Ceramic Matrix Composites – an Alternative for Challenging Construction Tasks

Ceramic Matrix Composites (CMC) are extremely valuable for applications with demanding thermal and mechanical requirements. CMC have been developed to achieve a damage tolerant quasi-ductile fracture behavior and to maintain all other advantages of monolithic ceramics at high temperatures.

Ceramic matrix composites (CMC) are produced from ceramic fibers embedded in a ceramic matrix. Various ceramic materials, oxide or non-oxide, are used for the fibers and the matrix. Also a large variety of fiber structures is available. So properties of CMC can be adapted to special construction tasks. They are especially valuable for components with demanding thermal and mechanical requirements.

Motivation

When new components are developed, usually Finite Element simulations are used to check the loads during operation and to optimize geometry. Databases are available, which allow a quick selection of the optimum material considering material properties, cost and process requirements [1]. If complex requirements are to be fulfilled, different material properties, which contribute to the same requirement can be combined to form a material index. Different requirements can lead to conflicting objectives, which are handled by constructing trade-off surfaces in material index charts [2].

As an example, a lightweight and stiff plate is considered which shall be used at temperatures above 600 °C. Brittle fracture of the plate is not allowed. Such plates can be used as material support in heat treatment processes. The first requirement leads to a minimization of specific weight ρ and a maximization of flexural modulus E. The respective material index which combines both properties is the ratio $I = \rho/E^{1/3}$. The best material for the first requirement is the material with the smallest index I. To fulfill the second requirement, i.e. to avoid brittle fracture, the fracture energy shall be maximized. Fig. 1 shows a selection of those materials – among a database of 4000 materials – which have promising

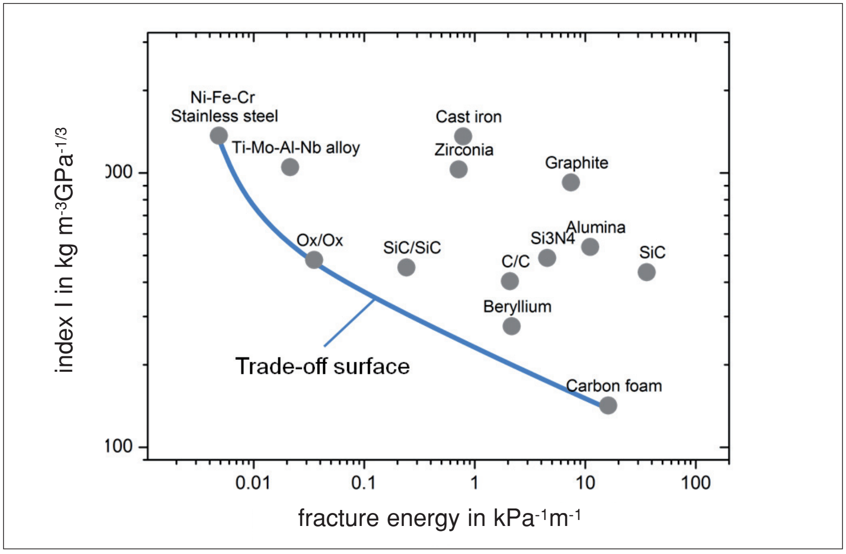

Fig. 1
Light-weight materials with maximum stiffness and maximum fracture energy selected from [1]. CMC dominate in a broad range of intermediate fracture energies and indices I, whereas stainless steel and Ni based alloys dominate at high fracture energies and carbon foam is superior for extremely small indices I

Keywords
Ceramic matrix composites (CMC), ceramic slurry infiltration, chemical vapor infiltration, alumina fibers, silicon carbide fibers

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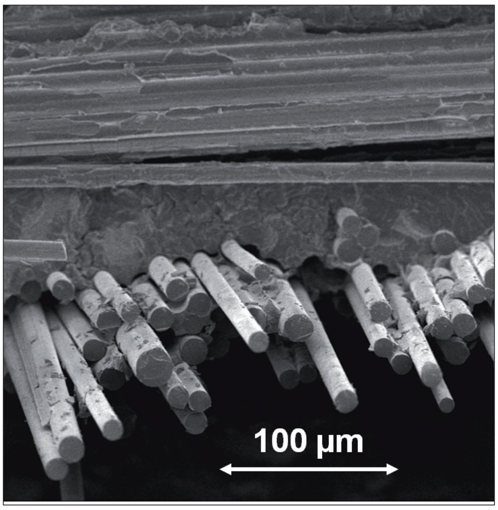

