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OXIDATION-RESISTANT INTERFACIAL COATINGS FOR CONTINUOUS FIBER CERAMIC COMPOSITES

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Abstract

Developing an oxidation-resistant interfacial coating for continuous fiber ceramic composites (CFCCs) continues to be a major challenge. CFCCs' mechanical behavior are influenced by the interfacial bonding characteristics between the fiber and the matrix. Finite element modeling studies suggest that a low-modulus interfacial coating material will be effective in reducing the residual thermal stresses that are generated upon cooling from processing temperatures. Nicalon[1]/SiC composites with carbon, alumina and mullite interfacial coatings were fabricated with the SiC matrix deposited using a forced-flow chemical vapor infiltration process. Composites with mullite interfacial coatings exhibited considerable fiber pull-out even after oxidation and have potential as a composite system.

Introduction

Continuous fiber ceramic composites are being developed for high temperature structural applications, many of which are in oxidative environments [1-2]. Such composites are attractive since they are light-weight and possess the desired mechanical properties at elevated temperature and in aggressive environments. The most significant

[1] Ceramic Grade Nicalon, Nippon Carbon Company, Tokyo, Japan

advantage is their toughness and their non-catastrophic failure behavior [3-4].

The mechanical properties of CFCCs have been characteristically linked with the nature of the interfacial bond between the fibers and the matrix [5-6]. Weakly bonded fiber-matrix interfaces allow an impinging matrix crack to be deflected such that the fracture process occurs through several stages: Crack deflection, debonding at the interface, fiber slip and pull-out and ultimately fiber failure [7]. Such a composite will fail in a graceful manner and exhibit substantial fracture toughness.

Generally, metal oxides are inherently stable to oxidation and possess thermal expansion coefficients relatively close to those of Nicalon and SiC. However, the metal oxides must also be chemically compatible with the fiber and matrix. If the fiber/interface/matrix system is chemically compatible, then the interfacial bonding stress is influenced by the thermal residual stresses that are generated as the composite is cooled from processing to room temperature. In this paper, thermomechanical computational results obtained from a finite element model (FEM) for calculating the thermal residual stresses will be discussed [8]. Then, the experimental evaluation of Nicalon/SiC composites with carbon, alumina, and mullite interfacial coatings will be presented.

Finite Element Modeling

A finite element model has been developed in order to understand the effect of interfacial coating materials on the profile of thermal residual stresses. The elementary cell comprises a fiber (radius =7 μm) surrounded by an interface, the matrix (radius = 11 μm) and the bulk material (Fig. 1). The bulk material is represented as having the average properties of the composite determined from the rule of mixtures. The fiber volume fraction is 40% and the interfacial and the matrix volume fraction varies with interfacial coating thickness.

The model is based on an axisymmetric system and the meshing was done with two dimensional elements (rectangular with eight nodes) in a plane. The boundary conditions are the following: 1. Displacement is permissible only along the axis of axisymmetry, 2. the bottom of the cell can not have any displacement in the direction of the axis of axisymmetry and the bulk can not rotate around this axis and has its outer surface free, and 3. a temperature differential of 1175 K is assumed from cooling from the processing temperature of 1473 K.

Experimental procedure

Fibrous preforms were prepared by stacking multiple layers of plain weave Nicalon cloth in a 30°-60°-90° sequence within the cavity of a graphite holder. The preform was compressed by hand and held within the graphite holder by a lid. The cloth sizing was removed by heat treatment at 973 K in argon for 2 h. The average fiber content of the resulting fiber preforms was 40 vol% with sample dimensions of 45 mm diameter and 12.25 mm thickness.

The carbon interfacial coating was deposited from an argon/propylene mixture at 1373 K and 3 kPa pressure. The alumina (Reynolds Grade RCHP-DBM) and mullite (Baikowski International Corporation, North Carolina) interfacial coatings were applied starting from powders using a novel colloidal process developed at Oak Ridge National Laboratory. Preforms with alumina and mullite interfacial coatings were then sintered at 1373 K in argon for 2 h.

