Low-Cost Ceramic Matrix Composites for Applications at Intermediate Temperatures

P. Vierhaus, J. Schmidt, A. Rüdinger, J. Maier

The basis for cost reduction of Ceramic Matrix Composites (CMC) is the use of low-cost basalt or glass fibres instead of ceramic or carbon fibres – in combination with low temperature fired or hardened matrices. Different from customary CMC, usually operating at temperatures above 1000 °C, these low-cost CMC are designed for use at intermediate temperatures between 300–800 °C. In this article, the authors present an overview of the field and highlight some related activities of Fraunhofer-Centre HTL.

Tab. 1 **Properties of commercially available ceramic low-cost fabrics and their market prices**

	Nextel™ 610 Fabric DF19	Carbon Fabric C T24-5.0/270-E100	Silica Fabric S300 LS	Basalt Fabric 014-0040
Supplier	3M	SGL Carbon	Hiltex	Final Advanced Materials
Filament number (in roving)	1000	24000	300 g/m²	500
Tensile strength (filament) [GPa]	2,9	5,0	300 N/cm ribbon of fabric	3,0
Young´s Modulus (filament) [GPa]	373	240	-	86
Price per m² fabric	~ 800 Euro	30 - 50 Euro	~ 15 Euro	15 Euro

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1 Introduction

CMC have high mechanical strength, fracture toughness, chemical resistance and low density, so that they are ideally suited as lightweight construction materials in harsh environments. Compared to monolithic ceramics, the main advantage of CMC is their high level of elongation under mechanical stress, which leads to damage-tolerant behaviour. CMC are prepared by embedding ceramic reinforcing fibres in a ceramic matrix. Usually, either non-oxidic or carbon fibres are used in combination with a non-oxidic matrix or oxidic ceramic fibres are embedded in an oxide ceramic matrix. The corresponding CMC are called non-oxidic or oxidic respectively.

To design the damage tolerance, a mechanically weak fibre-matrix interface or a weak matrix are required. Both lead to crack deflection or fibre pullout and the absorption of energy during fracture. They enable a rearrangement of the microstructure, when external stresses occur. The weak fibre matrix interface or the weak matrix are obtained by a fibre coating or by setting a porous matrix. Oxidic CMC can be used permanently at temperatures up to approx 1100 °C and non-oxidic CMC up to approx 1400 °C. Even higher operating temperatures can be achieved using thermal barrier coatings and cooling concepts. CMC are resistant to thermal shock and temperature gradients. Their properties can be custom-tailored depending on the fibre volume content, fibre placement and the interface and matrix properties. High fibre volume contents of approx 50 % and the alignment of fibres in the load direction lead to a high tensile strength. An overview on the properties of customary CMC was given in [1].

The drawback of customary CMC are their high costs. For one thing, these high costs are related to the prices of ceramic reinforcing fibres. The prices for several fibres, which are offered as 2D-laminates, are listed in Tab. 1. The most common oxide ceramic fibres for CMC applications are from 3M with the trade name Nextel™ 312, 440, 610 and 720. The price per kilogram or pound highly depends on the number of filaments and can vary for example for fabric out of Nextel™ 610 from >300 EUR/m^2 to >900 EUR/m^2.

Another type of oxide ceramic fibres are ALF from Nitivy/Hiltex with a price around 400 EUR/m^2 fabric. Commercially available non-oxide ceramic fibres are typically SiC-fibres from NGS – Nicalon NL, High Nicalon or High Nicalon Type S – or from UBE Industries – ZMI, LOX-M or SA4.

The price depends on the oxygen content and degree of crystallinity and can vary from >1000 EUR/kg for generation 1 and >8000 EUR/kg for generation 3. Therefore, the basis of low-cost CMC are low cost fibres, which are compared to a Nextel™ fibre fabric in Tab. 1.

These low-cost fibres are typically used for the manufacturing of carbon, glass or basalt fibres reinforced polymers (CFRP, GFRP and BFRP) and are available as rovings or 2D-laminates. However, the use of these FRP is limited to low temperatures up to 300 °C due to their plastic matrices. Furthermore, the use of carbon fibres is restricted by their vulnerability to oxidation.

