CMC MATERIALS AND BIOMORPHIC SiSiC FOR ENERGY APPLICATIONS

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ABSTRACT

Ceramic materials offer a high thermal and chemical stability and are therefore potential candidates for high temperature applications in severe environments, where metals can not longer be used. In future energy applications, high process temperatures > 1200 °C are required to increase the efficiency, to lower the fuel consumption, and to decrease the emissions. In order to achieve these goals, novel ceramic materials and manufacturing processes for complex structures are under development.

1. INTRODUCTION – CERAMIC MATERIALS FOR ENERGY APPLICATIONS

At DLR, three different classes of ceramic materials have been developed for the use in energy applications: Oxide/oxide and non oxide Ceramic Matrix Composites (CMC) as well as monolithic SiSiC materials.
The use of CMCs as liner material for gas turbines is a key concept to increase efficiency and reduce emissions. Replacement of metallic components by thermally stable ceramics allows reducing the amount of cooling air significantly. This will not only increase overall efficiency but allows lean combustion concepts. Moreover, ceramic components are required for future turbine technologies based on hydrogen combustion.
High temperature ceramic heat exchangers (HX) either in tube-in-tube or plate type design are promising candidates for the use in harsh corrosive and combustion environments. In contrast to tubes, plate-type HX with integrated flow channels can contribute to an increasing efficiency of the heat transfer. Those HX can be used for heat recovery processes, thermo chemical splitting reactions or within externally fired combined cycles.
For heating and drying processes porous burners can be used due to their high radiation output. The typically high brittleness and low thermal shock resistance of monolithic ceramics could be overcome by the build up of thin walled, highly porous SiSiC structures, offering structural integrity even at high temperature gradients, caused by extreme heating and/or cooling rates or by locally inhomogeneous temperature distributions inside the structure of such burners.
The main aspect of design and dimensioning of CMC combustion liners is the integration of CMC components into metallic structures. Therefore the different thermal expansion of the CMC components and the metallic support structure has to be taken into account carefully. Based on an anisotropic material model and a failure criterion suitable for the CMC material, Finite Element Analysis supports the design of the liner.

2. CMC HOT GAS LINERS FOR GAS TURBINES

Combustor materials require sufficient resistance to high temperature corrosion and thermal stability for operating times > 10,000 h at maximum surface temperatures of 1300 °C. A high resistance to cyclic fatigue and creep along with non-brittle, damage tolerant fracture behavior is mandatory. All-oxide ceramic matrix composites can meet these requirements and hence are promising materials for combustion liners in aircraft and stationary gas turbines with reduced cooling air consumption.
In institute-spanning, interdisciplinary projects oxide CMCs are being developed and tested for aircraft combustor liners. The main aim of these projects is the cooling air reduction in gas turbines, along with the development of specific cooling concepts for the ceramic composites having very low thermal conductivity. Performance was tested in model combustion chambers by the DLR Institutes of Propulsion Technology and Combustion Technology. The attachment concepts for the hot ceramic tiles onto the cold metallic support structure were developed at the DLR Institute of Structures and Design..
The CMC liner is composed of single curved shingles screwed together at radially oriented brackets (Fig. 1). The resulting CMC structure is positioned by the brackets in the metallic structure. However, both structures, the CMC liner and the metallic housing, are able to expand radially freely at any temperature during service.

