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Assessment of three oxide/oxide ceramic matrix composites: Mechanical performance and effects of heat treatments

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ABSTRACT

Mechanical performance of three oxide/oxide ceramic matrix composites (CMCs) based on Nextel 610 fibers and SiOC, alumina, and mullite/SiOC matrices respectively, is evaluated herein. Tensile strength and stiffness of all materials decreased at 1000 °C and 1200 °C, probably because of degradation of fiber properties beyond 1000 °C. Microstructural changes in the composites during exposure at 1000 °C and 1200 °C for 50 h reduce their flexural strength, fracture toughness and work of fracture. A literature review regarding mechanical properties of several oxide/oxide CMCs revealed lower influence of fiber properties on composite strength compared with elastic modulus. The tested composites exhibit comparable stiffness and strength but higher fracture toughness compared with average values determined from a literature review. Considering CMCs with different compositions, we observed an interesting linear trend between strength and fracture toughness. The validity of the linear relationship between fracture strength and flexural toughness for CMCs is discussed.

1. Introduction

Ceramic matrix composites (CMC) are designed to overcome the brittleness of monolithic ceramic materials while maintaining their advantageous high temperature stability, high specific strength and stiffness. Oxide/oxide composites additionally offer good stability against corrosive and oxidative environments, which makes them promising candidate for use in gas turbine applications aiming at higher process temperatures [1,2].

This potential led to the collaborative High Performance Oxide Ceramics (HiPOC) research project, which was funded by the German Federal Ministry of Education Research. The main objectives are based on the development and improvement of different oxide/oxide CMC materials that can be used in gas turbines for power generation and aerospace propulsion or as a spin-off in space applications such as thermal protection systems and hot structures.

Three oxide composites were developed and improved within this project. Two were based on the polymer infiltration and pyrolysis (PIP) process, whereas the third was manufactured by slurry infiltration. The slurry-infiltrated WHIPOX™ is a completely alumina-based composite material, whereas the PIP materials UMOX™ and OXIPOL contain small residual amounts of carbon in their mullite/SiOC and SiOC matrices. In the final stage of the project, two CMC combustors were validated to technology readiness level 4 (TRL) in a high-pressure tubular combustion rig [3,4].

The materials employed in this study are all based on reinforcement with Nextel® 610 (N610) alumina fibers, which exhibit the highest strength and stiffness of the commercially available oxide fibers [5–8]. However, because of its fine-grained structure the N610 is sensitive to creep and grain growth [9–14]. Schmücker et al. [12,14] and Cantonwine et al. [10,11] demonstrated a significant grain growth of these fibers during exposure to temperatures greater than 1100 °C. The grain coarsening reduces the tensile performance, but increases the creep resistance [13].

Depending on the matrix composition Schmücker et al. [15–17] found either more pronounced or nearly no grain growth of the N610 in a composite. In the case of pure alumina matrices they observed that SiO_2 diffused from the fiber into the matrix, resulting in accelerated grain coarsening. This phenomenon can be reduced by the addition of SiO_2 into the alumina matrix [16]. In case of SiOC-containing materials with fugitive coatings, recent studies by Hönig et al. [18] and Volkmann et al. [19] revealed embrittlement upon exposure to temperatures greater than

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1000 °C under an oxidizing atmosphere, which they attributed to the formation of silica bridges between the fiber and matrix [19].

The aim of the present study is to compare the composites of the HiPOC research project with respect to their quasi-static performance at room temperature (RT) and high temperatures and their long-term stability, with particular emphasis on toughness and notch sensitivity. Furthermore, we present a literature review to compare and classify the mechanical performance of the HiPOC CMCs and those of the CMCs reported in the literature. Key features within this overview are Ashby-like tensile strength vs. modulus, and flexural strength vs. toughness plots.

2. Materials

Table 1 provides a brief overview of the investigated composite materials. Additionally, the following section thoroughly describes the manufacturing process for each material.

