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Sol–Gel Coatings on Ceramic Fibers for Ceramic Matrix Composites

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Abstract

Different types of reinforcing components, i.e. SiC-filaments (Sigma, Tübingen, FRG), SiC-fiber bundles and plain weaves (Nicalon, Nippon Carbon, Japan) as well as C-fiber bundles (T-800, Torray, Japan), were coated using sol–gel techniques. As coating materials SiO_2, Nb_2O_5 *and* ZrO_2 *were chosen. The microstructure and the thickness of the coatings were examined using Auger electron spectroscopy, reflected light and scanning electron microscopy.*

It could be shown that with increasing complexity of the fiber architecture (filament–bundle–weave) a decrease in the coating quality was found. Nevertheless, using the coated reinforcing components in glass matrix composites the fiber-matrix interface could be influenced in an essential way. These components were produced using hot-pressing techniques and were tested in three-point bending. An increase in strength as well as a more controlled fracture behavior of the composites was attained by choosing the appropriate system of fiber, matrix and coating.

Verschiedene Typen von Verstärkungskomponenten, wie SiC-Filamente (Sigma, Tübingen, FRG), SiC-Faserbündel und verflochtene SiC-Fasergewebe (Nicalon, Nippon Carbon, Japan), sowie C-Faserbündel (T-800, Toray, Japan) wurden mittels Sol–Gel-Technik beschichtet. Als Beschichtungsmaterialien wurden SiO_2, Nb_2O_5 *und* ZrO_2 *gewählt. Die Mikrostruktur und die Dichte der Beschichtungen wurden mit Hilfe von Auger-Elektronen-Spektroskopie, Licht- und Rasterelektronenmikroskopie untersucht.*

Es konnte gezeigt werden, daß mit zunehmender Komplexität der Faser-Architektur (Filament–Bündel–Gewebe) die Qualität der Beschichtung abnimmt. Dennoch kann ein bedeutender Einfluß auf die Faser–Matrix-Grenzflächen ausgehen, wenn beschichtete Verstärkungskomponenten in Glas-Matrix-Verbunden eingebracht werden. Die Verbundwerkstoffe wurden mittels Heißpressen hergestellt und im Drei-Punkt-Biegeversuch geprüft. Wird ein geeignetes System aus Fasern, Matrix und Beschichtung gewählt, so kann sowohl eine Festigkeitssteigerung als auch ein kontrolliertes Bruchverhalten der Verbunde erreicht werden.

Différents types de composants de renforcement comme des filaments de SiC (Sigma, Tübingen, FRG), des faisceaux de fibres de SiC et des maillages plats (Nicalon, Nippon Carbon, Japan) ainsi que des faisceaux de fibres de C (T-800, Torray, Japan) ont été recouvert par des techniques sol–gel. Comme matériaux de recouvrement SiO_2, Nb_2O_5 *et* ZrO_2 *ont été choisis. La microstructure et l'épaisseur du revêtement ont été examinés par spectroscopie électronique Auger, microscopie optique et microscopie électronique à balayage.*

On a pu montré qu'avec une augmentation de la complexité de l'architecture des fibres (filament–faisceau–maillage) la qualité du revêtement diminue.

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Par contre le fait d'utiliser les composants de renforcement recouverts dans des composites ayant une matrice amorphe, peut avoir une influence déterminante sur l'interface fibre–matrice. Ces composants ont été produits par pressage à chaud et ont été testés par flexion trois points entaillés. En choisissant le système fibre–matrice–revêtement approprié, une augmentation de la résistance mécanique ainsi qu'un comportement à la rupture plus controllé ont été atteints.

1 Introduction

Fiber reinforcement of ceramic materials is developed with the central aim of reducing the brittleness. The basic mechanisms required for increasing the toughness are known from fiber-reinforced organic polymers: debonding, crack branching, multiple crack formation and pull-out. In ceramic matrices, these processes, which are of crucial importance for an increased work of fracture and the optimized crack propagation behavior, are even more strongly correlated with the fiber–matrix interface than in organic matrices. Hence, the influence on and the control of the interface structure are of decisive significance for a successful development of these composites as far as the mechanical properties are concerned. By a proper adjustment of the interface system, reactions and diffusions between the fiber and the matrix can be controlled. Barrier layers at the fiber–matrix interface can, for example, improve the thermal stability of the fibers.[1] The composite properties are affected not only by thermodynamic and reaction-kinetic aspects but also by the mechanical parameters such as the coefficient of static friction, Young's modulus, Poisson's ratio and the thermal expansion coefficient.[2]

