Oxide Ceramic Matrix Composites – Manufacturing, Machining, Properties and Industrial Applications

Oxide ceramic matrix composites (O-CMC) combine high temperature stability, low density, high strength and good corrosion resistance with a damage-tolerant quasi-ductile fracture behaviour enabling a variety of applications with demanding thermal and mechanical requirements.

Fig. 1
Oxide ceramic fibres as woven fabric

O-CMC components can substitute metallic components in high temperature applications leading to weight reduction, increased energy efficiency and prolonged service life time. With increasing number of applications, the manufacturing processes and the design layout are developed further enabling sophisticated component designs. The materials are entering more and more applications ranging from furnace parts to components in gas turbines. With increasing number of items produced, series production processes become a necessity.

Keywords
oxide ceramic matrix composites (O-CMC), fabrication techniques, material properties, industrial applications

Introduction

Ceramics generally show excellent temperature stability, low density, high hardness, good corrosion and wear resistance making them interesting materials for applications with demanding thermal and mechanical requirements. However, the use of monolithic ceramics as structural materials is often limited due to their brittle fracture behaviour. By reinforcing ceramics with ceramic fibres and tailoring the fiber-matrix interface, damage-tolerant quasi-ductile fracture behaviour can be achieved. These CMC materials can substitute metallic components in high temperature environments bringing advantages in terms of weight reduction, increase in thermal efficiency by increasing process temperatures or prolonged service life time and reduced maintenance costs [1, 2]. CMCs exist as non-oxide (NO-CMC) and all-oxide types (O-CMC). Comparing both types of CMC materials, O-CMCs exhibit lower maximum application temperatures, but are easier to fabricate, less expensive, and resistant to oxidation.

O-CMC materials are developed since some decades, have been continuously improved, and are currently commercialised by a few companies like COI-ATK/US, WPX Faserkeramik GmbH/DE and Walter E. C. Pritzkow Spezialkeramik (WPS)/DE. Improvement of O-CMC materials is constantly evolving with main efforts made in universities and research centers in the USA, France and Germany. Being a new class of material, O-CMC slowly entered into first applications like furnace components and flame tubes. These first applications demonstrated the potential of O-CMC materials and gave opportunities to develop the materials, their processing and the design layout of O-CMC components further. Currently, O-CMC components enter more and more applications and number items increase making series production processes necessary.

In this article some of the achievements are presented that have been made between WPS and Fraunhofer Institute for Silicate Research (ISC)/Center for High Temperature Materials (HTL)/DE who are collaborating in O-CMC development for more than 10 years.

Oxide ceramic matrix composites

O-CMCs are composite materials consisting of an oxide ceramic matrix reinforced by oxide ceramic reinforcing fibres. As reinforcing fibres, oxide fibres like Nextel TM 610 or 720 from 3M/US are typically used, often in form of textile fabrics

Walter Pritzkow
Walter E. C. Pritzkow Spezialkeramik
70794 Filderstadt – Sielmingen
Germany

Andreas Nöth, Arne Rüdinger
Fraunhofer Center for High Temperature and Design HTL
95448 Bayreuth, Germany

Corresponding author:
Walter Pritzkow
pritzkow-wps@keramikblech.com

(Fig. 1). As matrix components, different ceramic compositions like Al_2O_3 or mixtures like Al_2O_3–SiO_2, Al_2O_3–ZrO_2 are used. The materials exhibit low density, e.g. 1/3 of the density of high-temperature steels and super alloys, high bending strength, high thermal shock resistance and good stability in oxidising and moisture-rich atmospheres [3–6]. Applications of O-CMC materials are limited to about 1200 °C, because then degradation of the mechanical performance of the reinforcing fibres is observed [7]. The reason for the degradation of the mechanical properties is a coarsening of the ceramic grains of the fibres, which lead to reduced tensile strength values [8]. Thus, the maximum application temperature of O-CMC materials is limited to about 1150 °C for long-term use and up to 1200 °C for short term exposure. To achieve damage-tolerant fracture behaviour of O-CMC materials, a weak interface between the fibres and the matrix is required [9]. When the material is under load and starts to crack, the cracks are deflected at the weak fiber-matrix interface. These deflection mechanisms dissipate energy and catastrophic failure is shifted to much larger strain values. Thus, O-CMCs can show strain-to-failure values of up to 0,6 %, whereas monolithic ceramics exhibit strain-to-failure values below 0,1 % (Fig. 2).

