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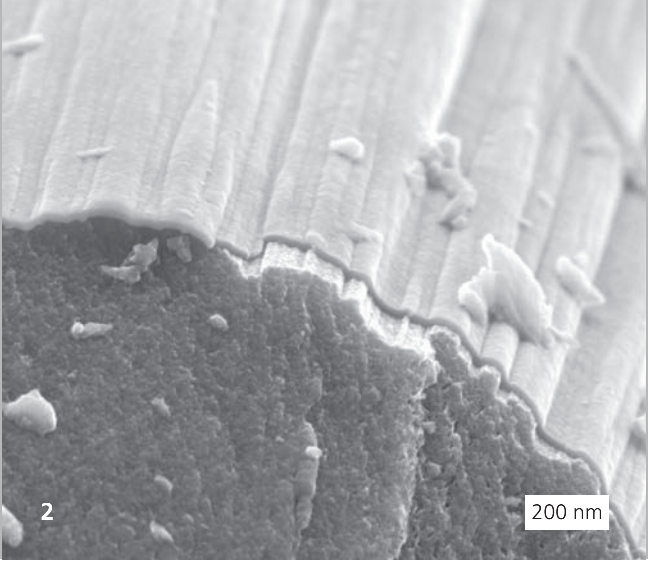

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FIBER COATING FOR THE DEVELOPMENT OF NEW COMPOSITE MATERIALS

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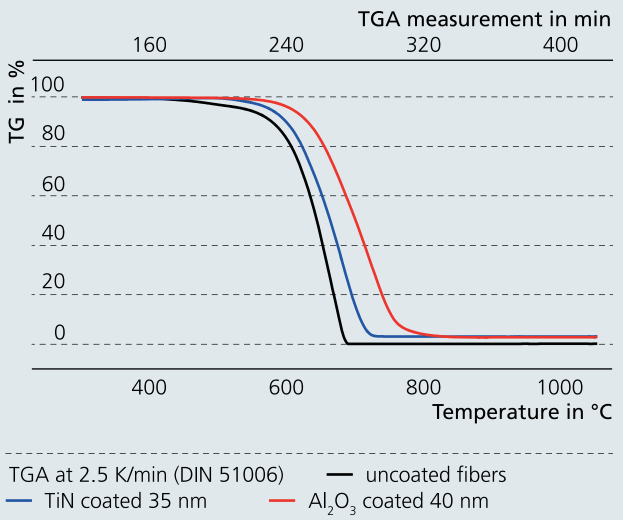
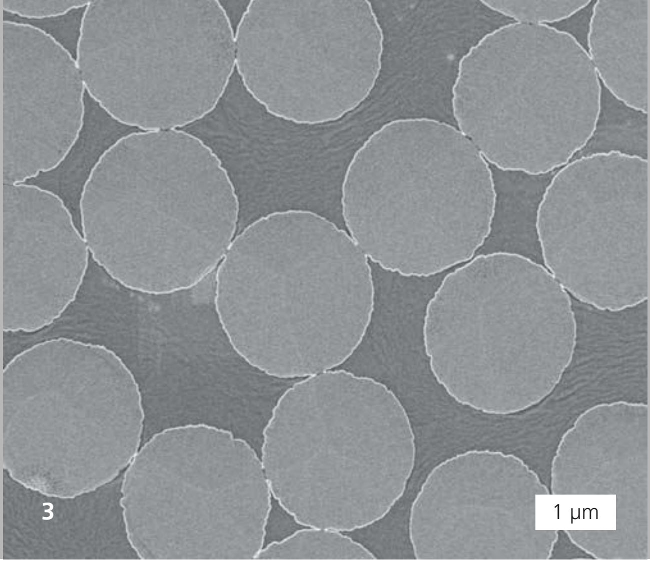
Fiber-reinforced composites are widely used in industry due to their variable design options. The utilized fibers have different functions. Aim of the combination of e.g. glass or carbon fibers with a ductile matrix like polymers or metals is the improvement of the strength and stiffness of such materials. In the case of ceramic composites, an increase of fracture toughness and damage tolerance can be achieved by reinforcing with ceramic or carbon fibers. For all composites, the fiber-matrix interface has a crucial role in the setting of optimal properties. Taylor-made fiber coatings offer manyfold opportunities, for example, a strong bonding with the matrix, an effective protection of the fiber from undesired reactions with the matrix and an adjustment of a weak fiber-matrix interface for a damage-tolerant failure behavior. Currently, coating opportunities for different fiber materials are extended at IKTS. In the future, the new coating equipment offers a batch processing mode for fiber textiles as well as a continuous operating mode using a roll-to-roll process for rovings and fibers. It enables novel technological possibilities for fiber and textile coatings using CVD and ALD processes.