Fig. 2
Fracture surface of a CMC with fiber pull-out

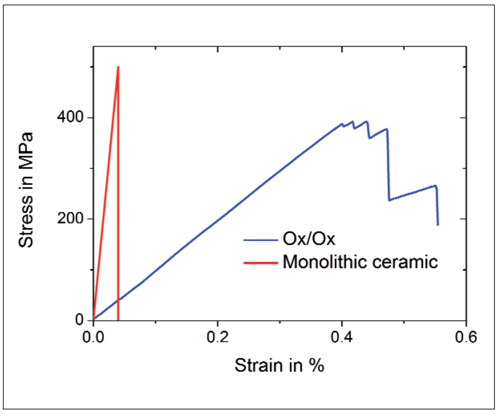

Fig. 3
Stress-strain diagram during fracture of an Ox/Ox CMC – indicated is the respective curve for monolithic ceramics

properties in terms of these two requirements. The trade-off surface is shown as well. If the focus is on high fracture energy customary metals like stainless steel can be selected, but if greater weight is attached to the first requirement, CMC materials like SiC/SiC and Ox/Ox are superior. With customary materials, i.e. polymers, metals and monolithic ceramics typical limitations occur in operational behavior. Polymers are rather weak and there use is limited to low temperatures. Apart from the refractory metals, which are expensive and brittle, metals can be used up to 1000 °C – some special alloys up to 1200 °C. A disadvantage of these metals is their low creep resistance and their susceptibility to oxidation. Monolithic ceramics can be used up to very high temperatures in the range of 1000 °C to 2000 °C. They have an excellent creep resistance and show high stiffness. The main disadvantage of monolithic ceramics is their low fracture toughness, which leads to brittle fracture and detrimental thermal shock resistance. CMC have been developed to achieve a damage tolerant quasi-ductile fracture behavior and to maintain all other advantages of monolithic ceramics.

CMC types and properties

There are many different types of CMC. Classification is usually done in terms of fiber and matrix materials – separated by a slash. E.g., C/SiC is a CMC made of carbon fibers and a silicon carbide matrix. Non-oxide fibers used in CMC are mainly made of carbon or silicon carbide, oxide fibers of alumina, mullite or silica. Non-oxide matrices are mostly silicon carbide, carbon or mixtures of silicon carbide and silicon. Oxide matrices consist of alumina, zirconia, mullite or other alumino-silicates. Usually oxide fibers are combined with oxide matrices and non-oxide fibers with non-oxide matrices. Thus, the main CMC types are C/C, C/SiC, SiC/SiC and Ox/Ox, where Ox represents one of the oxide materials mentioned previously [3]. In addition to matrix and fibers, most CMC contain pores – usually between 1 and 30 %.

CMC are further classified according to their fiber structure, which has a large impact on material properties. Ceramic fibers have a tensile strength between 1000 MPa and 7000 MPa – about an order of magnitude higher than the strength of the matrix. Likewise, the elastic modulus of the fibers, typically between 200 GPa and 900 GPa is higher than the elastic modulus of the matrix. The fiber type has to be carefully selected. Fiber degradation occurs between 1000 °C and 2100 °C depending on fiber material and fiber quality. It controls the maximum service temperature of the CMC. Continuous or short fibers are used for CMC manufacture. Fibers can be oriented unidirectional or planar to achieve special anisotropic properties. Woven or unwoven fabrics can be used, whereby textile techniques like breading allow for 3D structures with complex load characteristics.

The interaction between fibers and matrix during fracture provides the high fracture toughness of CMC. This interaction is carefully designed using two complementary concepts [4, 5]:

- Weak interface concept: the fibers are coated to reduce adhesion to the matrix. During fracture fibers are pulled out of the matrix and absorb fracture energy (Fig. 2).
- Weak matrix concept: the stiffness of the matrix is adjusted much lower than the stiffness of the fibers. During fracture cracks arise in the matrix and are deflected at the fibers, thereby increasing the fracture surface and elongation at break (Fig. 3).