The coated preforms were infiltrated with SiC matrix using the forced-flow chemical vapor infiltration (FCVI) process [2]. The SiC matrix was deposited from the decomposition of methyltrichlorosilane (MTS) in hydrogen. The process parameters are as follows: Top surface temperature of 1473 K; MTS flow of 0.307 g/min; hydrogen flow of 500 cm^3/min (STP); and exhaust pressure of 101 kPa. Typically, the matrix infiltration was completed within 20 hours.

The infiltrated Nicalon/SiC composites were cut into twenty-four flexural bars of average size 2.5 x 3.0 x 40 mm. The dimensions of the cut flexural bars were measured and they were weighed to determine densities. Half of the flexure bars were then heat treated at 1273 K for 24 h in air to determine their oxidation behavior. The bars were loaded perpendicular to the layers of the cloth and the fracture surfaces were examined using a Hitachi S-800 field emission gun SEM.

Results

The properties of Nicalon, SiC (matrix) and potential interfacial coating materials (carbon, aluminum titanate, barium zirconium phospate silicate or BaZPS, mullite and alumina) are summarized in Table 1 [9]. The finite element model computed the effect of carbon coating thickness on the radial thermal residual stresses (σ_x) at the fiber/interfacial coating interface and the interfacial coating/matrix interface is summarized in Fig. 2. The residual radial stress for the fiber/matrix interface without any coating is based on Hsueh's [10] model. With a thin coating (0.1 μm), the residual radial stresses at both of the interfaces are compressive, becoming tensile with increasing coating thickness. The effect of different coating materials on the radial stresses developed at the interfaces are shown in Fig. 3 and compared with that of carbon.

Fracture surface examination of composites with carbon interfacial coatings showed considerable fiber pull-out before oxidation (Fig. 4a). However, after oxidation for 24 h in air at 1273 K they exhibited brittle fracture with very little fiber pull-out (Fig. 4b). Similarly, the fracture surface of a composite with an alumina interfacial coating showed very little fiber pull-out after oxidation (Fig. 5). The fracture surface of the composite with a mullite interfacial coating. however, displayed considerable fiber pull-out before and after oxidation (Fig. 6).

Discussion

Based on the FEM results, among the three parameters, Young's modulus, coefficient of thermal expansion and poisson's ratio, the Young's modulus plays a more dominant role in the developed radial residual thermal stresses. For example, as the modulus is decreased (from alumina to aluminum titanate) the difference in residual stresses that are generated in the fiber/interfacial coating and interfacial coating/matrix interfaces are reduced (Fig. 3). Further, the materials with low Young's modulus (e.g., aluminum titanate) cause a reduction of compressive thermal residual stresses similar to that for 0.1 μm thick carbon coating. Moreover, for interfacial materials with the same modulus, a material with a higher thermal expansion coefficient than that of the fiber and matrix is more effective in reducing radial stresses than is a material with a lower or similar thermal expansion. Trends similar to those reported here were observed with Hsueh's [10] model as well.

Composites with carbon interfacial coatings exhibit brittle fracture after oxidation due to the oxidation of the carbon interlayer and the subsequent formation of silica that bonds fiber and matrix [5, 11].

Composites with alumina interfacial coating showed brittle fracture after oxidation and Langley et al. [12] reported that the tensile strength of Nicalon fibers coated with alumina by plasma CVD were reduced by 30-40% compared to fibers similarly coated with carbon. The fiber damage was attributed to either chemical reaction or mechanical damage resulting from the thermal expansion mismatch between fiber and coating, or a combination of both. Walukas [13] observed that sol-gel derived alumina interfacial coating reacted with silica in the Nicalon fiber during composite densification to form mullite.

Composites with mullite interfacial coating exhibited considerable fiber pull-out even after oxidation, however, the non-uniformity of coatings is a problem, and regions with considerable fiber-pull out adjacent to regions of brittle fracture were observed (Fig. 7). The accumulation of coating material around the fibers in certain areas also resulted in the lack of matrix in those areas. Preliminary thermodynamic calculations indicate that mullite coatings are likely to be stable with the Nicalon/SiC system. Process development is underway to deposit mullite coatings on Nicalon fabrics using a sol-gel route.