Controlled interface systems can be produced by the in-situ generation of interfaces. Another method would be the coating of single fibers, fiber bundles and fabrics. The in-situ generation can be selected, if fiber–matrix reactions or reactions of the fiber constituents are possible, e.g. formation of a C-rich layer when introducing SiC-fibers with an over-stoichiometric C-content.[3] In the event that more stable fiber materials with a higher purity are to be used, the fiber surface can be modified by means of coating techniques, i.e. CVD methods.

Using these methods, a multitude of coating materials and layer specifications can be achieved in an almost ideal manner.[4] Major drawbacks of the CVD methods are due to process technology: only small coating rates can be attained, as a result of which the fabrication procedures are very tedious.

A promising coating technique, which has received little notice so far with respect to composites, is the sol–gel method. It is characterized by high coating rates, variable layer compositions and a simple process technology. This explains the wide application of the method for the production of coated flat glasses, heat-reflecting glasses, shop window panes and optical filters.

It is the objective of the present work to demonstrate the feasibility of sol–gel coating of ceramic reinforcing components for composites in terms of technological aspects. The complexity of the coating task increases with the transition from mono-filaments to fiber bundles of increasing number of filaments, fabrics and composites, respectively.

2 Experimental

2.1 Reinforcing components used

The reinforcing components used and their properties are listed in Table 1. The number of filaments in a fiber bundle is a very important parameter, which also determines the price of the fiber. The fibers used vary by more than four orders of magnitude as far as this parameter is concerned. On the basis of Table 1, the influence of this parameter on the coating behavior can be studied. Furthermore, a fabric made of SiC-fibers (Nicalon, Nippon Carbon, Japan) was used. Fabrics are of great interest for composite production, as anisotropy of the composites can be reduced using a relatively simple technology.

2.2 Coatings of fibers and production of composites

SiO_2, ZrO_2 and Nb_2O_5 were selected as coating materials. This selection was based on the thermal expansion coefficient, which increases from SiO_2 to Nb_2O_5 and ZrO_2, respectively. Moreover, SiO_2 was to provide a good adhesion to the silicate matrices. Nb and Zr are not constituents of the matrix, thus their content and distribution in the composite material can be determined correctly. When using ZrO_2, no reaction with the fiber takes place.[13,14]

The SiO_2 coating solution was produced as follows. Distilled water and acetic acid were added to tetraethoxysilane (TEOS) in proper amounts. At a viscosity of the solution of 3·2 dPas, the hydrolytic reaction was slowed down by dilution with ethanol. The resulting viscosity was ranging from 2·0 to 2·4 dPas and proved to be very suitable for the coating tasks. The ZrO_2 and Nb_2O_5 coating

Table 1. Major parameters of the reinforcing components used

Type of fibre	SiC-Fiber (Sigma)	SiC-Fiber (Nicalon)	C-Fiber (T-800)
Producer	Sigma Verbundwerkstoffe Tübingen	Nippon Carbon, Japan	Toray, Japan
Production route	CVD	Polymer precursor	PAN, polymer precursor
Chemical composition (mass %)	SiC with W-core	Si = 56·9 C = 30·6 O = 11·3	C ≥ 95[a]
Number of fibers per bundle	Mono-filament	500[a]	12·000[a]
Diameter (μm)	100[a]	14 ± 8	7[a]
Density ρ (g/cm^3)	3·5[a]	2·45	1·81[a]
Youngs' modulus (GPa)	420[a]	200[a]	294
Tensile strength σ (GPa)	3 600[a]	3 000[a]	5 490[a]

[a] manufacturers' specifications.

solutions were prepared analogously on the basis of the alkoxides and halogenides available. The coating properties of all solutions have remained the same for weeks.