Tab. 1 shows material properties of typical CMC. Due to anisotropy and different CMC qualities a broad range is covered [1, 4]. Note that the properties cannot be arbitrarily combined within the given range. The composition and microstructure of CMC components has to be carefully designed according to the respective use. Compared to metals, the most important advantages of CMCs are a significantly smaller density, which is important for lightweight constructions, and a much higher maximum operating temperature. For many applications also its resistance to wear and aggressive chemicals is important. Costs of CMC strongly depend on composition and manufacturing route. They vary between some hundred and some thousand EUR/kg. So, CMC are expensive compared to other materials and the high price has to pay off by longer service life or by a unique performance in value-added products.

If non-oxide CMC components are used in oxidic atmospheres at high temperatures, the components can be protected from oxidation using environmental barrier coatings (EBC). Compared to carbon, silicon carbide is less sensitive to oxidation because it forms a protective layer of silicon dioxide. In addition to the EBC, non-oxide fibers used in CMC are often protected by a fiber coating to avoid attack of oxygen molecules diffusing through the pore channels of the matrix.

Applications

CMC are used in many high temperature processes. They have a very high thermal shock and creep resistance, which enables designs with large mechanical and thermal loads. As an example, Fig. 4 shows some

Tab. 1
Material properties of typical CMC at ambient temperature, the range reflects minimum and maximum of the respective property in different directions or for different CMC qualities (Ox/Ox covers CMC with alumina fibers and alumina or alumino-silicate matrix) [1,4]

Property	Unit	SiC/SiC	C/SiC	C/C	Ox/Ox
Fiber content	vol.-%	40–60	10–70	40–60	30–50
Porosity	vol.-%	10–15	1–20	8–23	10–40
Density	g/cm^3	2,3–2,9	1,8–2,8	1,4–1,7	2,1–2,8
Tensile strength	MPa	150–360	80–540	14–1100	70–280
Bending strength	MPa	280–550	80–700	120–1200	80–630
Strain-to-failure	%	0,1–0,7	0,5–1,1	0,1–0,8	0,12–0,4
Young's modulus	GPa	70–270	30–150	10–480	50–210
Fracture toughness	$MPa \cdot m^{1/2}$	25–32	25–30	5,7–,3	58–69
Thermal conductivity	W/m·K	6–20	10–130	10–70	1–4
Coefficient of thermal expansion	ppm/K	2,8–5,2	0–7	0,6–8,4	2–7,5
Maximum service temperature	°C	1100–1600	1350–2100	2000–2100	1000–1100

Ox/Ox hot gas valves used to control the gas flow in gas fired high temperature furnaces. Compared to metallic valves, the service life of the CMC components is much longer and over-compensates their higher purchasing costs. CMC components, used as batch carriers in metal hardening are another example (Fig. 5). These C/C-grids have small heat capacity – thus reducing energy consumption and allowing fast heating and cooling cycles. Different from metallic batch carriers, they show no creep deformation providing much longer service life. Other applications of CMC in high temperature processes are flame tubes, heat exchangers, protective tiles, and various high temperature holders.
The high wear resistance and the favorable friction properties of CMC lead to applications as sliding contact bearings, brakes and clutch-plates. As an example Fig. 6 shows a C/SiC brake disk used in passenger cars. It has a life time longer than the life time of the car and a much smaller weight than customary brake disks made of cast iron. So, the higher costs of the CMC brake disks are compensated by reduced fuel consumption and elimination of service costs for the renewal of the brake disks.