On the other hand, the manufacturing process of CMC is expensive, because it still includes many manual process steps. In addition, slow and expensive gas phase processes such as Chemical Vapour Deposition (CVD) or Chemical Vapour Infiltration (CVI) are often used for fibre coating and matrix formation. Curing and compaction of the matrix often is supported by autoclave processing, which is expensive due to its low throughput.

Presently, wider use of high temperature CMC is prevented by their prohibitive costs. There is still a great need for novel CMC filling the gap between FRP and customary CMC, i.e. operating at temperatures in the range between 300–800 °C. Many thermal processes in the metal, glass, chemical and energy industries require corrosion resistant and damage tolerant materials in this temperature range. However, customary CMC are too expensive for wide use in this field. A drastic reduction of manufacturing costs is already achieved by substituting the ceramic reinforcing fibres by glass or basalt fibres (Tab. 1). However, these fibres cannot withstand temperatures above 1000 °C. Therefore, infiltration of a ceramic slurry and subsequent sintering at high temperatures, which is used in customary production of oxidic CMC to obtain appropriate matrix strength [2], is unfeasible in general.

As an alternative matrix, geopolymers are available. They are cheap and can be hardened at room temperature. Moreover, other cheap precursors or suspensions with low curing respectively sintering temperatures can be used. In order to provide a stable and cheap manufacturing, roll-to-roll processes and injection moulding are proposed.

The major benefit comes from automated and continuously working processes for important steps such as fibre coating, 2D- or 3D-textile manufacturing and prepregging (Fig. 1). Furthermore, out-of-autoclave techniques such as tape winding and axial pressing are to be used consequently to keep the production costs low.

2 Technical basis for producing low-cost CMC

In addition to the use of inexpensive raw materials and the avoidance of high-temperature processes, the basis for the production of cost-effective CMC components is the complete automation of all production steps. Fibre matrix interphases can be applied by wet chemical coating in a fast roll-to-roll process. The process set-up is shown in Fig. 2. In contrast to CVD coatings, the deposition speed is much faster at about >500 m/h. Another advantage is the possible multilayer deposition of a one coating material within one cycle with up to eight layers as well as the integration of the thermal treatment such as desizing and pyrolysis.

A high variety of oxide and non-oxide ceramic coatings can be applied as interphase material. The applied coatings must have a very good bonding to the surface, so that they can be handled in the following weaving step without any mechanical damage. Furthermore, the coatings need to have a

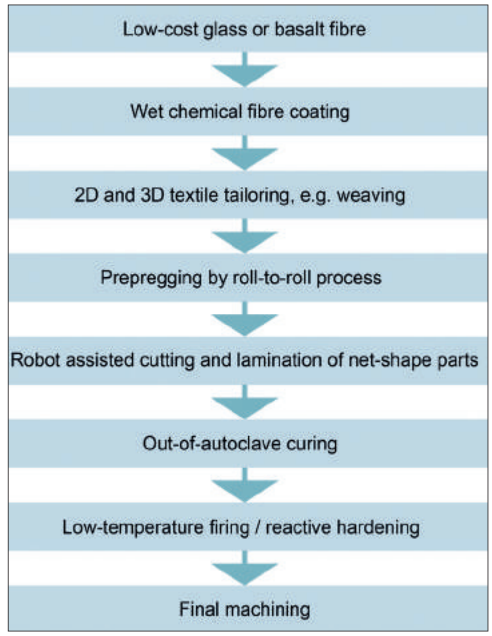

Fig. 1 Process chain for the manufacturing of low-cost CMC in a closed process cycle