The weak fibre-matrix interface is basically realized by two concepts. First, the ceramic fibres are coated with a ceramic layer, which provides the weak interface between the fibre and the matrix material ("weak interphase concept") [10]. This concept is realized when rather dense O-CMC materials are needed [3, 11]. More typically, the matrix of the O-CMC material is porous and less stiff than the reinforcing fibres ("weak matrix concept") [12]. In this case, the weak fibre-matrix interface is given due to the fact that the matrix is only partially bonded to the fibre [13]. Thus, no fibre coating is needed.

A disadvantage of using a porous matrix is its low intrinsic strength which brings limitations to the matrix-dominated properties of the composite. If a higher strength of the matrix is desired, the porosity needs to be lowered. This can be realized by sintering the O-CMC material at higher temperatures. One problem caused by the higher sinter temperatures is crack formation in the matrix. At high sintering temperatures the matrix shows significant volume shrinkage, whereas the reinforcing fibres or fabrics form a rigid network. Thus, matrix cracks occur with this approach, which limits the mechanical performance of the composite materials. The approach of WPS and Fraunhofer ISC/HTL is to maximize the strength of the ceramic matrix and while minimizing its volume shrinkage during sintering. This is achieved by realizing a multiscale design of the matrix microstructure using different grain size fractions. In this case a solidification of the matrix without cracking is possible, which leads to O-CMC materials with good mechanical performance.

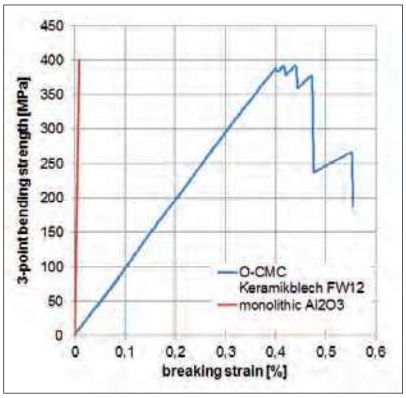

Fig. 2
Stress-strain curve of monolithic ceramic in comparison to O-CMC material

Manufacturing processes of textile-based oxide ceramic matrix composites

WPS and Fraunhofer ISC/HTL use three different techniques to fabricate components made of textile-based O-CMC materials. The manufacturing methods are well-established for fibre-reinforced plastics and have been adapted to the requirements for producing O-CMC components.

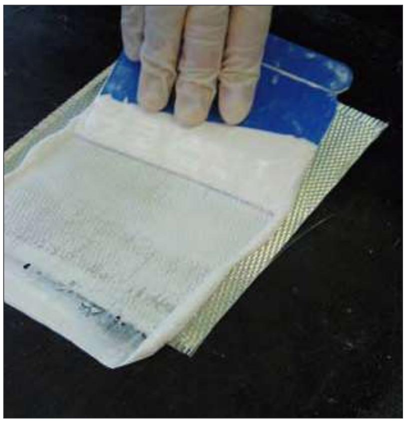

Fig. 3
Infiltration of ceramic fabric with matrix slurry for lamination process

Lamination process (method 1)

In this process, fabrics of oxide ceramic fibres are first infiltrated with a slurry of matrix material. Then, the infiltrated fabrics are draped on a tool. Different layers of draped fabrics are pressed using a scraper or a roller (Fig. 3). This method leads to the lowest fibre volume contents resulting in the lowest strength values of the materials. Nevertheless, the process is very simple and fast, and is used for components with lower requirements on mechanical performance.