Fig. 4
Hot gas valve made of Ox/Ox CMC used to control gas flow in gas fired furnaces (source: Walter E.C. Pritzkow Spezialkeramik)

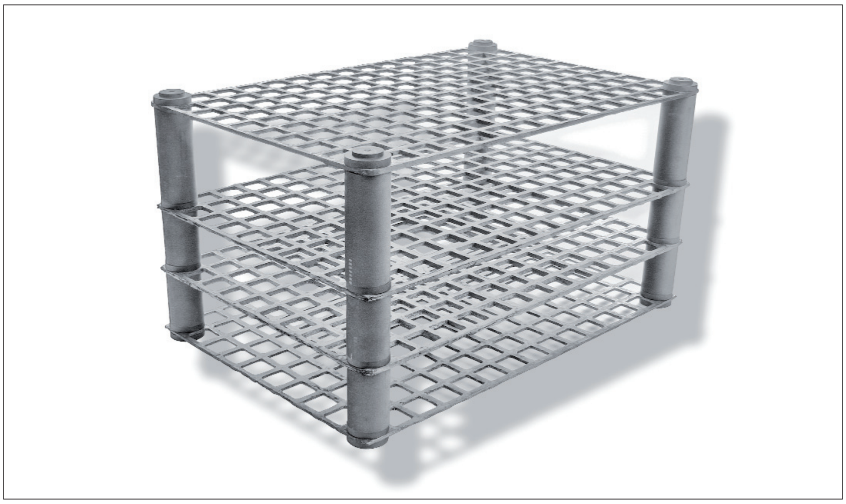

Fig. 5
C/C batch carriers for metal hardening (source: Schunk group)

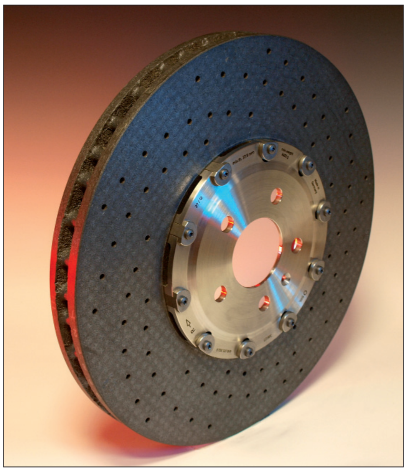

Fig. 6
Brake disk made of C/SiC CMC (source: Brembo SGL Carbon Ceramic Brakes)

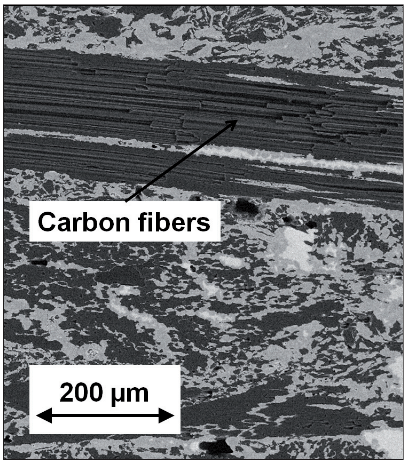

Fig. 7
Structure of a short fiber bundle reinforced C/SiC CMC

CMC can also be used in extreme environments like gas turbines. Operating temperatures of gas turbines have been increased to improve energy efficiency. Moreover, new designs of the turbines require blades with very high rotational speeds. The lightweight and high-temperature properties of CMC are ideal for this application. Tests have already been performed in working gas turbines and first products shall be ready in 2016 [6]. Other CMC applications in aerospace are body flaps, shrouds and thermal protection systems.
The anisotropic thermal expansion of C/SiC can be used to design components with zero thermal expansion in one or two directions of space. These components are used as support in precision optics, e.g. in satellite communication or microelectronics, or for calibration of dimensional control tools.