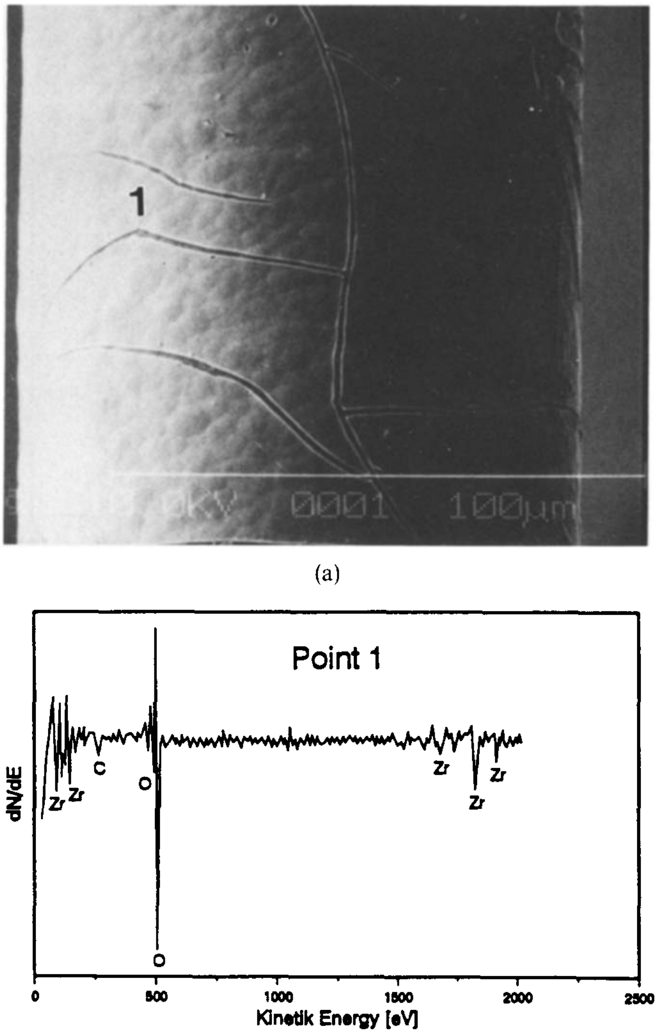
The mono-filaments were received without any organic protection layer (sizing). Hence, cleaning with ethanol was sufficient for the preparation of these fibres. The mono-filaments of about 25 cm in length were immersed in the coating solution and withdrawn straight up at about 10 cm/min. For the removal of the solvent, the fibers were then dried at room temperature for a period of 2 h. Subsequent heat treatment was carried out at 600°C in air for a period of 20 min. For increasing the layer thickness, this process could be repeated up to ten times.

The fiber bundles used and the SiC-fiber fabric were subjected to a treatment of about 30 s (fabric: 5 min) at 600°C in air in order to remove the sizing. The fibers were then immersed in the strongly agitated coating solution for several minutes. Then they were dried at 110°C for 20 min and subjected to a heat treatment at 500°C (C-fiber) and 550°C (SiC-fiber) in air, respectively, for a period of 20–30 s.

In Refs 5 and 6 the production of the composites is described in detail. After removal of the sizing, the fiber bundles were pulled through the slurry pool containing a suspension of glass powder and the respective sol–gel solution. On a hexagonal drum, the fibers were wound in parallel and on top of each other to prepreg. plates and subjected to subsequent hot pressing. Borosilicate glass (Duran) with a low thermal expansion coefficient, produced by Schott Glaswerke, Mainz, FRG, was selected as the matrix material.

2.3 Characterization methods

Characterization was carried out by means of light microscopy, scanning electron microscopy (SEM) and high-resolution Auger electron spectroscopy (HRAES). For the latter, a device supplied by the Perkin Elmer company (PHI 600) was used. The typical excitation conditions were primary electron current of about 20 nA at an accelerating voltage of 3–10 keV. Depth profiling was carried out by means