Carbon fiber-reinforced metal-matrix composites

Production of modern metal-matrix composites apply 3D and 2D carbon fiber fabrics, which consist of fiber bundles with thousands of single filaments in each bundle. Protective layers made of titanium nitride (TiN) and aluminum oxide (Al_2O_3) are deposited on the carbon fiber fabrics in order to prevent undesired reactions between the fibers and the metal matrix. At Fraunhofer IKTS, two coating technologies for deposition of protective layers are applied: chemical vapor deposition (CVD) and atomic layer deposition (ALD). Figure 1 shows a new coating equipment offering the possibility of a continuous operation in both ALD and CVD processes. So far promising results have been obtained with ALD-Al_2O_3 coatings as well as CVD-TiN coatings, which were prepared at different laboratory scale facilities. In the ALD process, the precursors are sequentially injected and separated by purge gas pulses. At IKTS, Al_2O_3 deposition is carried out with an ALD process with substrate temperatures below 300 °C. The used precursors are trimethylaluminium (TMA) and ozone or water. However, preparation of the TiN protective layer is conducted by means of CVD. The deposition is carried out with a gas mixture of $TiCl_4$, N_2 and H_2 in the temperature range between 800 °C and 850 °C. With both methods, a homogeneous coating on all single fibers in the fabric could be obtained. In Figure 2, the fracture surface of a single fiber coated with a conformal and well-adherent ALD-Al_2O_3 layer is shown. Figure 3 demonstrates a homogeneous coating of a whole fiber bundle, which is taken from the 3D fabric. The Al_2O_3 layer has an amorphous structure with a smooth surface whereas the TiN layer has a nano-crystalline structure. Both layers increase the oxidation resistance of the carbon fibers. The best protection against oxidation is offered by Al_2O_3 layers as illustrated by thermographimetric analysis in the figure below.

TGA analysis for determining oxidation resistance





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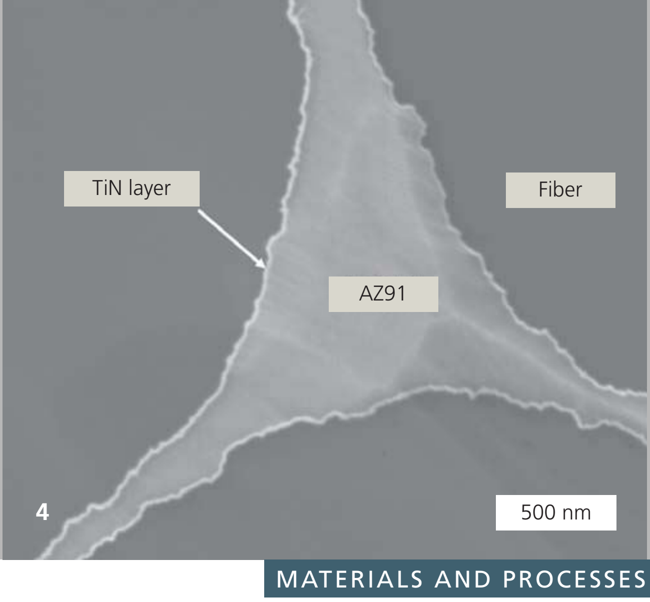