Conclusions

FEM analysis revealed that a low modulus interfacial coating will be effective in reducing radial residual stresses that result from cooling from processing temperatures. Further, for the interfacial materials with the same modulus, a material with a higher thermal expansion coefficient than that of the fiber and matrix is more effective in reducing the radial stresses than is a material with a lower or similar thermal expansion coefficient.

Composites with carbon and alumina interfacial coatings exhibited brittle fracture after oxidation. However, a composite with a mullite interfacial coating retained considerable fiber pull-out, suggesting that it may be a desirable interfacial coating. Colloidal application, however, resulted in non-uniform mullite coatings. Potentially, the use of sol-gel methods may result in coatings with much better uniformity.

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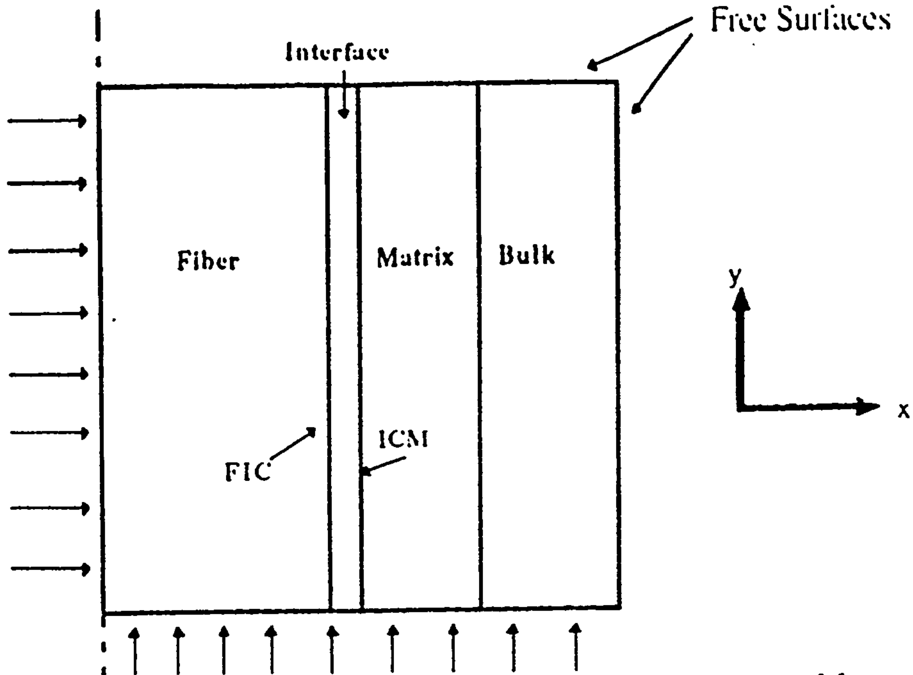

Fig. 1 Schematic of an elementary cell in the finite element model

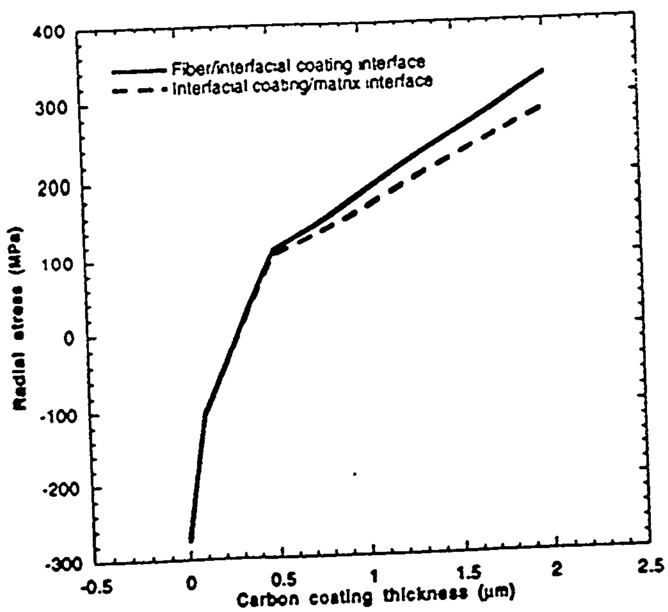

Fig.2 Effect of carbon coating thickness on the calculated residual radial thermal stresses using finite element model