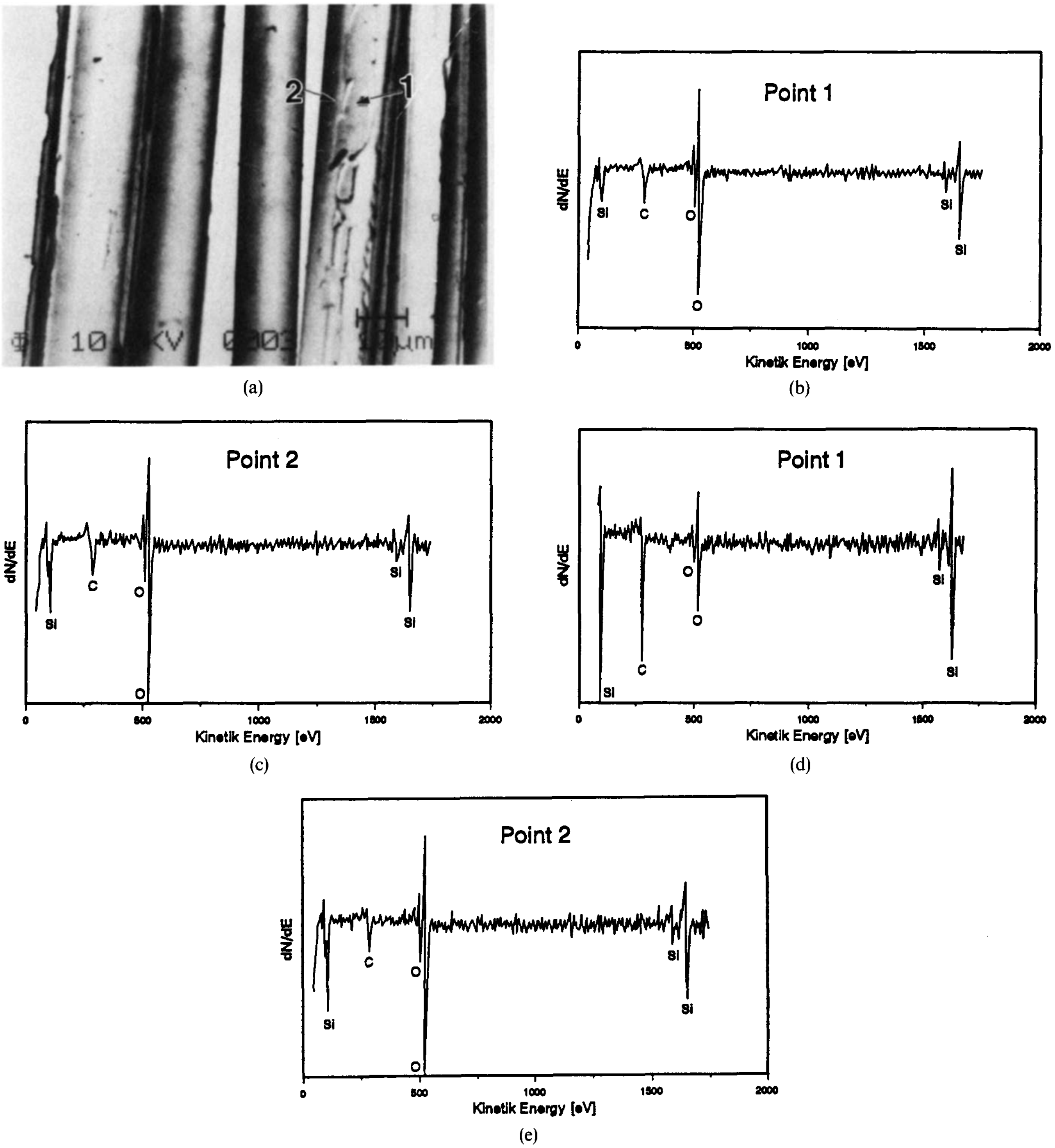
(a)

(b)

Fig. 1. HRAES investigation of a ZrO_2-coated SiC-fiber (Sigma). (a) Secondary electron micrograph; (b) point analysis at point 1 after a sputter depth of 34 nm.

of a scanning Ar ion beam with a primary ion energy of 6 keV at an angle of incidence of 45° to the normal of the specimen. The sputter depth was calibrated by a SiO_2 standard. The microstructure was investigated using an illuminating microscope (Zeiss) and a scanning electron microscope (Jeol, JSM 840). The latter was equipped with an energy-dispersive analyzer (Kevex Quantum Detector).

The bending strength of the composites was determined by means of a three-point bending test with a support $L = 80$ mm and a specimen thickness $d = 3$ mm. The high L/d ratio is required for the reduction of the shear stress.[7] Testing was carried out using a universal testing machine, Instron model 4301, with a load cell of 5 kN. The tests were performed at a constant cross-head speed of 1·2 mm/min. The deflection was determined from the crosshead displacement.



