was 1:1. The density and viscosity of the sols were 1.12 g/cm^3 and 6 mpa s, respectively.

2.2. Sample preparation

Mixtures of propylene and argon gas were used to deposit PyC on fiber fabrics with size of about 60 mm × 100 mm at 1000 °C by CVD. The coatings were deposited for 1, 4 and 8 h, with the resulting thickness of about 0.15, 0.42 and 1.00 μm. Then coated fabrics were stacked to a thickness of about 4 mm. Finally, the 3D architecture was finished by Z-stitching the stacked fabrics with Nextel™440 fiber yarn in a 2.5 mm × 2.5 mm space in Changzhou Bolong Aerospace Technology Ltd., China. The fiber volume fraction of the preform is approximately 40%.

3D N440/AS composites were prepared by the sol–gel method according to our previous work [20]. The composites were sintered at 1000 °C with a heating rate of 10 °C/min. Composites with PyC interphases were denoted according to their coating thickness as C0.15, C0.42 and C1.00. Samples were fired at 600 °C under air atmosphere for 2 h to oxidize PyC. Composites with fugitive PyC coatings were denoted as FC0.15, FC0.42 and FC1.00.

2.3. Characterization

The density and porosity of the samples were determined by the Archimedes principle, using distilled water as the immersion medium. The theoretical density was calculated from the ratio of the alumilosilicate matrix and the fiber volume fraction. The tensile strength of the PyC-coated fibers was tested at room temperature on a universal strength machine (Testometric, M3505CT) equipped with a 5 N load cell. The gauge length and crosshead speed were 20 mm and 0.2 mm/min, respectively. Three-point bending tests (test bars $50^l \times 4^w \times 3^t$ mm^3) were carried out at room temperature, with support span of 40 mm and cross-head speed of 0.5 mm/min in an INSTRON 1342 testing machine, using the number of five specimens. The flexural stress (σ) and elastic modulus (E) were calculated from Eqs. (1) and (2), respectively:

$$\sigma = 1.5PL/wt^2 \quad (1)$$

$$E = 0.25mL^3/wt^3 \quad (2)$$

where P is the load at a point of deflection of a stress/displacement curve in the test, L is the support span, w is the specimen width, t is the specimen thickness and m is the slop of the tangent to the initial linear portion of the load–deflection curve.

Microstructure analysis of PyC-coated fibers and composites after mechanical tests was done by a scanning electron microscope (SEM, Hitachi FEG S4800). The pullout fiber surface of the composites was analyzed by EDS equipped with SEM.

3. Results and discussion

3.1. Fiber surface coatings

Fig. 1 shows SEM images of uncoated and PyC-coated Nextel™440 fibers formed by CVD. The fibers were well coated; with thicknesses of about 0.15, 0.42 and 1.00 μm. The surfaces of PyC-coated fibers were smooth and uniform, without relation to the coating thickness. As shown in Fig. 1(c) and (a) narrow gap appeared between the fiber and PyC coating during the CVD cooling procedure, due to the different thermal expansion coefficient (fiber, 5.3 × 10^{-6}/°C; carbon, 2.5 × 10^{-6}/°C). The inference was that the coatings couldn't isolate the fibers from matrix completely. That is to say, interfacial reaction between the fibers and the matrix might occur, and strong interfacial bonding might be obtained.

Single fiber tensile tests were used to evaluate the fiber tensile strength, and the strength distribution was evaluated by the two-parameter Weibull model [21]. Weibull plots of uncoated and PyC-coated fibers are shown in Fig. 2, and the corresponding Weibull parameters are listed in Table 2. In the Weibull model, larger m values of the fibers mean fewer defects and lower dispersion of the tensile strength [22]. The m value decreased as the coating thickness increased, indicating higher distribution of the tensile strength in coated fibers. Fibers with 0.15 μm PyC coating showed higher strength compared with uncoated fibers, while fibers with 0.42 and 1.00 μm PyC coatings showed lower strengths. The strength increase in 0.15 μm PyC coating might be attributed to the ability of this coating to heal surface flaws, as reported by Chawla et al. [23]. In the case of fibers with thick PyC coatings, fiber