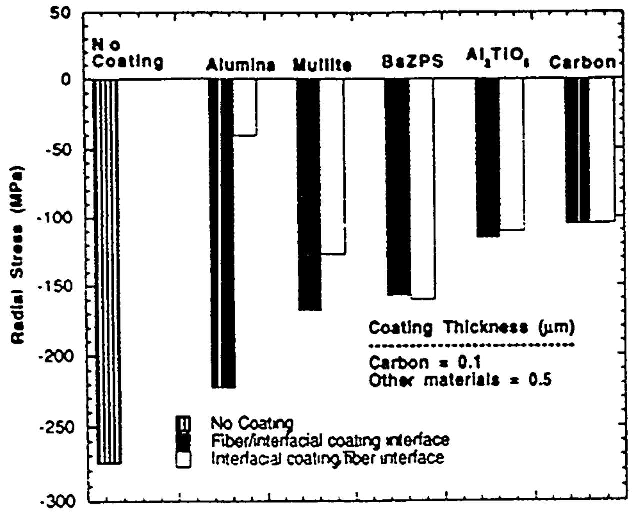

Fig. 3 Finite element computations indicate that low modulus interfacial coatings reduce compressive residual radial stresses

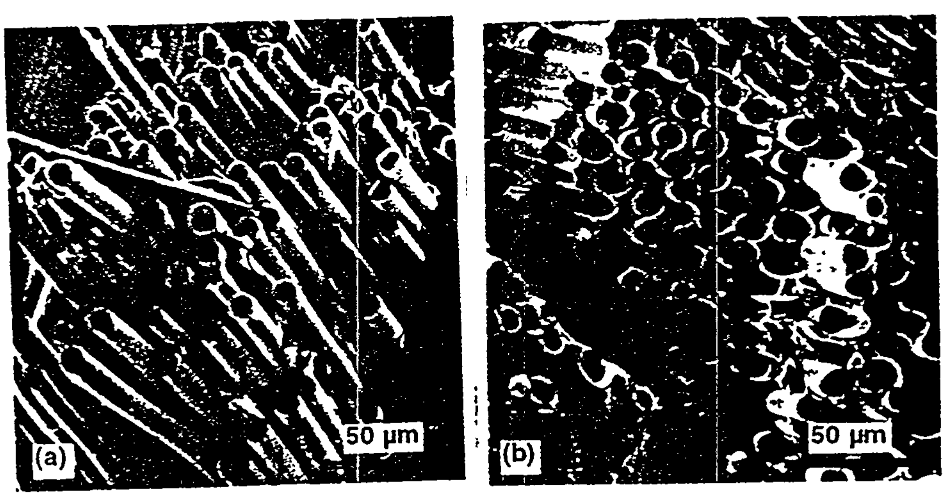

Fig.4 Fracture surface of a composite with a carbon interfacial coating (a) before oxidation and (b) after oxidation in air for 24 h at 1273 K