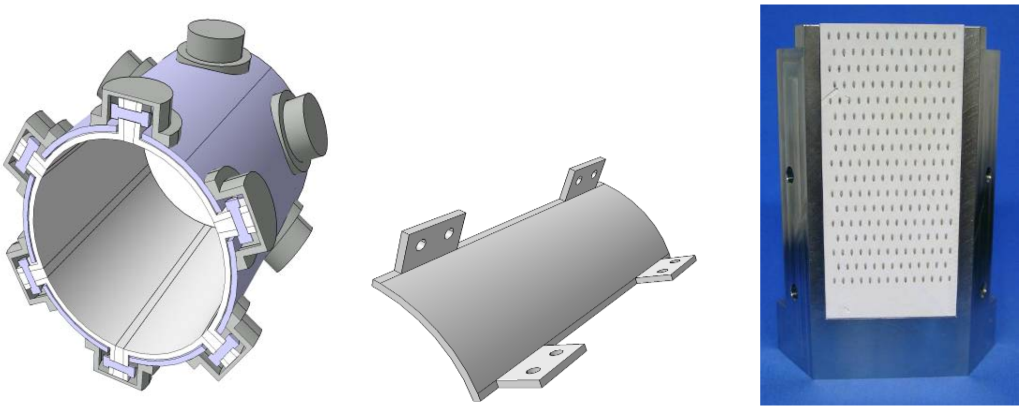


Figure 1. Schematic view of a design concept for CMC combustion chambers, based on joined segments (left and center). WHIPOX combustion chamber shingle with laser drilled cooling channels for rig testing (right).

At the DLR Institute of Materials Research an all-oxide CMC (WHIPOX = wound highly porous oxide) consisting of alumina fibres Nextel 610 or mullite based fibre (Nextel 720, both 3M) and an alumina or mullite matrix, respectively, has been developed in recent years [1, 2].
Mullite-based CMCs typically offer higher creep stability than alumina-based composites but display lower thermal conductivity. Lower thermal stability of alumina-based materials, however, can be accepted, since service temperature is significantly lower for these materials as a result of the better cooling efficiency. Therefore material development was focused on alumina CMCs, i.e. Nextel 610 fibres and virtually pure alumina matrices.
The chemical stability of mullite and alumina is a serious issue for long-term application of oxide/oxide CMCs in combustion environments due to the presence of water-vapour rich (exhaust) gases. Under highly dynamic flow conditions of powerful industrial burners and

combustors, mullite and alumina are prone to decomposition and volatilization. The application of chemically resistant environmental barrier coatings (EBCs) is considered a solution for the corrosion problem. Due to its thermodynamic compatibility and low recession rate up to high temperatures (>1400°C), yttria stabilized zirconia (Y-ZrO_2, YSZ) is another attractive EBC material for alumina- and mullite-based CMCs. Low thermal conductivity of ZrO_2 coatings additionally provides thermal protection. At DLR, different types of ZrO_2-based coatings were developed for WHIPOX-type oxide/oxide CMCs [2].
Mechanical tests using bending, tensile and compressive load conditions including the determination of elastic constants of the orthotropic material were carried out under room and high temperature conditions. For creep tests in tension four testing devices were established and creep tests longer than 6,000 h were carried out with different CMC qualities. The WHIPOX CMCs show much better creep resistance compared to state-of-the-art metallic combustor materials.
Calculations and tests in a high pressure cooling rig shortly will demonstrate the reduction of cooling air using the all-oxide CMC WHIPOX as thermal protection system in combustion chambers.

At the DLR Institute of Structures and Design the activities are focused on the development of non-oxide CMC materials and structures for hot gas liners in gas turbines. Within the "Engine 3E" project, which was financed through the German Aviation Research Programme (Luftfahrtforschungsprogramm), the first investigations on the development of SiC long fibre reinforced ceramic tiles for use in the combustion chamber of an aero engine started in 1995. Thereby highly efficient gas turbines with staged combustion were in the focus, leading to demanding operation conditions: The material used must have suitable properties which withstand long operating times of up to 20,000 hours, at high temperatures (1300-1600 °C) and in high corrosive or oxidative stress environment.
The application conditions require the use of fibre reinforced materials which, in addition to a high thermal and oxidative stability, also have sufficient processability through the availability of textile products. Carbon fibres are not suitable due to their low oxidation resistance, because a long-term oxidation protection under the given transient operating conditions with high temperature gradients (thermal shock) is not possible. Therefore research studies were conducted with commercially available SiC fibres (e.g. Nicalon NL 207, Tyranno Lox M). These fibres demonstrate a good thermal and chemical resistance and are available as drapeable 2D fabrics. Using the Liquid Silicon Infiltration process (LSI), composites were produced, whose matrices were largely free of unreacted carbon. The precursors used were chosen so that their remaining shares of carbon after pyrolysis could be completely converted to silicon carbide during the siliconization step, or later removed via oxidation. Due to their limited thermal resistance and their tendency to recrystallize at elevated temperatures, the implementation of the SiC fibres under normal conditions of the LSI process, would have lead to complete fibre degradation. Accordingly, the conditions of siliconization (temperature, holding time) as well as the porosity and its distribution within the matrix had to be adjusted. By varying the temperature of pyrolysis or fibre pretreatment, microstructures were realized which enabled a successful conversion to so-called SiC/C-SiC materials.
The prequalification of these materials was carried out by static and cyclic oxidation tests at 1200-1300 °C. First test components (80 x 30 x 3 mm) were produced (Fig.2) and successfully tested on the high pressure sector test rig at DLR. The test conditions chosen - 20 cycles at 20 bar, approximately 1200 °C, in air for a total duration of 4 hours - are representative for operating conditions.