Fig. 4
Green body of O-CMC material after pressing in mould

Mould pressing (method 2)

Infiltrated fabrics are laminated upon each other, put into a press mould and compacted by applying pressure (Fig. 4). Compacting can be performed under defined pressure or to a defined thickness of the infiltrated fabrics by using mechanical stoppers. After pressing, the part is dried in a drying oven under moderate temperatures. Alternatively, the part can also be warm-pressed so that the drying process is not necessary. Using this method, higher and well-defined fibre volume contents can be realised in comparison to method 1. The method is used for high-quality components, allows near-net shape manufacturing, but is limited to parts with rather low complexity.

Fig. 5
Formation of O-CMC green body by vacuum-assisted lamination process

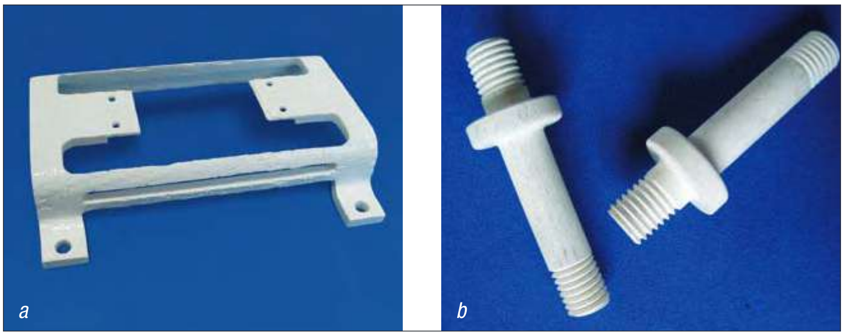

Fig. 7 a–b
O-CMC parts machined with diamond tools

Fig. 6
Fabrication of prepregs at the lab

Vacuum-assisted lamination process (method 3)

Like in method 1, infiltrated layers of fabrics are draped on a tool. Then, peel foils are put around the fabrics. The part is put into a bag which is evacuated (Fig. 5). Using this method, high fibre volume contents, high densities of the matrix and complex shapes can be realized. The technique is used to fabricate components with high complexity and very high strength values.

Fabrication of prepregs for O-CMC lamination

The lamination process (method 1 to 3) is suitable for individual items and small series production. With an increasing number of items components and increasingly demanding specifications for components, for example O-CMC parts for gas turbines, automated, reproducible and standardized production methods become a necessity. For these reasons, WPS and Fraunhofer ISC/HTL are currently developing a prepreg production process for O-CMC parts. The process allows a defined infiltration of fabrics in terms of mass and volume using an aqueous suspension of ceramic powders and organic binders. During the infiltration process the fabric is directly put between two carrier foils. The produced prepregs can be stored for several weeks at room temperature (Fig. 6).

Machining of fibre-reinforced oxide ceramic matrix composites

The classical method to machine fibre-reinforced oxide ceramic matrix composites is by using diamond tools like diamond wire saws, diamond cut-off wheels, diamond drill bits or mounted points. The methods are used to carve out arbitrary shapes or hole patterns from complex 3-dimensional components or to realise threads (Fig. 7a, b). Another option is to carve out complex shapes with smooth surfaces from thick O-CMC plates. In this case a lot of waste is produced which should be avoided if possible.

The material can also be machined by using milling cutters based on high-speed steel (HSS cutters) or polycrystalline diamond (PCD cutters) (Fig. 8). The method can be used to machine complex shapes, is faster than diamond based grinding