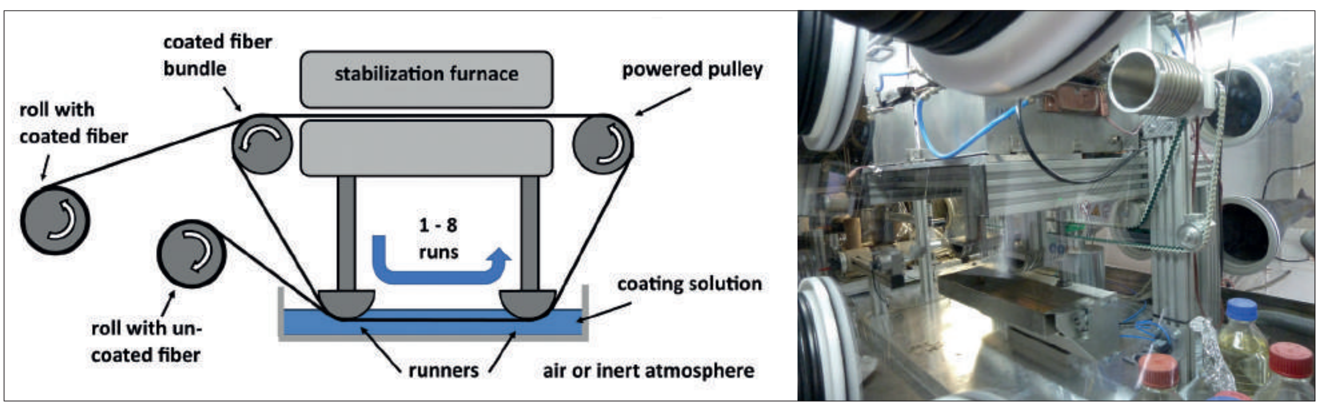

Fig. 2 Fibre coating by wet chemical deposition in a fast roll-to-roll process (Source: Fraunhofer-Centre HTL)

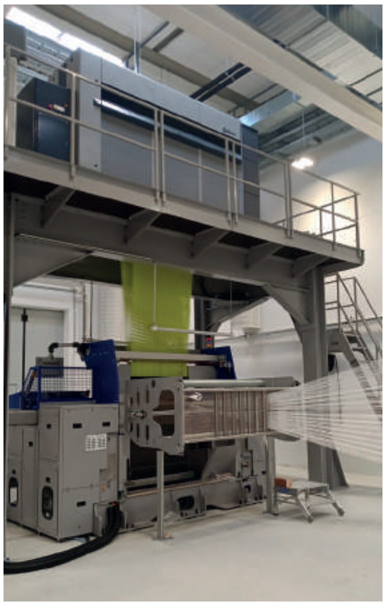

Fig. 3 **Double rapier weaving machine with single-thread operation (Source: Fraunhofer-Centre HTL)**

low degree of bridging between the fibres to avoid fibre or coating breakage [3]. In the next step, textile preforms are made from the fibres. New designs can be manufactured using 3D-weaving and braiding. In this way, semi-finished products custom-tailored to a specific application can be produced, which lead to cost-effective production.
Fraunhofer-Centre HTL offers a wide range of machinery for textile manufacturing processes, e.g., a double rapier weaving machine with single-thread operation offers a new option for the manufacture of fabrics (Fig. 3). Textile processing of inorganic and carbon-based fibres is developed on this weaving machine. In the braiding area, variation braiding technology is used to manufacture very complex braids for diverse fields of application (Fig. 4).

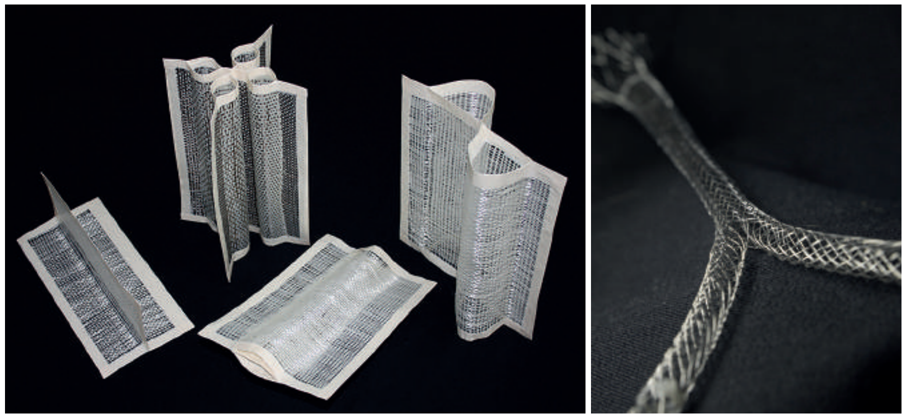

Fig. 4 **Examples for fibre preforms made by 3D-weaving and braiding (Source: Fraunhofer-Centre HTL)**