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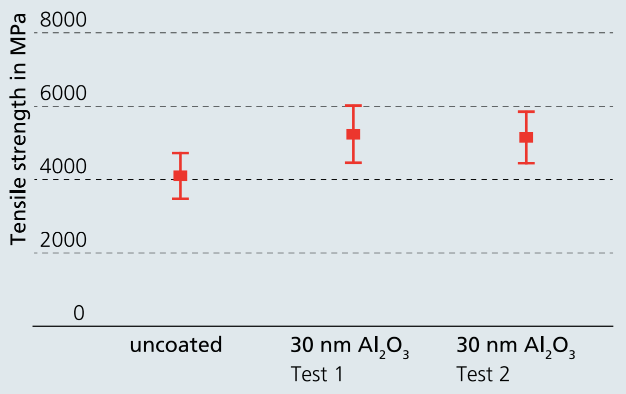
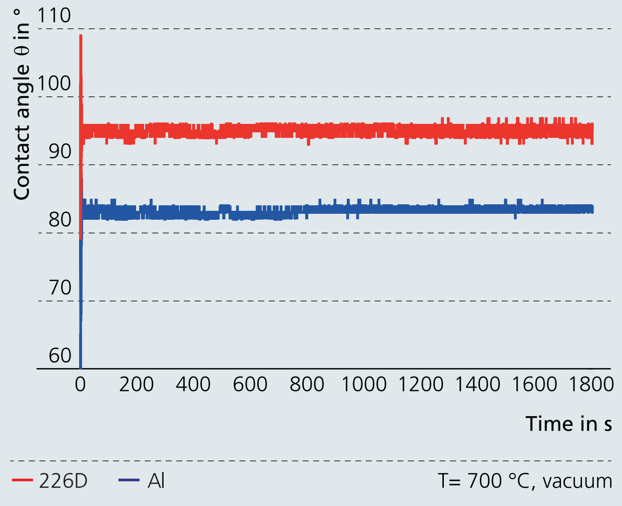
However, the coating affects tensile strength of the fibers. A significant decrease in the tensile strength is observed for TiN-coated fibers. At a coating temperature above 850 °C, formation of a brittle TiC_xN_y intermediate layer favors and reduces tensile strength of the fiber dramatically. Applying a thinner layer (about 30–35 nm) at low deposition temperature can minimize this behavior. An acceptable tensile strength of 2000 MPa is achieved when TiN layer thickness is limited to 30 nm and a coating temperature of 850 °C is not exceeded. Al_2O_3-coated carbon fibers show no loss of strength. In the case of high modulus carbon fibers, the tensile strength is slightly improved after the deposition as can be seen in the diagram below. This is caused by the low deposition temperature of ALD (below 300 °C) and by the thin layer thickness of 30 nm. The preparation of composites is performed by infiltration of coated 2D and 3D fabrics with molten metal of aluminum and magnesium alloys. Both coatings (Al_2O_3 and TiN) show good wetting behavior with metal melts. However, based on measurements at FRI Krakow, contact angle with pure Al and Al alloys show significant differences for both types of layers. The measurements for comparing the two layer systems with pure Al showed a contact angle of 83 ° for the Al_2O_3 layer and approx. 130 ° for TiN layer in conjunction with pure Al. The better wettability of the Al_2O_3 layer is an advantage for manufacturing MMC with Al alloy.

Gas pressure infiltration (GPI) was employed to infiltrate coated textiles using commercial Mg-Al-alloy (AZ91) and Al-Si-alloy (226D). Infiltration was carried out in corporation with the Institute for Lightweight and Polymer Engineering at the Technical University Dresden. The Al_2O_3- as well as TiN-coated fabrics were successfully infiltrated with both alloys. Investigation of infiltrated Al_2O_3-coated 2D carbon fiber fabrics shows a dense composite with low porosity. The undesired aluminum carbide formation is completely avoided. The same is observed for a TiN protective layer. A composite of TiN-coated 3D fabric infiltrated with magnesium-aluminum alloy AZ91 also shows a dense structure without Al_4C_3 formation at the fiber-matrix interface. Both TiN and Al_2O_3 layers are effective diffusion barriers and protect carbon fibers from the aggressive molten metal in the MMC manufacturing process.

