100 Years of Textile and Fibre Research and 30 Years of Ceramic Fibre Research in Denkendorf

Double birthday – this year, the DITF Denkendorf celebrate their 100th anniversary as well as 30 years of ceramic fibre research. Ceramics and fibre do not sound compatible at first. Nonetheless, R&D in the field of high-performance oxide ceramic fibres has been successfully carried out at the DITF since 1990, not least due to their expertise in the textile and fibre sector. An industrially suitable process has been developed that enables the continuous production of oxide fibres of different compositions. In addition to the production-ready corundum and mullite fibres, further zirconium oxide stabilised fibre types have been developed. With the help of in-house expertise in weaving technology, an adapted weaving process was established for the shear-sensitive oxide fibres.

Ceramic fibre research as a unique feature

The German Institutes of Textile and Fibre Research in Denkendorf are Europe's largest textile research centre. At the research centre, a wide variety of issues along the entire fibre and textile manufacturing chain can be addressed using state-of-the-art technologies on an area of more than 25 000 m^2. For a long time now, the focus has not only been on apparel textiles, but to a large extent on technical applications of fibre-based textile structures. This means that nowadays applied R&D, like the one carried out in Denkendorf, forms the basis for various enabling technologies in which fibres and textiles play a decisive role. Therefore, it is not surprising that for 30 years now, continuous research has been devoted to the development of ceramic fibres, which are the crucial component in fibre-reinforced ceramics, so-called CMCs (Ceramic Matrix Composites). In terms of developments and technological status in the field of oxide ceramic fibres, the DITF occupy a leading position worldwide and these activities constitute a unique feature in the landscape of textile research institutions in Europe.

Keywords
ceramic fibres,
continuous production on pilot plants,
development of new compositions,
ceramic matrix composites

Research activities focus on the production of alumina- and mullite-based high-performance ceramic fibres, with the emphasis on material development on the one hand and the development of a manufacturing process suitable for industrial use on the other. So far, only two types of fibres from 3M (USA) are commercially available for the production of high-quality CMCs, so there is a strong need for the availability of other oxidic fibres. The alumina fibre developed in Denkendorf (OxCeFi A99) corresponds to one of these commercial fibres, but the newly developed pure mullite fibre (OxCeFi M75) represents a novelty, since fibres with this composition and structure have not previously been available on the market. This also illustrates the research strategy in Denkendorf, which aims to develop ceramic fibres based on new compositions and with improved and extended property profiles and to transfer this know-how to industrial partners.

Last but not least, the further success of the still relatively young material class of fibre-reinforced ceramics depends not least on the availability and price-performance ratio of ceramic fibres. This article aims to provide a brief overview of the many years of activities and the state of the art at the DITF in this field.

History

The starting signal for ceramic fibre research at the DITF was the participation of the Denkendorf institutes in the Keramik-

Bernd Clauß, Stephanie Pfeifer
German Institutes of Textile and
Fibre Research Denkendorf (DITF)
73770 Denkendorf, Germany

Michael R. Buchmeiser
German Institutes of Textile and
Fibre Research Denkendorf (DITF)
73770 Denkendorf, Germany

Chair of Macromolecular Compounds
and Fibre Chemistry
Institute of Polymer Chemistry (IPOC)
University of Stuttgart
70569 Stuttgart, Germany

Corresponding author: B. Clauß
E-mail: bernd.clauss@ditf.de

Fig. 1
OxCeFi A99 fibres

verbund Karlsruhe-Stuttgart (KKS), which was founded by the State of Baden-Württemberg in 1989. This association was established to improve the coordination of research activities in the field of ceramic materials. Since then, research in the field of ceramic fibres for fibre-reinforced ceramic materials has been an integral part of the institutes' portfolio. In the course of time, the competences have been continuously expanded through a large number of research projects carried out, predominantly in the field of oxide ceramic fibres.

Today, sound basic knowledge is available on the production and rheology of spinnable, ceramic-forming systems, on spinning processes for pre-ceramic green fibres and on structure formation during the subsequent thermal processes. This forms the foundation for further developments.