(a) (b) (c) (d) (e)

Fig. 2. HRAES investigation of SiO_2-coated SiC-fiber bundle (Nicalon). (a) Secondary electron micrograph; (b), (c) point analysis of the coated fibers in the as-received state; (d), (e) point analysis after a sputter depth of about 50 nm.

3 Results

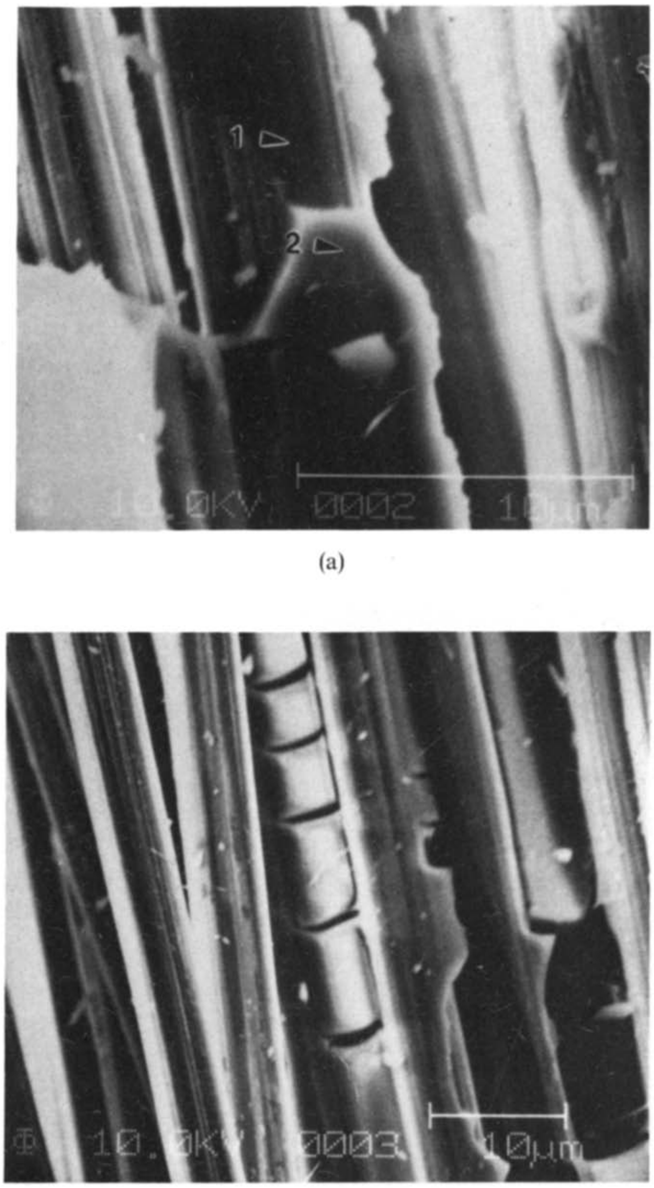
3.1 Mono-filament

To work out the principal steps of the coating technology, experiments with mono-filaments were first carried out. Figure 1 shows the ZrO_2 coating of the mono-filament (SiC-fiber, Sigma, Tübingen, FRG). In this case, the coating had a thickness of about 0·5 μm, as a result of which the roughness and the topography of the filament were also taken up by the coating (Fig. 1(a)). Moreover, the secondary electron micrograph shows characteristic contraction cracks both in circumferential and axial directions relative to the longitudinal axis of the fiber. These cracks are attributed to the volume reduction of the sol–gel layer due to annealing. At the crack base a small amount of Zr is still detectable. In the ZrO_2 layer, carbon is contained in addition to zirconium and oxygen. This carbon represents the impurity in the solvent (Fig. 1(b)). These coatings were exposed to solidification at 550°C in air. Preliminary drying at about 110°C did not affect the quality of the coating. Similar results were also obtained for SiO_2 and Nb_2O_5 coatings of SiC-fibers.