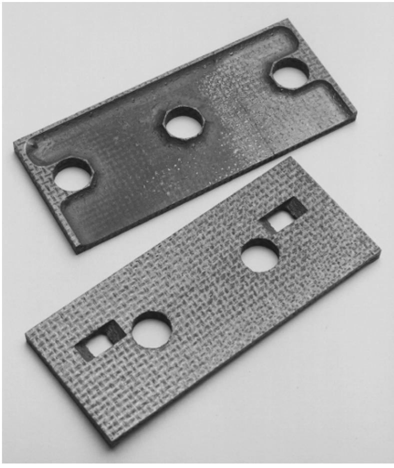


Figure 2. SiC/C-SiC combustion chamber shingles for rig tests, manufactured via LSI.

Due to the fact, that SiC fibres without coating were used, the fibres were partially attacked by the highly reactive Si during siliconization. The resulting SiC/C-SiC material was characterized by low fracture toughness and damage tolerance as well as by a high brittleness. Currently, new SiC/SiC materials based on high temperature resistant SiC fibres, like Tyranno SA, are in development. To protect the fibres during the LSI process and to obtain a weak fibre matrix interphase the fibres are PyC coated via rapid CVI.

3. HIGH TEMPERATURE HEAT EXCHANGERS

In the scope of the European project "Prediction of the Lifetime Behaviour for C/C-SiC Tubes as High and Ultrahigh Temperature Heat Exchangers" (HITHEX, CEC contract No. G5RD-CT-2000-00218) ceramic tubular components have been manufactured and tested. These tubes shall be used in bayonet type heat exchangers (HX) (Fig. 3), e.g. in the Externally Fired Combined Cycle (EFCC) processes. For the long term use, the hot gas turbine must be isolated from the combustion gases by integrating an HX system. The ceramic HX should be creep resistant, gas-tight, thermo-shock resistant and stable against hot gas corrosion and oxidation at temperatures of about 1200-1400 °C. Ceramic HX tubes made of C/C-SiC were already tested in coal combustion chambers. These tests have shown that the attack of water vapour and coal ashes at high temperatures limits the lifetime of the HX components. The corrosion of the uncoated CMC was mainly due to the presence of metals like iron or alkali metals like sodium. When liquid coal slag comes in contact with the surface, silicides or silicates are formed and especially attack the SiC matrix. On the other hand samples with an applied multilayer BoraSiC®-cordierite outer surface coating are much more resistant. The corrosion of the ceramic components by water vapour can be reduced by such improved environmental barrier coatings (EBCs) [3].
Silicon melt infiltrated and gas-tight C/SiSiC is one favourite material for the development of an inexpensive compact HX in plate design (Fig. 3) for the thermo chemical hydrogen production. The compact offset fin plate heat exchanger concept has been developed to meet the functional and cost goals, which will serve as the intermediate heat-exchanger (IHX) to transfer high temperature heat from a helium-cooled high temperature nuclear reactor to a liquid salt intermediate loop, which couples to hydrogen production loops. The IHX uses offset fin (OSF) structures with fin widths and heights in the mm scale. The de-

tailed local and global thermal mechanical stress analyses show that the OSF design can tolerate large pressure and temperature difference from two fluid sides. Leak-tight pyrolytic carbon coatings have been successfully applied on C/SiSiC specimens and excellent helium hermeticity was obtained [4].