Research objectives

The aim of the research activities at the DITF was and is to develop oxide ceramic fibres that are on a par with the few commercially available fibres in terms of performance and can thus be used as an alternative. Based on this, ceramic fibres with new compositions are realised and investigated in order to improve the property profile of the fibres with respect to high temperature stability. The limit of long-term temperature stability of oxide ceramic fibres under mechanical load is mainly determined by undesired grain growth and creep deformation.

In this respect, these are the starting points for fibre optimization. However, issues such as processability of the fibres with textile processes are also relevant, since the fibres are introduced in the form of woven fabrics in most of the currently used manufacturing processes for CMC.

Spinning process and design of the spinning dope

From the very beginning, the focus of the scientific work at the DITF has been on developing a technical spinning process for these special fibre materials and on understanding the structure formation processes in the ceramic fibres based on alumina, mullite and later also zirconia [1–5]. This fundamental work on spinning dope design, in which the rheology of the spinning systems plays a decisive role in addition to precursor selection, now forms the basis for all new developments.

While in the past some attempts were made to produce ceramic fibres from ceramic powders, at the DITF the focus was already at the beginning on fibre formation from colloidal sols, as well as from molecularly disperse, aqueous solutions of ceramic-forming precursors. The high homogeneity of the precursors at the molecular level enables the realisation of small grain sizes of the target ceramics in the submicrometre range and thus the formation of very thin individual fibre diameters in the range of 10 µm. Small grain sizes are essential to ensure high tensile strengths of the oxide ceramic fibres.

However, the requirements for such spinnable ceramic-forming precursors are manifold. On the one hand, the precursors must form the target ceramics in the desired stoichiometry during thermal treatment; on the other hand, the spinning dopes must meet further requirements such as sufficient thread forming capacity and adequate rheological flow properties. Water-soluble polymers such as poly(vinyl alcohol) or poly(vinyl pyrrolidone) are used as spinning aids and ensure the spinnability as well as the stability of the spinning dopes even at high viscosities over a period of several days. In addition, complexation reagents are added as stabilizers in more complex spinning systems to prevent the tendency of the spinning masses to gel. For the production of green fibres, a dry spinning process was developed in Denkendorf and optimized over the years, so that for ten years now, the production of preceramic continuous multifilaments from 20–30 kg spinning dope can be carried out on an industrial scale dry spinning plant.

The plant is used both for OxCeFi A99 corundum fibre and OxCeFi M75 mullite fibre, which have been optimized to production readiness, and for all new developments. 500 individual filaments are spun out at the same time and dried in a controlled manner in a 7 m long spinning shaft before being taken up. The adjustment of the rheological behaviour and the setting of suitable spinning process parameters (spinning shaft temperature, draw down ratio, humidity, etc.) are the key to success.

From green fibre to ceramic fibre

The continuous multifilament green fibres obtained are then converted into ceramic fibres via thermal treatment. Due to the composition of the spinning dopes (aqueous solutions of ceramic-forming precursors, water-soluble polymer), a significant mass loss of approx 50 % occurs during the thermal conversion from preceramic green fibre to ceramic fibre. This is not the only reason why enormous caution is required during thermal treatment, which shall lead to a compact non-porous ceramic fibre. The structure formation processes, which include pyrolysis in addition to calcination and sintering are being studied for each ceramic composition in detail at the DITF.

This is necessary to define adequate process parameters for the calcination and sintering temperature regimes. While ceramic fibre production in the first years of research activities was mainly carried out in batch trials, investigations on continuous temperature treatment of preceramic green fibres have been carried out since 2003 [6].

Years of optimization supported by extensive analytical methods for structural investigation (STA-MS, XRD, SEM) and mechanical characterisation (tensile strength measurements at RT and after thermal treatment) finally led to the installation of furnaces, which since 2018 has enabled continuous conversion of preceramic green fibres to ceramic fibres on a pilot scale. In further research activities, it has been possible to increase the productivity of the thermal processes to such an extent that high-quality ceramic fibres can be produced continuously on a 10–15 kg/lot scale (Fig. 1).