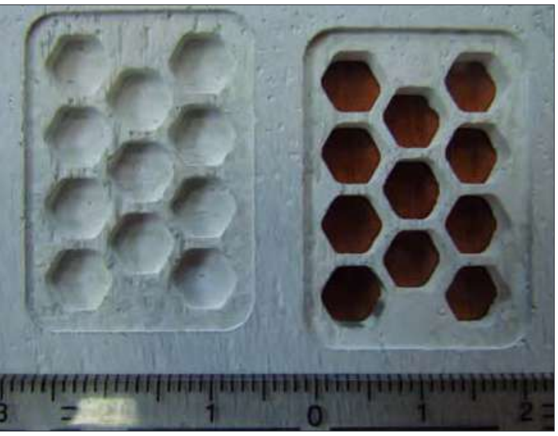

Fig. 8
Example of machining O-CMC parts with PCD cutters

Fig. 9
Example of a tube with a hole pattern done by laser machining

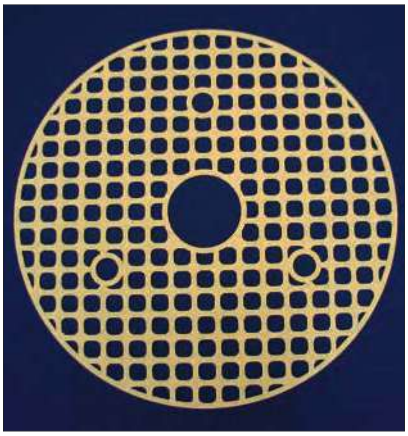

Fig. 10
Kiln furniture (diameter = 690 mm) done by waterjet machining

methods, but the surfaces are also slightly rougher.

Another method to machine O-CMC components is laser machining. It is used to realise complex hole patterns in plates and tubes in a fast and cost-effective manner (Fig. 9). The method provides high precision. In contrast to diamond grinding, laser machining can be used for large number of items.

Waterjet cutting is an alternative to laser machining (Fig. 10). Typically, an abrasive medium is added to the water to be able to cut the ceramic materials. Due to the abrasive media, the cutting line is less smooth when compared to laser cutting. Another disadvantage is the possible occurrence of material delamination due to the waterjet.

Properties of O-CMC materials

Recently, two standard high-end O-CMC materials, named Keramikblech® FW12/30 and Keramikblech® SA12 have been developed by WPS and Fraunhofer ISC/HTL (Tab. 1). Fig. 11 shows a comparison of the performance of different types of commercially available O-CMC materials.

Industrial applications of O-CMC components

O-CMC components can substitute metallic parts in high temperature processes. The advantages of using O-CMCs are

Tab. 1
Mechanical properties of standard O-CMC materials developed by WPS and Fraunhofer ISC/HTL

	CerOx AZ-N6-F Keramikblech® FW12	**CerOx AS-N7-F Keramikblech® SA12**
Manufacturing technique	Lamination & mould technique	Lamination & mould technique
Fibre type	NextelTM 610 / corundum DF11 woven fabric	NextelTM 720 / corundum-mullite EF11 woven fabric
Matrix composition	Al_2O_3/ZrO_2	Al_2O_3/SiO_2
Density [g/cm³]	2,9	2,5
Fibre volume content [%]	35-45	35-40
Open porosity [%]	25-35	30-35
3-point bending strength at RT [MPa] (DIN EN 658-3)	300-500	150-200
Interlaminar sheer strength ILS at RT [MPa] (DIN EN 658-5)	20	12

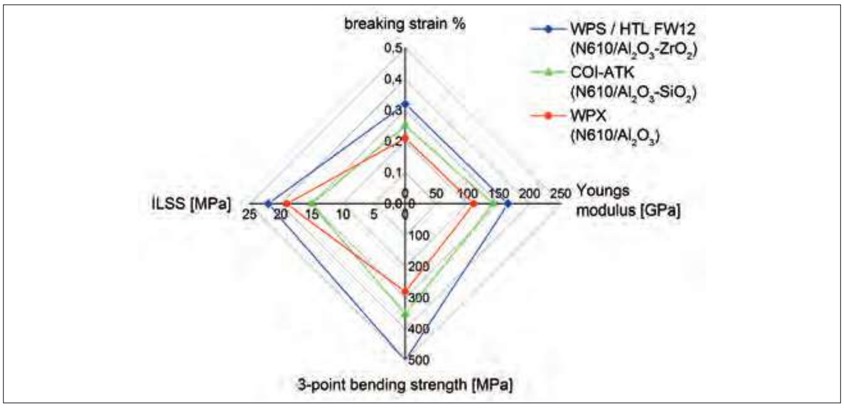

Fig. 11
Spider web comparing properties of commercially available O-CMC materials [14–16]