The focus of development in both areas concentrates on multidimensional textile preforms for load-conforming component design. Supported by a finite element simulation, the fibre reinforcement is optimally designed for the stress on the later component and implemented in a targeted manner during the manufacture of the preform. Both the textile manufacturing of complex shapes and the load conforming fibre arrangement reduce costs by saving costly fibres and by avoiding joining steps in final system integration.
At Fraunhofer-Centre HTL, a fully automated prepreg system is available to provide the required fibre prepregs inexpensively and in large quantities (Type KTF-S, Mathis/CH) (Fig. 5). The system is based on a roll-to-roll process, in which fibre fabric tapes up to a maximum width of 600 mm are continuously soaked and coated from the roll with a liquid medium, forming the so-called matrix. The resulting prepreg is then dried and rewound as roll goods. Precursors in liquid form, e.g. geopolymers, which can be varied by adding fillers, are impregnated during the process and used after thermal processing to form the matrix. Fully impregnated wet prepregs with weights per unit area of up to 700 g/m² can be achieved with glass and carbon fibre fabrics. A pad-mangle unit is used to impregnate the fabric with the precursor. The homogeneity of the prepregs across the web width and length can be verified in accordance with DIN EN 2557. The deviations are <5 %. The prepregs can be pressed into flat and delamination-free plates using axial hot pressing technology, or they can also be laid out using tape spreaders. The homogeneous distribution of the matrix in the prepreg and its ability to bind in the composite material can be verified by testing the interlaminar shear strength in accordance with DIN EN ISO 14130.
CMC components are tested non-destructively during their development and – on a random basis – during production (Fig. 6).

Fig. 5 **Fabric prepreg plant at Fraunhofer-Centre HTL (Source: Mathis AG)**

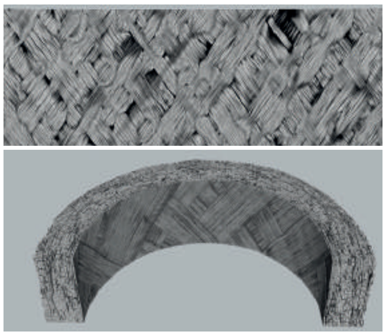

Fig. 6 CT analyses of CMC Material (Source: Fraunhofer-Centre HTL)

Fig. 7 Fibreglass reinforces casting launder

Fig. 8 Fibreglass reinforced casting launder, shielded by a steelcase (Source: InovaCeram)

Fraunhofer-Centre HTL operates a state-of-the-art Computer Tomography (CT) system for this purpose. The system consists of a combination of three X-ray tubes and a fast area detector, which means that examinations on large components as well as microstructural analyses on small material samples can be carried out. Delamination and fibre breaks as well as other structural defects can already be detected in the production chain, allowing for an efficient elimination of production faults [4].

3 Low-cost CMC systems for intermediate temperatures

Two companies, Pyrotek/US and InovaCeram/DE already offer low-cost CMC for metal casting. They are based on glass fibre reinforcement. Pyrotec uses different matrices of calcium or zirconium silicate, fused silica or silicon carbide under the trademark of Reinforced Fibreglass Material (RFM®). The material can be manufactured in thin walled complex shapes [5]. Also, InovaCeram is a provider for aluminium casting devices using glass fibres embedded in alumina-silica matrices [6] (Figs. 7–8).

Within the joint project BaMox, Fraunhofer-Centre HTL currently develops low-cost CMC for metal casting, which are based on basalt fibres embedded in geopolymer matrices: so-called GMC. Project partners are TU Chemnitz/DE, InovaCeram and Metallgießerei Chemnitz/DE.

Within the project tensile strength, fracture toughness and tribologic properties are optimised using different basalt fabric qualities in combination with different geopolymer matrices. The development of a hand casting crucible and a casting funnel as test devices, shall show the possibilities, this newly designed material will provide. Thermal and chemical resistance is verified under real use in aluminium casting (Figs. 9–10). Thereafter, the manufacturing method is to be transferred into automatization. For that, TU Chemnitz develops an injection moulding process, where the precursor is pressed into the inlayed basalt fabric. Besides pouring crucibles, feeder boxes and pouring channels for use in the aluminium casting industry will also be produced. The GMC should be inexpensive and long-term resistant to attack by the melt and deposits and should enable optimal casting success supported by low heat dissipation. In addition, its non-metallic surface should not contaminate the melt through flaking or leaching, which is an important benchmark for a high quality standard.