Tensile strength of Al_2O_3-coated high modulus carbon fiber



Contact angle measurement of Al_2O_3 layer with molten Al und 226D alloy

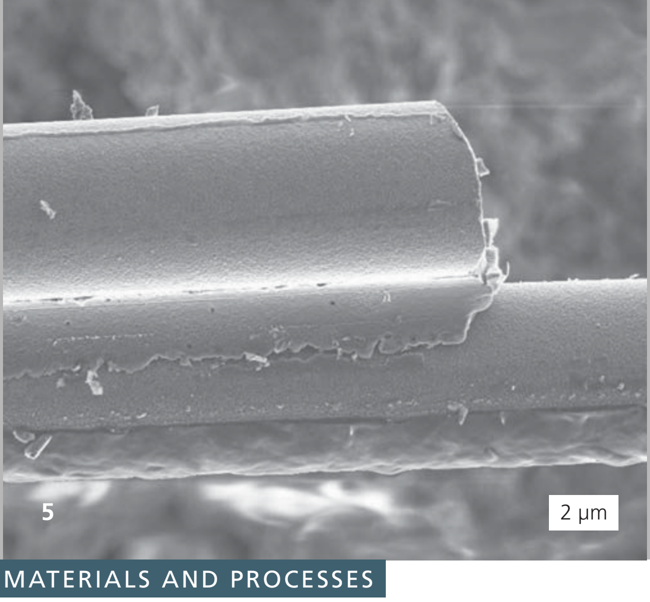


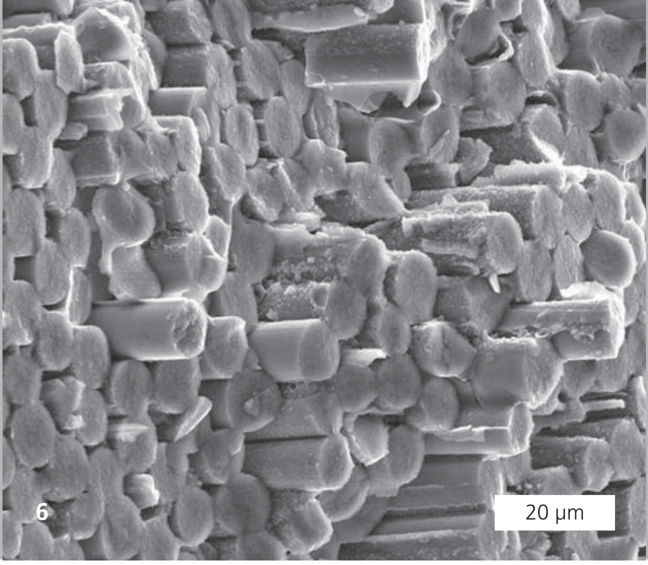
1 *New equipment for continuous fiber coating.*

2 *Al_2O_3-coated single fiber.*

3 *Cross-section of fiber bundle with homogeneous Al_2O_3 coating.*

4 *SEM micrograph of a composite from TiN-coated carbon fiber infiltrated with AZ91 alloy.*





Ceramic matrix composites

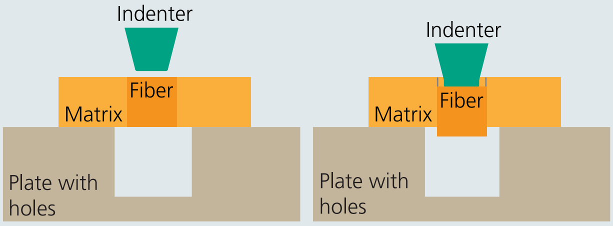
Even in ceramic fiber composites (CMC), used e.g. as lightweight material or in high-temperature processes, fiber coatings are needed. Besides the reliable oxidation and corrosion protection of the ceramic fibers, the guarantee of a damage-tolerant composite behavior is the main function of the fiber coating. Thus, in contrast to other composite materials with a ductile matrix, like carbon fiber reinforced plastics (CFRP) or metals (MMC), the focus of the material design of CMC must be placed on the adjustment of a weak bonding between fiber and matrix, which allows crack propagation in the fiber-matrix interface.

Usually, a strong bonding between fiber and matrix was obtained as a consequence of chemical reactions in the heat treatment during the fabrication of the composites. These reactions prevent toughening mechanism, such as crack deflection or fiber pull-out and finally a damage-tolerant behavior of the composites. With an additional coating of the fibers, however, the bonding at the interface between fiber and matrix can be purposefully adjusted.