Fig. 12 a–c
Flame tubes: a) O-CMC flame tube under operation; b) metallic flame tube; c) metallic flame tube after 1000 h of operation; d) O-CMC flame tube; e) O-CMC flame tube after more than 20 000 h of operation

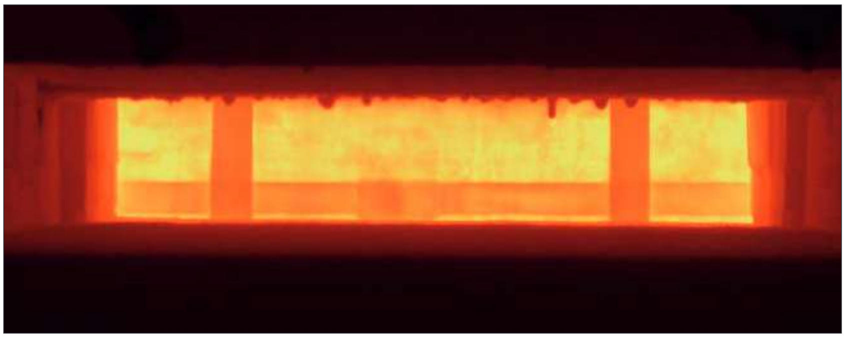

Fig. 13
O-CMC lift gate in sinter metal production plant operating at 1250 °C

weight reduction due to reduced density and mass, increase in thermal efficiency by increasing process temperatures or prolonged service lifetime and reduced maintenance costs.

The initial higher purchase costs of O-CMC components often amortize during operation bringing overall cost savings. Moreover, O-CMC components can enable high temperature processes being not possible with metallic parts (see lift gates in following sections).

Flame tubes based on O-CMC

O-CMC materials can be used for flame tubes in industrial applications as a substitute for metallic flame tubes leading to a tremendous increase in service lifetime (Fig. 12). For example, in a baking line for producing crispbread, metallic flame tubes were used that had a service lifetime of about 1000 h. The replacement of these components necessitated 6 shut-downs of the production plant per year leading to long production downtimes and huge costs. Searching for an alternative, the metallic flame tubes were exactly rebuilt by a 1 : 1 copy using O-CMC materials. The O-CMC flame tubes could be directly integrated into the production plant. The service lifetime of the O-CMC flame tubes is larger than 60 000 h. This results in enormous cost savings due to less production downtimes and lower maintenance efforts. Due to these cost savings, the higher purchase costs of the O-CMC flame tubes in comparison to the metal based counterparts charged off quickly. Also in other industrial applications O-CMC flame tubes have demonstrated largely increased service lifetimes in comparison to metallic flame tubes (Fig. 12).

Lift gate for sinter metal production plant

The potential of O-CMCs is also demonstrated in form of a lift gate in a sinter metal production plant (Fig. 13). The lift gate separates the debinding zone and the sintering zone. In the debinding zone temperatures of 600 °C and oxidizing conditions are used, whereas in the sintering zone temperatures between 1100 °C and 1280 °C and a N_2/H_2 atmosphere are used. Because of these harsh conditions, the gate could not be realised with metallic materials. Carbon/carbon composites were tested, but showed insufficient service lifetimes. A solution could be provided by building the lift gate from SiO_2-free O-CMC materials. With the O-CMC lift gate more than 1 000 000 open/close cycles have been demonstrated without interruption. For cycles times of 2 min, this means that the lift gate was used more the 40 months without interruption under these harsh conditions.

O-CMC hot gas distributers

In high temperature test rigs for testing sealings and exhaust systems for automotive applications, thin-walled and thermoshock resistant structures are needed for distributing the hot gas. Together with a thermally insulating intermediate layer, these structures are integrated in metallic frames. Hot gas with temperatures of 1200 °C produced by a fan burner is injected on one side of the distributors and is led through the structures to the test components. The flowing hot gas in the distributors simulates the gas flow in gasoline and diesel engines. When buildt completely from metallic materials, the distributors needed to be repaired several times during a 100 h test cycle because of cracked welded joints or extreme deformation of the metallic components. Using O-CMC materials for the distributors, several long time test runs were possible without any need for replacement or repair (Fig. 14).