Fig. 2
Weaving of OxCeFi fibres

OxCeFi A99 and OxCeFi M75

The research activities of the DITF on the fibre types OxCeFi A99 (corundum) and OxCeFi M75 (mullite), which have meanwhile been optimized to production maturity, date back to the 1990s. Already at that time, the declared goal was to develop a viable alternative to the oxide fibre types still available only from 3M, especially for the European market.

While initially the focus was mainly on the development of a suitable spinning process as well as the spinning dope design together with the characterisation of the structure formation processes [1, 2], in the further course of the work a continuous process for fibre production was developed [6]. This process, in addition to the optimization of the fibre properties [7], also includes aspects such as handling and storing of the green fibre multifilaments (development of a spin finish), recycling of process waste and increase of productivity by increasing the production speed or higher filament count per roving.

The OxCeFi A99 corundum fibre developed at DITF is similar in composition to the commercially available Nextel™ 610 corundum fibre from 3M. The fibre consists of 99 % corundum (α-Al_2O_3), but iron oxide is not used for controlled structure formation as in 3M, and other additives and precursors are used [7]. The corundum fibre is designed to have a high tensile strength, which is provided by very small grain sizes.

There is no counterpart from 3M to the pure mullite fibre OxCeFi M75 developed at DITF. While the Nextel™ 720 fibre usually used for comparison is a mixture of corundum and mullite, OxCeFi M75 consists of 96 % mullite.

Fibre development was supported by extensive analytical studies, resulting in the successful production of an approximately stoichiometric mullite fibre for the first time [8–13]. The OxCeFi M75 mullite fibre achieves the high creep resistance of the Nextel™ 720 fibre but is superior to it due to its particular high temperature stability [10–12].

Alternative compositions – ZrO_2, YAG, OxCeFi ZTA and OxCeFi ZTM

The DITF have also been involved in the development of alternative compositions of oxide ceramic fibres, since undesired grain growth and creep deformation are the challenges faced by oxide fibres in their application, especially in the case of alumina-based fibres, and limit the long-term temperature resistance under simultaneous mechanical stress. The increased requirements regarding the mechanical and chemical resistance of oxide fibres, especially in recent years, underline the need to explore new fibre compositions.

Promising candidates for improving the properties of alumina fibres are mainly ZrO_2 and Y_2O_3. While the addition of ZrO_2 allows for an increase in (flexural) strength, fracture toughness, corrosion resistance and thermal shock resistance, Y_2O_3 is of interest with respect to creep resistance and corrosion resistance. Early research on pure zirconia fibres [3–5] was carried out at DITF, and later the binary systems Al_2O_3–ZrO_2 and Al_2O_3–Y_2O_3 were also studied in detail [14–16]. The Al_2O_3–SiO_2–ZrO_2 ternary system is in the focus of current R&D activities [17].

The process for continuous production of oxide ceramic fibres established during many years of development and optimization of corundum and mullite fibres at DITF Denkendorf is very well transferable to these fibre types.

The research work on pure zirconium oxide fibres, which was already carried out in the 1990s, showed that the stabilization of the tetragonal modification of the ZrO_2 can be achieved by the addition of Y_2O_3. Due to the limited stability of the spinning dopes, no technical process for the production of Y_2O_3-stabilized zirconia fibres could be established at that time [3, 5]. Fibres of pure yttrium aluminium garnet (YAG, $Y_3Al_5O_{12}$) are particularly attractive due to the chemical composition and its properties and have been researched at DITF for many years [14, 15]. The very low mobility of grain boundaries in the YAG structure is associated with extremely high creep resistance and therefore promises to improve the long-term temperature stability of such oxide fibres. However, these very properties stand in the way of the fabrication of compact pore-free fibres, so that the development of mechanically stable YAG fibres remains a challenge, although the fabrication