Another application of low-cost CMC are supporting structures for metallic components, which are vulnerable for creep at intermediate temperatures. For example, in another joint project, FaRo CMC reinforcements were developed for highly stressed steel pipes in power plants. Project partners are Schunk Kohlenstofftechnik/DE, Bilfinger Piping Technologies GmbH/DE, TÜV SÜD Industrie Service GmbH/DE, Großkraftwerk Mannheim/DE, Technion Israel Institute of Technology/IL, Materialprüfungsanstalt Stuttgart/DE and Universität Bayreuth/DE.

In steam power plants, these steel pipes are subjected to high internal pressure of 350 bar at temperatures of 650 °C. Under these conditions, steel shows tertiary creep, which can be stopped by a CMC structure wrapped around the pipe (Fig. 11), because the CMC has a much better creep resist-

Fig. 9 Metallic casting crucible

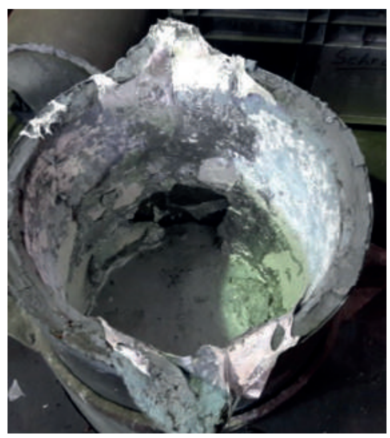

Fig. 10 Used casting crucible with ceramic fabric lining (Source: Metallgießerei Chemnitz)

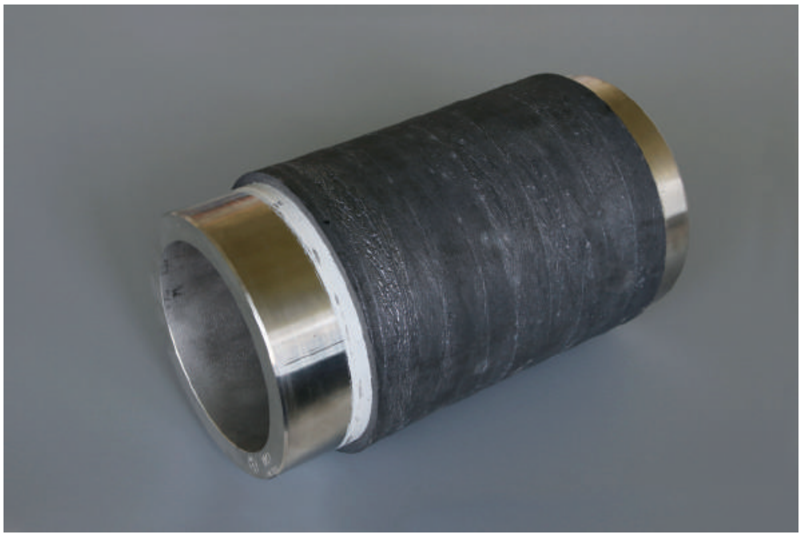

Fig. 11 CMC reinforcement for power plant steel pipes (Source: Fraunhofer-Centre HTL)

ance. This CMC can be manufactured from different fibre and matrix systems and their combinations depending on the requirements. In addition to high-priced fibre types from the corundum or mullite system, basalt fibres or glass fibres can be used in many applications. The matrix is made of precursors such as polysiloxanes, polycarbosilanes or polysilazanes, which are transferred into amorphous ceramics in a temperature range between 350–800 °C [7], which is compatible to the low-cost fibres.

Regardless of the precise market demands, there are various opportunities for the use of low-cost CMC at intermediate temperatures. Their high temperature versions, they need high fracture toughness and good chemical resistance.

Design concepts already developed for customary CMC can be directly transferred to the low-cost composites, e.g.: weak interfaces or weak matrices control fracture toughness; load conforming fibre arrangement increases strength.

Compared to customary CMC, production costs contribute more to total costs, since raw material costs are significantly lower. It is assumed that low-cost CMC will create a driving force for cheaper and more automated CMC production, which may be transferred to high temperature CMC thereafter as well.

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