Modular design of O-CMC components

There are many applications were a modular concept for a component or a component assembly is meaningful to minimize effects of thermal stresses. Beside the re-

Fig. 14 a–c
Hot gas distributors fabricated from O-CMC

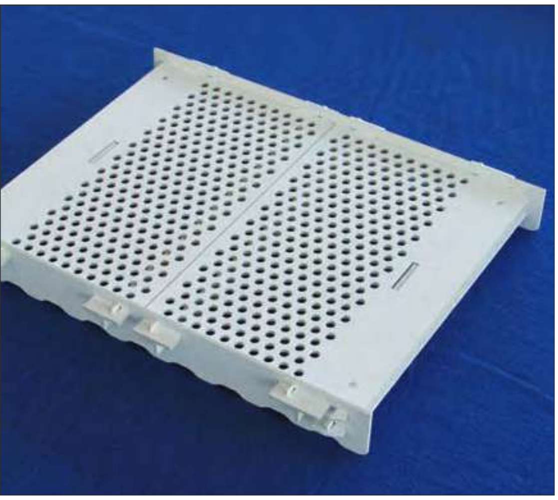

Fig. 15
O-CMC charging rack for sintering process of metallic parts

Fig. 16
Large-sized O-CMC thermal protective tube built with modular design

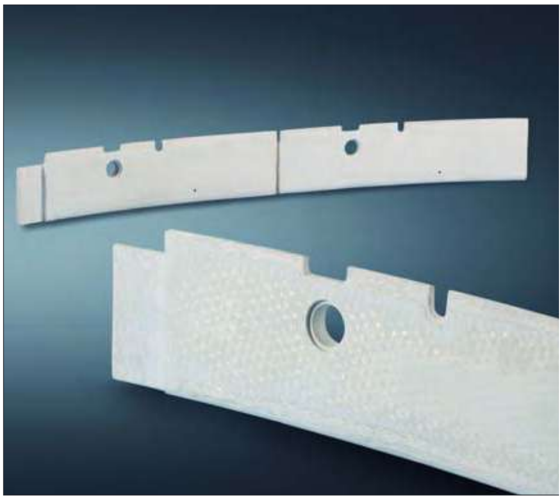

Fig. 17
O-CMC liner segment for an aero-engine

quirement of using a thin-walled, thermoshock resistant material, also the design layout is an important aspect for successful application of the components or the component assembly.

Charging racks for heat treatment processes

An example for the need of a modular component design is given by charging racks used in heat treatment processes for metallic parts with extreme cooling rates. In this case, metallic racks rapidly deform due temperature cycling. As a consequence of the deformation of the racks the automated production process is hindered because the robot cannot find the desired position for putting the parts to be heat-treated. When using carbon/carbon racks, the metal parts to be heat treated react with the carbon at high temperature leading to undesired changes of the metal parts. Oxides ceramic coatings that avoid a reaction between carbon and the metal parts can be used, but they are not longtime stable and peel off. A solution is the use of O-CMC components.

One concept is to use plates or trays that are placed on the carbon/carbon racks or the rack is fully built from O-CMC material (Fig. 15).

Large-sized thermal protective tubes

The modular concept is also chosen when the components are so large that they cannot be processed with textile fabrics in one part or a sintering furnace large enough is not available. An example is a thermal protective tube with a length of 3,3 m, a diameter of 250 mm and a wall thickness of 3 mm (Fig. 16). The tube was assembled from tube segments of 850 mm length by using bushings. The single segments were cemented to the bushings and additionally interlocked by bolts. The O-CMC protective tube replaced a monolithic SiC tube, which failed too often under operation. In contrast to the SiC tube, the O-CMC tube could be installed without crane by only one person due to its low weight.