In case of non-oxide composites, layers of carbon or boron nitride have prevailed since their hexagonal-layered structure resulting in crack propagation at the fiber-matrix interface promoting the pull-out. However, these layers are not suitable for long-term use at elevated temperatures in air, as they do not have sufficient oxidation stability. For this reason, the focus of future CMC developments must be placed on new coating material systems featured by a superior chemical and mechanical resistance at temperatures > 1000 °C.

Two different technologies for continuous fiber coating were applied at IKTS. In case of the CLPC method, continuous liquid phase coating, a liquid precursor as coating material was used. During thermal treatment, the precursor was pyrolized to a thin ceramic layer. Pyrocarbon-coated SiC fibers are shown in Figure 5 as an example of these processes. The microstructure of the fracture surface of a SiC_F-Si_3N_4 composites with carbon fiber coating is demonstrated in Figure 6. The damage tolerant behavior was obtained by pull-out of the fibers from the ceramic matrix.

Description of single fiber push-out test



Position of sample and indenter before testing

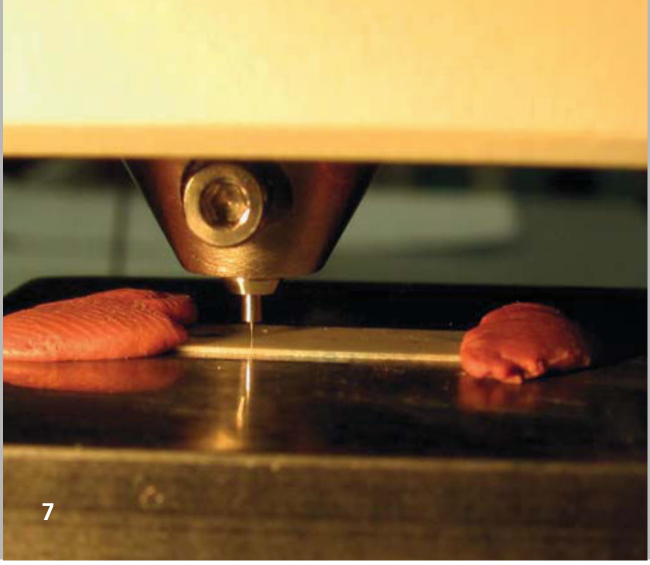
Fiber displacement after debonding the loaded fiber

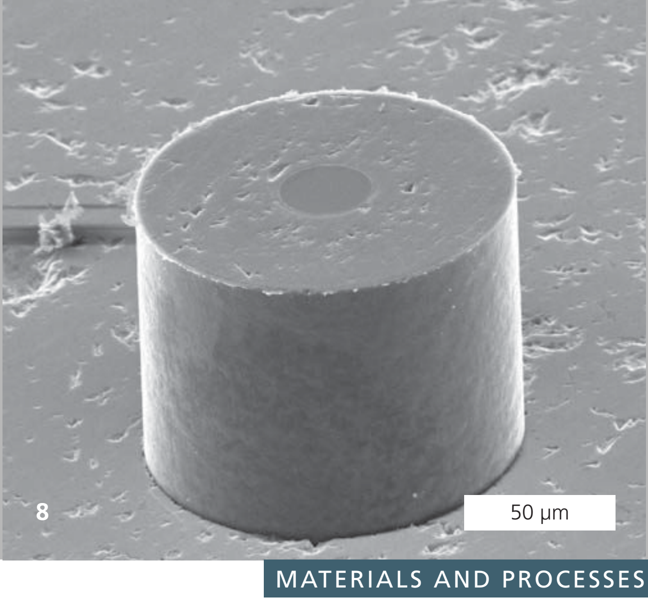
By separating the fibers, a damage-tolerant crack behavior is realized. Fiber coating by means of chemical vapor deposition (CVD) is another method. Advantages of this method include the layer deposition by transporting materials via vapor phase into the smallest intermdiate space so that coatings are also detectable in the fiber bundle or in fabrics. Thin, homogenous layers can be created, as shown in Figure 3.