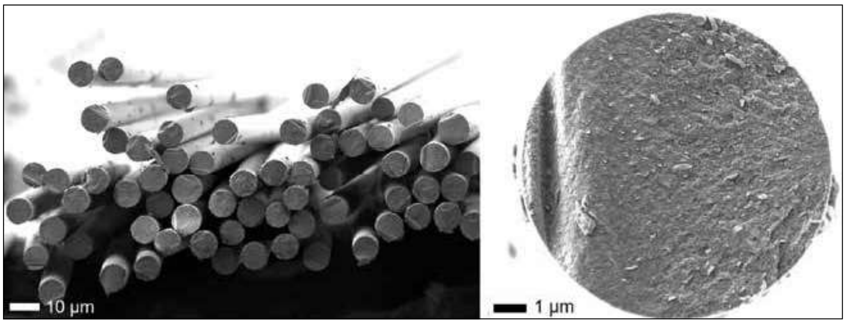

Fig. 3
SEM photos of ZTM fibres

of green fibres has already been successful.

In contrast, the incorporation of ZrO_2 into alumina fibres was much easier to accomplish, leading to the successful development of zirconia-toughened alumina (ZTA) fibres, which we call OxCeFi ZTA [16]. The fibres consist of a duplex structure of corundum and ZrO_2 localized at the grain boundaries. It has been possible to transfer the process for ceramic fibre production, including technical spinning and continuous thermal treatment, to this type of fibre.

Currently, further variations of the composition are being investigated and the fibre properties will be further optimized. By incorporating ZrO_2 into the microstructure of α-Al_2O_3 a duplex microstructure can be obtained, which improves the long-term temperature stability (reduced grain growth) of the fibres. In addition, the increase in fracture toughness had a positive effect on the textile processability of the ceramic fibres. The ZTA fibres have already been processed into fabrics (Fig. 2) and their performance has been successfully tested in OCMCs. Based on the promising results, the issue of reinforcing mullite fibres with zirconium oxide finally became the focus of R&D activities. Zirconia-toughened mullite (ZTM) fibres (Fig. 3) can be obtained analogously to the previously developed fibre types [17]. For this purpose, as for ZTA fibres, certain adjustments of process parameters during dry spinning as well as during thermal treatment are essential.

The incorporation of ZrO_2 into the mullite structure leads to a significant improvement of the room temperature tensile strength of the fibres (Tab. 1 and Fig. 4) as well as to an increased flexural strength, which also has a positive effect on the textile processability. As these zirconia-toughened mullite fibres, which we call OxCeFi ZTM, are a novelty in the field of oxide ceramic fibres, both the composition and the manufacturing process have been patented by DITF [18].

Tab. 1
Properties of OxCeFi fibres

Fibre Type	OxCeFi M75	ZTM3	ZTM15	OxCeFi A99	ZTA3
Weibull strength [MPa]	1320	1390	1740	2140	1960
Weibull Modulus	9,5	7,1	9,0	8,6	7,5
Young's Modulus [GPa]	190 ± 3	220 ± 8	210 ± 3	339 ± 7	332 ± 14
Diameter [µm]	10,3 ± 0,4	9,9 ± 0,3	9,7 ± 0,4	9,2 ± 0,4	10,2 ± 0,6