2.1. UMOX™

UMOX™ is the standard oxide-based CMC used at EADS Innovation Works/Airbus Group Innovations (Munich, Germany), where it has been developed over the last 20 years, including a successful flight test within a Do 228 aircraft jet engine equipped with exhaust components. The matrix is based on commercial micron-sized mullite powder and polysiloxane precursor. Coated continuous N610 alumina fibers (3M, St. Paul, US) were employed as reinforcing material. Removal of the coating after composite manufacturing results in a gap between the fiber and matrix that prevents crack propagation (fugitive interface) [20,21]. The oxide CMC was manufactured by the PIP process [22]. Oxide fibers were infiltrated with a liquid pre-ceramic matrix slurry (Liquid Polymer Infiltration, LPI) and were subsequently wound onto a constantly rotating drum or mandrel (up to 1.5 m in diameter). The unidirectional prepregs were stacked in a symmetrical, bidirectional lay-up consisting of 16 layers. After being dried the impregnated fibers are vacuum packed and consolidated in an autoclave ($p > 10$ bar, $T > 423$ K). Conversion of the preceramic matrix to a ceramic is achieved by pyrolysis under an argon atmosphere at temperatures greater than 1470 K. Two re-infiltration cycles of the composite with a polymeric precursor, followed by further high-temperature treatment reduced the open porosity to 12 vol.%. The final composite exhibited a raw density of 2.46 g/cm^3 and a fiber volume content of ~50 vol.%.

2.2. WHIPOX™

Oxide/oxide CMCs with porous matrices and without an interphase between the fiber and ceramic matrices have been developed since 1995 [23]. These CMCs possess porous matrices that typically consist of alumina or aluminum silicates. Reinforcing potential within these materials is ensured by crack deflection in the weak matrices, thereby rendering expensive fiber coatings and elaborate matrix densification techniques unnecessary. WHIPOX™ CMCs [24,25] were manufactured by filament winding at the DLR, Cologne (Germany) and are composed of N610 fibers in a pure alumina matrix. The matrix is derived from a commercial pseudo-boehmite/amorphous silica phase assemblage with an Al_2O_3 content of 70–100 wt.%. At the beginning of the process, a heat-cleaned fiber tow was continuously infiltrated with a water-based matrix slurry. The infiltrated tow was then predried to stabilize the matrix and was finally wound in 1D–2D orientation on a mandrel. Processing of moist green bodies allowed subsequent stacking, forming, or joining of the prepregs. After being formed into their final shapes, the green bodies were sintered free-standing in air at approximately 1570 K. The fiber orientation and content in the CMC were chosen as ±30° and 37 vol.% with respect to the desired combustor application in the program, respectively. The WHIPOX™ employed in this study possessed a density of 2.72 g/cm^3 and a total porosity of 28% (matrix porosity 46%).

2.3. OXIPOL

OXIPOL, a recently developed oxide composite, was manufactured at the DLR Institute of Structures and Design (Stuttgart, Germany) via PIP process. It consists of N610 fibers and a SiOC matrix derived from polysiloxane precursors [26]. A high damage tolerance is guaranteed via fugitive coating, which weakens the fiber/matrix interface.

The preparation process started with the application of a phenolic coating on the N610 fiber fabrics, which was subsequently dried at RT and cured at 448 K for 2 h. After drying, fabric sheets and layers of resin powder (MK, Wacker Chemie, Germany) were stacked into a laminate and warm-pressed. Thereby, the fabrics were infiltrated with the polymer, which was cured under axial load and at low pressure (50 mbar). For the following densification steps, the pyrolysed ($T \approx 1374$ K) preform was then plunged into a liquid polysiloxane precursor assisted by near-vacuum. Five PIP cycles were performed to reduce the CMCs' porosity. The resulting CMC exhibited a total porosity of 15 vol.% and a raw density of 2.36 g/cm^3. A fiber orientation and content of ±0/90° and 43 vol.% were used for the investigated materials.

3. Methods

3.1. Preparation of specimens and heat treatment

Dog-bone-shaped specimens for tensile tests were prepared using water jet cutting. Samples for flexural and single-edge notched bend testing (SENB) were cut using a diamond disc precision cutter CUTO 1 (Jean Wirtz, Düsseldorf, Germany) with a diamond-coated disc rotating at 1000 rpm. The notches for the SENB samples were prepared with a Well™ 6234 (Well, Mannheim,

Table 1
Overview of the investigated composites; the ID consists of the first letter of the material and the reinforcement orientation.

Property/ID	U090	W30	W60	O090
Material	UMOX™	WHIPOX™		OXIPOL
Manufacturer	EADS, Munich	DLR, Cologne		DLR, Stuttgart
Manufacturing	PIP	Slurry based filament winding		PIP
Lay up	0/90 Cross ply	±30° Wound	±60° Wound	0/90 Twill fabric
Reinforcement	Nextel 610: ≈99 % α-Al_2O_3/0.67% Fe_2O_3/0.35% SiO_2			
Matrix	Mullite/SiOC	Alumina		SiOC
Interface	Fugitive	None		Fugitive
Fiber volume content in %	50	37		43
Porosity in %	12	25		15
Raw density in g/cm^3	2.46	2.72		2.36