As mentioned above, the purposeful adjustment of the fiber-matrix interface strength was found to be the essential factor influencing the damage-tolerant fracture behavior of the composite. Single fiber push-out tests have been performed at IKTS in order to characterize the mechanical interaction between fiber and matrix. The measurement of interfacial shear strength on a CMC sample with a microhardness tester is shown in Figure 7. In this way, it is possible to characterize the fiber-matrix connection in dependence on the type of coating and coating technology and to define the requirements for the development of such materials.

By purposeful preparation of thin samples of model composites, it was possible to obtain reproducible force-displacement curves via the described test and to calculate the characteristic shear stress for fiber debonding. A low shear strength is characterized by a weak fiber-matrix interaction. The fiber can be pushed out quite easily as shown in Figure 8. The weak interaction was the consequence of the homogeneous fiber coating. In case of uncoated fibers, however, a strong interaction with a high shear strength was obtained.

The results of the push-out tests are demonstrated in the diagrams on the right-hand side. A significant displacement of the indenter was observed in the composite with fiber coating re-

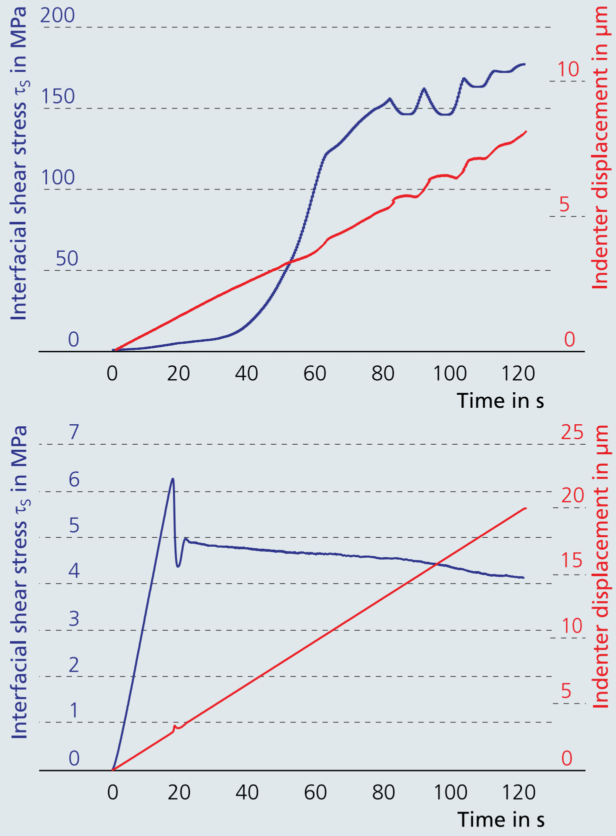




sulting in a shear stress of 6 MPa. Much higher stresses were found in the uncoated material with strong fiber-matrix interaction. There, a significant displacement of the indenter was not observed up to a stress level of about 120 MPa.

The formation of cracks observed inside the fibers show that the compression strength level of the fiber was reached. A brittle failure behavior should be expected in case of such a strong fiber-matrix connection. In this way, correlations between the interface properties and the macroscopic mechanical behavior of the composites can be determined. Based on the results and interpretation of these tests, the fiber-matrix interface of CMC's can be designed. According to the application and the chemical and mechanical requirements, oxide or non-oxide fiber and matrix systems will be chosen. The coating composition and technology will be selected in the last step of the composite design in order to realize a damage-tolerant behavior of the composites. Thus, it is possible to fabricate composites with reproducible properties.

Interfacial shear stress over time for weak fiber-matrix bonding and strong fiber-matrix bonding



Services offered

- Functional design of fiber-matrix interface of CMC
- Continuous fiber coating by CLPC, CVD and ALD processes, coating of textile structures
- Fabrication and characterization of MMC and CMC

5 *SiC fiber coated with CLPC pyrocarbon.*

6 *Fracture surface of CMC with coating.*

7 *CSM equipment: Measuring instrument for push-out test.*

8 *SiC–SCS with low fiber-matrix bonding after push-out test.*

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