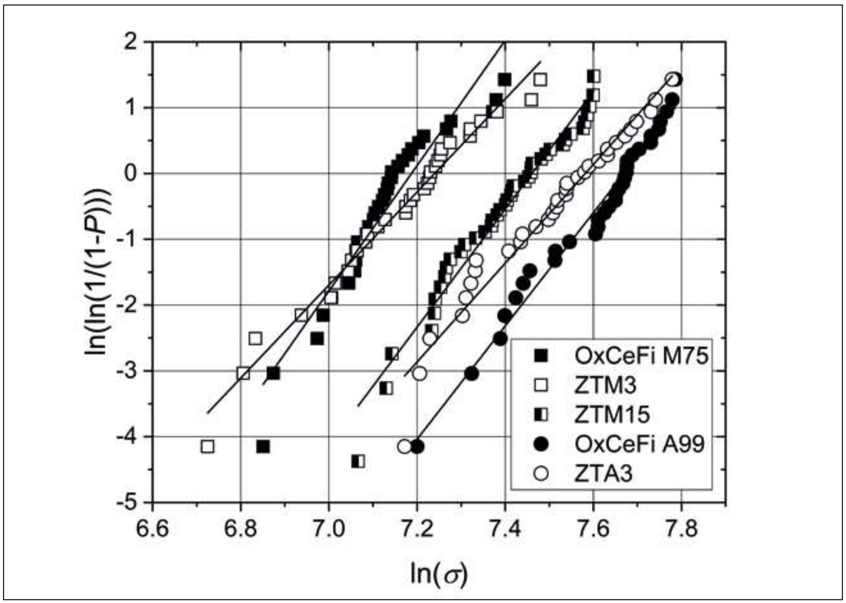

Fig. 4
Weibull plot of different OxCeFi fibres

Textile fabrics from ceramic fibres

In most manufacturing processes for Oxide Fibre Reinforced Ceramics (OCMC), the fibres are introduced into the composite in the form of fabric layers. This usually involves infiltrating several fabric layers with ceramic slurry and then forming them into the shape of the desired component, drying them and finally firing them. Therefore, it was obvious to tackle the production of fabrics from our own ceramic fibres at DITF. In Denkendorf, extensive equipment is available for a wide variety of weaving processes, and experience was already available with the processing of other high-performance fibres. However, the weaving of the shear-sensitive oxide ceramic fibres presents a particular challenge. After some technical adjustments on a 3D rapier weaving machine with Jacquard technology, it was possible to process OxCeFi A99 corundum fibres as well as OxCeFi M75 mullite fibres in larger quantities into fabrics (Fig. 2 and Fig. 5), from which OCMC components could subsequently be manufactured by industrial partners (Fig. 6). The newly devel-

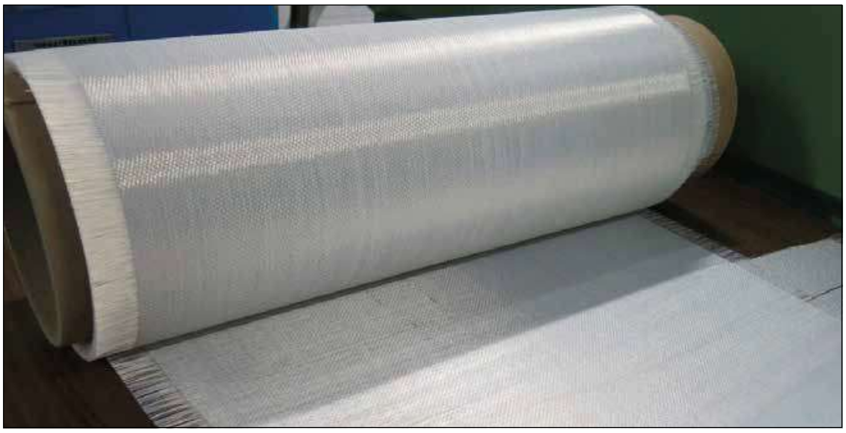

Fig. 5
OxCeFi A99 fabric

Fig. 6
Burner nozzle made of OxCeFi A99 fabric by Walter Pritzkow Spezialkeramik

oped ZTA and ZTM fibres have also been successfully used to produce fabrics.

Summary and outlook

The process for the direct production of oxide ceramic fibres, which has been established in the course of many years of development and optimization of corundum and mullite fibres at the DITF Denkendorf, includes the spinning dope preparation in a solution process, the formation of preceramic green fibres in a dry spinning process and the continuous conversion to oxide ceramic fibres via thermal processes and is very well transferable to other fibre types.

Thus, in addition to the production-ready OxCeFi A99 and OxCeFi M75 fibres, it has been possible to develop other fibre types such as OxCeFi ZTA and OxCeFi ZTM, which can help meet increased requirements in terms of long-term temperature stability and processability and ultimately also open up new markets.

In addition to the development of new fibre compositions, the DITF will also focus in the future on the realisation of higher filament counts in order to be able to reduce the costs for fibres and fabrics in the medium term. The aim is to transfer the know-how of the technology to industry in order to meet the long-standing call for a "second source" for oxide fibres in Europe.

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