CMC manufacturing
CMC are produced using ceramic fibers in a thickness range of 3 to 20 µm. The small fiber diameters provide flexibility of the fibers during further textile processing. Fibers are usually manufactured as yarns with some hundreds up to several ten thousands of filaments. Prices increase from carbon fibers over oxide ceramic fibers to silicon carbide fibers from 20 EUR/kg for the cheapest carbon fibers up to 10 000 EUR/kg for the most expensive silicon carbide fiber type. CMC preforms are produced from the fibers either by cutting the yarns and forming short fiber bundles (Fig. 7) or by textile structuring of continuous fibers with techniques like weaving, knitting and braiding (Fig. 8). Also non-woven structures like uniaxial or multiaxial fabrics, fleeces and felts are used. Some non-woven structures can also be produced directly from short fibers, which are made by disk spinning – avoiding the more expensive nozzle spinning and cutting of endless fibers. The preforms have a one-, two- or three-dimensional fiber structure. This structure controls the anisotropic properties of the final CMC. It can be designed to bear exactly the anisotropic loads expected during use of the CMC components.
The matrix material is introduced into the preform via a fluid phase – either gaseous or liquid. Liquids are infiltrated as slurry with ceramic particles, as polymers or as metallic melts. Usually silicon is used for metallic melt infiltration. Silicon melts at 1414 °C, is soaked into the preform by capillary forces, and reacts with carbon in the preform to form silicon carbide. This process is called liquid silicon infiltration (LSI).
Alternatively, polymers are introduced as organometallic compounds either in dissolved or molten state to achieve sufficient low viscosities. External pressure can support the infiltration. During a subsequent heat treatment the polymers are pyrolysed and the final structure of carbon or silicon carbide is formed. Since the volume of the polymers decreases during pyrolysis, this so called polymer infiltration and pyrolysis process (PIP) has to be repeated typically 3 to 10 times to achieve high densities of the final CMC.
As a further variant using liquids, slurries with ceramic particles are infiltrated into the preforms at ambient temperatures. This impregnation allows a quasi ductile manufacturing of complex shapes (Fig. 9) analogous to the processing of sheet metals. After drying of the preforms, a heat treatment is required to obtain enough strength within the ceramic matrix by a sintering process. Usually sintering is interrupted in the initial stage because excessive shrinkage of the matrix would lead to cracks in the CMC structure. Ceramic slurry infiltration (CSI) leads to matrices with an open porosity between 20 and 50 %.
Unlike using liquids, the matrix can be introduced via a reactive gas. This chem-

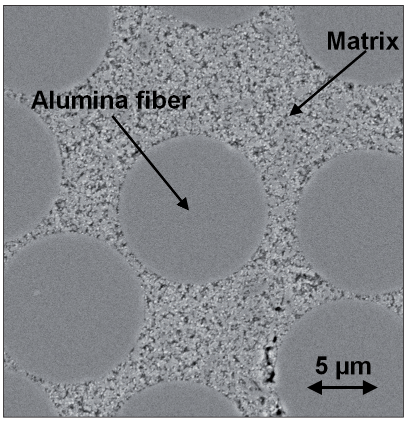

Fig. 8
Cross section through an Ox/Ox CMC reinforced by a 2D woven fabric

Fig. 9
Distributor for testing exhaust systems made of Ox/Ox CMC (source Walter E.C. Pritzkow Spezialkeramik)

ical vapor infiltration (CVI) is similar to the well known CVD process. It is performed in a controlled atmosphere of the reactive gases at temperatures above 800 °C and needs infiltration times of several hours up to some days to achieve sufficient densities. An advantage of the CVI process is its capability to apply coatings on the fibers before introducing the matrix. Using the liquid infiltration routes the coatings are applied either via an additional CVD process or by – cheaper wet chemical routes.

Trends

Costs of CMC are controlled to a large extent by the costs of ceramic fibers. With carbon fibers a dramatic decrease of prices was already achieved when mass production started within the last decades. The production volumes of alumina and silicon carbide fibers are still small and the world market is shared between few companies located in North America and East Asia. With increasing use of CMC, additional companies, especially in Europe, will enter the market [7, 8]. So it is expected that fiber prices decrease medium-term. Another source of high production costs of CMC components is the generation of the matrix, which needs expensive batch processes at high temperatures – usually in controlled atmosphere. Currently large activities in R+D consider more efficient infiltration processes [9]. Further benefit is expected from standardization of CMC components for serial production. Large scale production of simple shapes like plates and pipes would eliminate manual processing steps. More complex components can be built via joining techniques, which are currently developed.

A driving force for the increasing demand for CMC is the computer based design of new components. FE simulations provide complex technical requirements like highly anisotropic loadings. The competitive advantage of CMC is highest with such complex demands. Currently, intense research is done to understand CMC behavior from its structure on micro- and meso-scale and to predict life time of CMC components under operating conditions (compare e.g. [9]). This will help to further improve performance of CMC components and to convince construction engineers through both, economical and technical reasons to use CMC in additional applications.

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