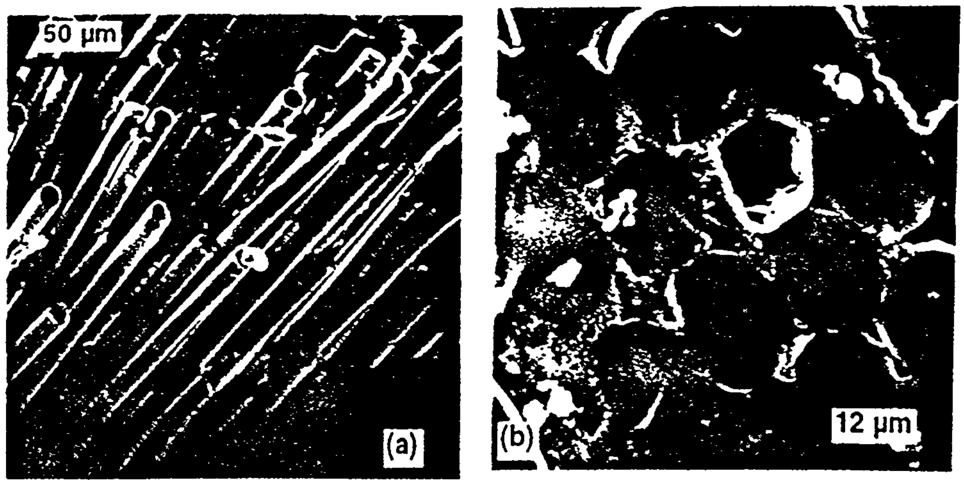

Fig. 5 Fracture surface of a composite with an alumina interfacial coating (a) before oxidation and (b) after oxidation in air for 24 h at 1273 K

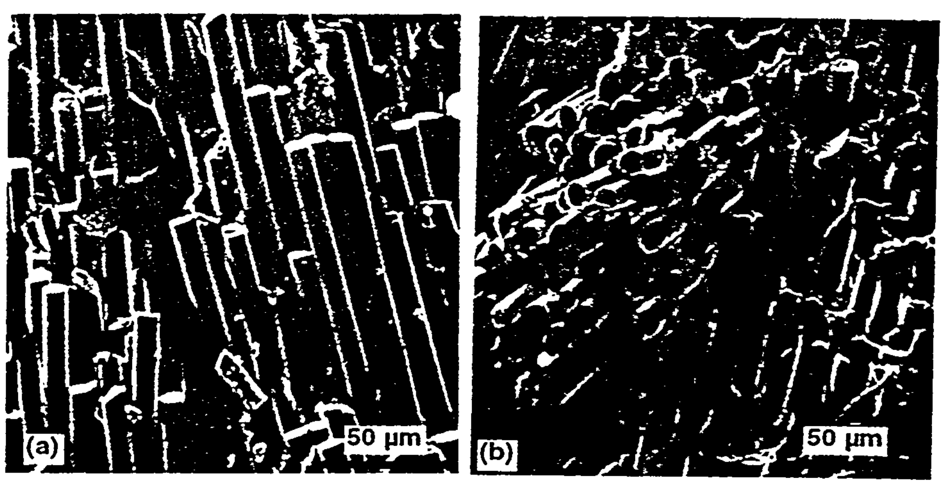

Fig.6 Fracture surface of a composite with a mullite interfacial coating (a) before oxidation and (b) after oxidation in air for 24 h at 1273 K

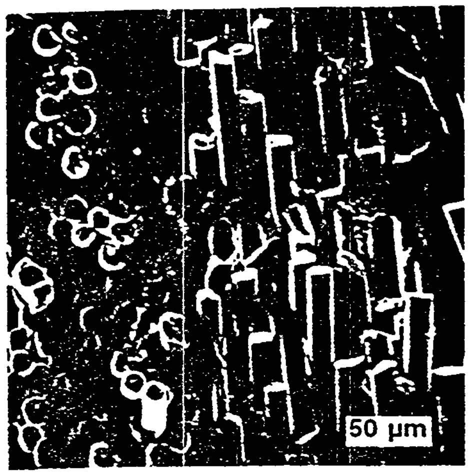

Fig. 7 Non-uniformity of the mullite interfacial coating resulted in fiber pull-out in certain regions and brittle fracture in other areas

Table 1. Material properties utilized for the FEM study [9]

Material	Young's modulus, E (GPa)			Coefficient of thermal expansion, α ($x10^{-6}/K$)			Poisson's ratio, ν		
	E_x	E_y	E_z	α_x	α_y	α_z	ν_x	ν_y	ν_z
Nicalon	200	200	200	3	3	3	.12	.12	.12
SiC	350	350	350	4.6	4.6	4.6	.2	.2	.2
Carbon	12	40	40	28	2	2	.4	.12	.12
Alumina	380	380	380	8.3	8.3	8.3	.22	.22	.22
Mullite	220	220	220	5	5	5	.27	.27	.27
BaZPS with x=0.25	50	50	50	1	1	1	.2	.2	.2
Al_2TiO_5	11	11	11	1	1	1	.22	.22	.22