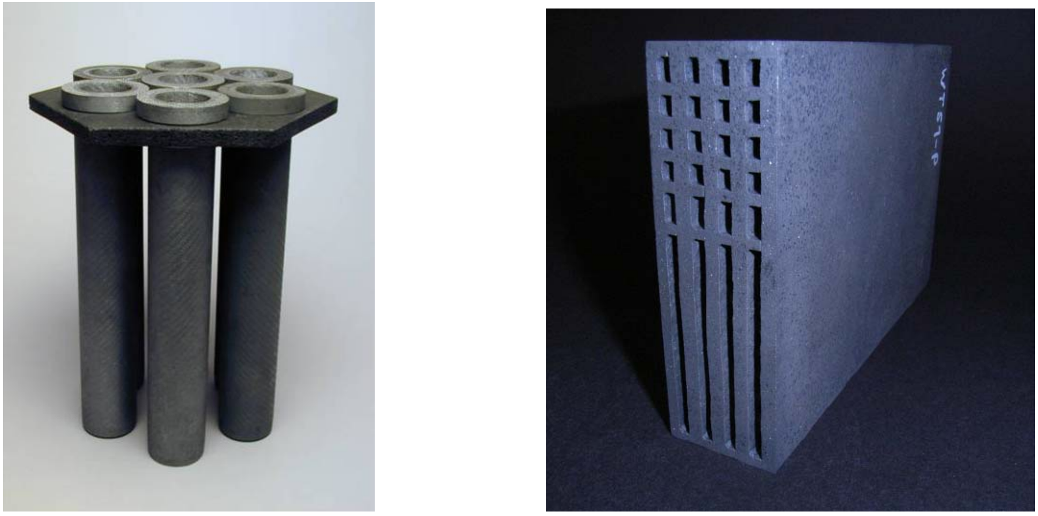
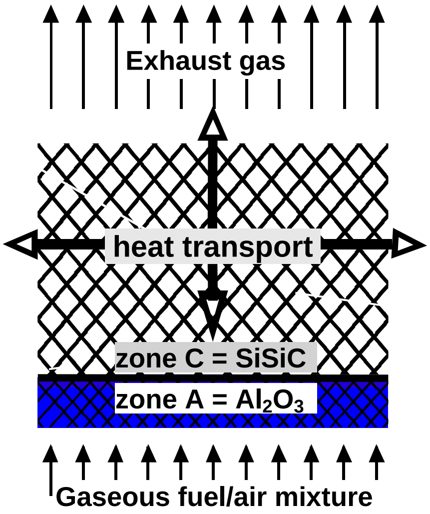


Figure 3. Bayonet type heat exchanger assembly (left). Prototypical ceramic HX stack in plate design (right)

4. RADIATION HEATERS BASED ON HIGHLY POROUS SiC BURNERS

For heating and drying purposes, e.g. in paper industry, ceramic porous burners are currently under development. The porous burner technology is based on the stabilization of combustion reactions within an inert open cell porous ceramic structure (Fig. 4). The materials should be stable against thermal cycling (thermal gradient > 100 K/s) and active oxidation. In comparison to conventional free flame burners the combustion in porous structures offers exceptional advantages, e.g. low emissions, high power modulation range, small scale sizes and high radiation output. Within the German funded BMWi-project CERPOR (Optimization of ceramic components for the porous burner technology, FKZ 16INO182) degradation mechanism were investigated and the results were used to create novel ceramic structures with an improved durability.
The most promising material for the combustion area (zone C) is Si-infiltrated SiC, which should have a pore size distribution of about 8-10 ppi (pore diameter ~3 mm) so that lateral flame propagation is possible and the combustion is stabilized. For the fabrication of such porous SiSiC ceramics DLR carried out a new technology based on C/C sheets and lamellae. These basic materials can be combined to lightweight (porosity ~80 Vol.-%, density ~0.6 g/cm³) 3D stacks. Through the variation of the amplitude and number of lamellae per inch, the porosity and orientation of the pore channels could be tailored in a wide range. Best results from durability tests were obtained with structures, which are composed of oriented pore channels. Suitable structures should have angles (α) of about $\alpha = 50 \pm 10°$. The results from burner rig tests (Fig. 4) with improved components are very promising, since no significant oxidation or degradation could be observed after 1.939 h and 10.800 start-ups [5]. From the industrial point of view a lifetime of about 3 years and some thousands cycles are required and probably can be fulfilled by these structures.