O-CMC liner segment for aero-engines

In the framework of the EU project Clean-Sky, WPS and Fraunhofer ISC/HTL developed and produced a liner segment for the low pressure exhaust area of an aero-engine together with MTU Aero Engines/DE (Fig. 17). This O-CMC part serves as a thermal insulation and impact tolerant housing. The prototype is based on the O-CMC material Keramikblech® FW12. The part was manufactured near net-shape by combining several production techniques like lamination and mould pressing. Only the cavities were drilled and the steps within the holes were grinded. In beginning of 2015 MTU Aero Engines made a successful application test of these liner segments within an aero-engine. In the second half of 2015 the first hot gas ground-based test of the liner segment in an aero-engine will be started.

Summary

O-CMC materials combine the excellent mechanical and thermal properties of ceramics with a damage-tolerant quasi-ductile fracture behaviour making them attractive materials for the application in high temperature processes. Possible benefits of substituting metallic parts by O-CMC components are weight reduction, increased thermal/energy efficiency and prolonged service lifetime. O-CMC components like flame tubes, lift gates or charging racks have demonstrated their potential in various industrial high temperature applications. O-CMC parts for gas turbines are currently developed and tested.

References

[1] Raether, F.: Ceramic matrix composites – an alternative for challenging construction tasks. Ceramic Applications **1** (2013) [1] 45–49

[2] Steyer, T.E.: Shaping the future of ceramics for aerospace applications. Int. J. Appl. Ceram. Technol. **3** (2013) [10] 389–394

[3] Jefferson, G.; et al.: Oxide/oxide composites with fiber coatings. In: Krenkel, W. (Ed.). Ceramic Matrix Composites. Weinheim 2008, 187–204

[4] Keller, K.; Jefferson, G.; Kerans, R.: Oxide-oxide composites. In: Bansal, N. (Ed.). Handbook of Ceramic Composites: New York 2005, 377–421

[5] Zawada, L.P.; et al.: Characterization and high-temperature mechanical behavior of an oxide/oxide composite. J. Amer. Ceram. Soc. **6** (2003) [86] 981–990.

[6] Zok, F.W.: Developments in oxide fiber composites. J. Amer. Ceram. Soc. **11** (2006) [89] 3309–3324

[7] Bunsell, A.R.: Oxide fibers, in: Bansal, N. (Ed.). Handbook of Ceramic Composites. New York 2005, 3–31

[8] Schmuecker, M.; Mechnich, P.: All-oxide ceramic matrix composites with porous matrices. In: Krenkel, W. (Ed.). Ceramic Matrix Composites. Weinheim 2008, 205–229

[9] Chawla, K.K.: Interface. In: Chawla, K.K. (Ed.). Ceramic Matrix Composites. Boston, MA, 2003, 139–167

[10] Koch, D.: Microstructural modeling and thermomechanical properties. In: Krenkel, W. (Ed.). Ceramic Matrix Composites. Weinheim 2008, 231–259

[11] Kaya, C.; et al.: Development and characterisation of high-density oxide fibre-reinforced oxide ceramic matrix composites with improved mechanical properties. J. Europ. Ceram. Soc. **9** (2009) [29] 1631–1639

[12] Mattoni, M.A.; et al.: Effects of matrix porosity on the mechanical properties of a porous-matrix, all-oxide ceramic composite. J. Amer. Ceram. Soc. **11** (2001) [84] 2594–2602

[13] Levi, C.G.; et al.: Processing and performance of an all-oxide ceramic composite. J. Amer. Ceram. Soc. **11** (1998) [81] 2077–2086

[14] Data sheet from COI-ATK, URL: http://www.coiceramics.com/pdfs/3%20oxide%20properties.pdf; 20.07.2015

[15] Data sheet "WHIPOX-A" from WPX Faserkeramik GmbH, URL: http://wpx-faserkeramik.de/downloads/; 20.07.2015

[16] Göring, J.; Hackemann, S.; Schneider, H.: Oxid/Oxid-Verbundwerkstoffe: Herstellung, Eigenschaften und Anwendungen. In: Krenkel, W. (Ed.) – Keramische Verbundwerkstoffe. Weinheim 2002, 122–148