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Microstructure and flexural properties of multilayered fiber-reinforced oxide composites fabricated by a novel lamination route

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Abstract

All-oxide ceramic matrix composites produced by a novel route based on the lamination of thermoplastic prepregs are investigated. This route allows for the production of composites with very homogeneous microstructures and a reduced amount of matrix cracks. Nextel^{TM} 610 alumina woven fabric is used here to reinforce a porous oxide matrix composed of 80 vol% Al_2O_3 and 20 vol% ZrO_2. The mechanical behavior of composites submitted to different heat treatments is investigated under 4-point bending and short beam shear. Results show that composites with low interlaminar shear strength present a graceful failure under 4-point bending, characterized by a stepwise stress reduction upon straining beyond the peak stress. The fracture of such composites is accompanied by a series of interfacial delamination events, which enhance energy dissipation during failure. An increase of the interlaminar shear strength due to matrix densification causes a loss of the stepped stress–strain behavior. Nevertheless, fiber-related toughening mechanisms such as crack deflection and bridging still ensure inelastic deformation up to failure of these composites.

Keywords: Ceramic matrix composites; Thermoplastic prepregs; Lamination; Alumina; Zirconia

1. Introduction

Continuous fiber-reinforced ceramic matrix composites (CMCs) were developed to overcome the inherent brittleness and consequent catastrophic failure of ceramics [1]. The energy released during the failure of CMCs is enhanced by a series of toughening mechanisms such as crack deflection at fiber–matrix interfaces or interphases, crack bridging and fiber pullout, normally leading to a quasi-ductile fracture behavior [1–3].

Among the different classes of CMCs, much attention has been drawn to all-oxide systems because of their chemical stability in oxidizing environments [3,4]. Toughness is typically achieved in these materials by a weak, porous matrix that enables debonding at fiber–matrix interfaces [3,5]. These composites are usually produced by liquid infiltration techniques, in which matrix particles are impregnated into fiber tows, fabrics or preforms via aqueous slurries or sols [3,6–8]. After drying the liquid carrier, the matrix is sintered at moderate temperatures (< 1300 °C) to avoid strength degradation of the polycrystalline oxide fibers [3,7], as well as to ensure a partial sintering of the matrix, leading to the porosity necessary for damage tolerance [5]. One of the challenges of this process is the consolidation of flawless matrices, since the constrained shrinkage imposed by the rigid network of fibers causes the formation of matrix cracks during drying and sintering [1,3,6]. These flaws may not just be detrimental to the mechanical properties of the composites [8–10], but also compromise their thermal shock resistance by decreasing the thermal conductivity of the material [11,12].

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To produce crack-free CMCs, both drying and sintering-related cracks must be mitigated. Consequently, shrinkage should be avoided in both processing steps [10]. When conventional liquid infiltration routes are used to produce 2D-woven composites, cracking occurs already during the extraction of the liquid carrier, mainly in matrix-rich regions located at the crossover between fiber tows [6,7]. An alternative to mitigate these drying cracks was proposed by Levi et al. [7] and Yang et al. [13] and consists in reducing the amount of unreinforced matrix regions by filling the large inter-tow spaces with chopped fibers or large particles, respectively. Another possible method was proposed by Mah et al. [10] and is based on the freeze casting of camphene-based slurries used for the infiltration of fiber fabrics or preforms. Although promising results were obtained by these methods, the viability of using them to produce all-oxide CMCs in large scales should yet be proved. With regard to the sintering-related cracks, they can be avoided by using matrix particle networks that do not shrink at sintering temperatures of interest [4,6,7].

In this work, a novel lamination route is used to manufacture 2-D woven all-oxide CMCs with a reduced amount of matrix cracks. This is achieved by (i) employing a two-step impregnation process, which allows for an enhanced filling of void spaces within the fiber textiles, thereby decreasing the amount of shrinkage cracks in the green state and (ii) using an alumina-zirconia matrix that presents very low shrinkages at the selected sintering temperatures, preventing the formation of sintering-related cracks. In this novel route, fiber fabrics are first impregnated with a low viscous, ethanol-based slurry that guarantees a good infiltration of fiber bundles. In a subsequent step, the large inter-tow voids are filled with a softened paraffin-based suspension used for the manufacture of thermoplastic prepregs (at ~115 °C). After the solidification of paraffin, such prepregs are stable and easy to handle at room temperature. On the contrary of conventional routes based on liquid infiltration, the thermoplastic prepregs produced here can be stored under normal room conditions, giving more time flexibility for the manufacturing process. Moreover, such prepregs present thermoformability, which enables shaping and joining of different composite parts in the green state to produce complex-shaped CMC components.