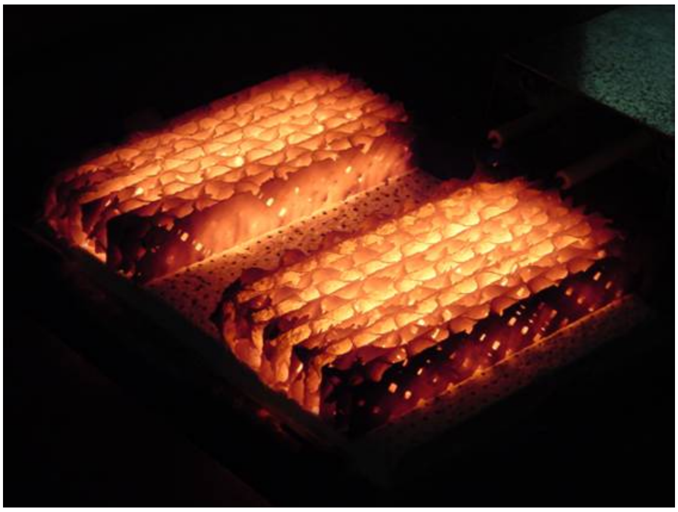


Figure 4. Schematic setup of a porous burner for drying and heating purposes (left). 3D cardboard like ceramic SiSiC structure on the test bench at 1400 °C (right)

5. SUMMARY AND OUTLOOK

At DLR, oxide and non oxide CMC as well as not fibre reinforced SiSiC materials and structures have been developed successfully for energy applications. In first rig tests.WHIPOX materials and also nonoxide SiC/C-SiC materials showed a high potential for the use as combustion chamber shingles in gas turbines, due to typical CMC properties like high temperature and thermal shock resistance.

C/C-SiC tubes for high temperature heat exchangers in coal combustion chambers could withstand highly aggressive environments including water vapour and liquid coal slags, especially coated with multilayer EBC based on B_4C, SiC and Cordierite.

Thin walled structures made of C/SiSiC and SiC materials based on biocarbon and carbon/carbon preforms showed excellent long term stability in porous burner systems and are in development for high temperature heat exchangers in plate design.

For combustion chamber shingles, future work will be focused on environmental and thermal barrier coatings for oxide and nonoxide CMC, to obtain long term stability and to increase service temperatures and overall efficiency. Additionally, CMC materials based on newly developed nonoxide fibres, like SiBNC are a main topic. Intensive testing at realistic conditions will be necessary for further development and a future integration of CMC materials in gas turbines. At DLR an interdisciplinary team of scientists in different institutes are working together in internal programmes as well as in close cooperation with potential industrial users. Thereby the whole spectrum including material research, structural design, component manufacturing and rig testing as well as quality assurance and non destructive testing are available for a goal oriented development.

References:

1. J. Göring, B. Kanka, M. Schmücker, H. Schneider, A Potential Oxide/oxide Ceramic Matrix Composite for Gas Turbine Application, Proc. ASME / IGTI Turbo Expo; 2003

2. M. Schmücker, P. Mechnich, All-Oxide Ceramic Matrix Composites with Porous Matrices, in W. Krenkel (ed.) "Ceramic Matrix Composites, Fibre-Reinforced Ceramics and their application" Wiley-VCH, Weinheim, 2008, 205-229

3. J. Schmidt; J. Schulte-Fischedick; E. Cordano, C. Mao, V. Liedtke, R. Fordham: CMC tubes based on C/C-SiC with high oxidation and corrosion resistance, Proceedings of the 5th international conference on high temperature ceramic matrix composites, ed. by M. Singh, R. Kerans, E. Lara-Curzio, R. Naslain, published by the American Ceramic Society, p. 531-536, 2004

4. P. Peterson; H. Zhao; F. Niu; W. Wang; J. Schmidt; J. Schulte-Fischedick: Development of C-SiC ceramic compact plate heat exchangers for high temperature heat transfer applications, Proc. of AIChE Annual Meeting,12.-17. November, San Francisco, 2006

5. J. Schmidt; M. Scheiffele: Fabrication and Testing of corrugated 3D SiSiC ceramics for porous burner applications, Industrial Ceramics, Vol. 27, No. 2, S. 127-130, 2007