Focus is given here to the microstructure and mechanical properties of composites produced by this novel route. They are investigated after three different heat treatments, involving sintering at 1200 °C and 1300 °C and an ageing treatment at 1100 °C for 500 h. Mechanical behavior is investigated by 4-point bending (4PB) and short beam shear (SBS) tests. The effect of heat treatment on the mechanical properties is discussed considering the resulting stress–strain curves, fracture surfaces and predictions of crack deflection according to the well-known He and Hutchinson model.

2. Experimental procedure

2.1. Materials and preparation of suspensions

Both ethanol and paraffin-based suspensions were prepared using a powder mixture consisting of 80 vol% alumina (Ceralox HPA 0.5, RWE-DEA, Hamburg, Germany) and 20 vol% yttria-stabilized zirconia (TZ-3Y, Tosoh, Toyama, Japan). This powder mixture is hereafter designated by A8Z2. According to the respective suppliers, the alumina powder has a median particle size (D50) of ~0.4 μm and a surface area of ~9 m^2/g, whereas the yttria-stabilized zirconia has a D50 of ~0.6 μm (with a crystallite size of ~27 nm) and a specific surface area of ~16 m^2/g.

The use of two different suspensions in the composite manufacture leads to the formation of two different matrices in the composites: an *intra-bundle matrix* (IB), originated from the ethanol-based slurry used to infiltrate the fiber bundles, and an *inter-textile matrix* (IT), originated from the paraffin-based suspension used to manufacture the thermoplastic prepregs.

For the paraffin-based suspension, batches of 120 g of the A8Z2 mixture were homogenized at 500 rpm for 30 min in an attrition mill. A 500 cm^3 alumina crucible was used, together with 1300 g of 3 mm zirconia balls and 200 ml ethanol as the wetting media. The powder mixture was subsequently dried and sieved for deagglomeration. The composition of the paraffin-based suspension, as well as the materials used for its production is shown in Table 1. The binder system is composed of a paraffin wax medium, together with different polar surfactants used to achieve appropriate rheological properties. These additives contain polar carboxylic or amine end-groups that physisorb or chemisorb on the oxide particle surfaces, while their lipophilic polymeric chains extend into the nonpolar paraffin medium. This promotes a sterical stabilization of the suspension. Details on the development of this binder system, as well as on the composition of the different surfactants are presented elsewhere [14]. This binder system was primarily developed to manufacture alumina and metal-ceramic components via low-pressure injection molding. According to Leverköhne et al. [14], the combination of short and long-chain molecules used in this binder system presents advantages over the use of a single surfactant such as stearic acid, particularly when processing powder mixtures containing milled metallic powders.

For the preparation of the paraffin-based suspension, all organic ingredients were preheated at 100 °C and mixed in a glass beaker. Then, the A8Z2 powder was gradually added, while mixing the suspension with a glass stirrer. Further homogenization was achieved by passing the suspension through a three roller mill (EXAKT 120S, EXAKT, Norderstedt, Germany) heated at 95 °C. After solidification, the suspension was granulated using mortar and pestle, so as to facilitate its handling during the subsequent processing steps.

Table 1
Composition of the paraffin-based suspension used in this work.

Material	Producer	Density (g/cm^3)	Volume Content (%)
A8Z2 powder	(produced in this work)	4.13[a]	58
Paraffin KX1313	Zschimmer & Schwarz	0.9	35.44
Octadecylamine	Sigma-Aldrich	0.9	2.96
Licowax OP	Clariant	1.0	2.52
Solsperse	Zencca	0.9	1.08

[a]Measured by gas pycnometry after drying and sieving the powder.