3.2 Fiber bundles

HRAES investigation of the SiO_2 coating on a SiC-fiber bundle (Nicalon) is shown in Fig. 2. According to the point analyses, a SiO_2 layer is to be found on all fibers (Fig. 2(b) and (c)). The shift of the Si peak from 92 to 76 eV indicates an oxidic bonding of Si.[8] After a sputter depth of about 50 nm, SiO_2 still exists at point 2 (Fig. 2(e)), while the C/O/Si peak ratios of the analysis at point 1 (Fig. 2(d)) already correspond to those of the SiC-fiber (Nicalon) in its initial state.[9] This also indicates that no chemical modifications of the fiber surface took place during coating. Two layer thicknesses have been achieved during coating: a thickness of about 50 nm and a thickness of several hundred nm. Furthermore, small carbon fractions are detected in the coating. They represent residues of the solvent.

The C-fiber bundles (T-800, Toray, Japan) exhibit another behavior. The SiO_2 layer on this type of fiber is shown in Fig. 3. In this case, the maximum layer thickness is up to 1 μm (Fig. 3(a)). With this high number of fibers per bundle an enrichment of the coating solution takes place between the fibers (Fig. 3(b)). The space between the fibers can be regarded as a capillary, into which the solution is drawn. As a result, SiO_2 intermediate layers with a thickness of up to 10 μm were obtained. In these enriched areas, contraction cracks occur (Fig. 3(b)). The resulting agglutination of several fibers may also cause the surface to peel off during further handling for composite production, such that a SiO_2 layer can no longer be detected on parts of the fiber. Thus, no homogeneous coating could be obtained for the fiber with 12 000 filaments per bundle. In C-fiber bundles more fiber agglutinations and a higher number of thicker layer regions (several μm) exist than in SiC-fiber bundles.



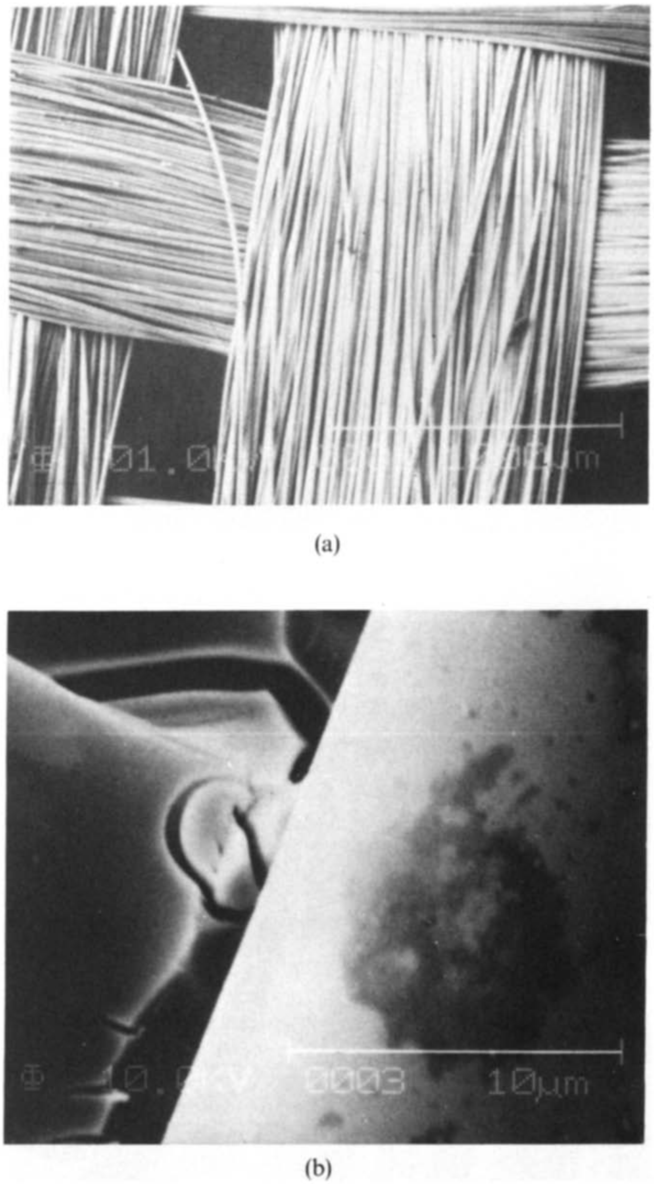
(a)

(b)

Fig. 3. (a), (b) Secondary electron micrographs of the SiO_2-coated C-fiber bundle (T-800).

3.3 Fabrics

The results of fabric coating are represented in Fig. 4 for a Nb_2O_5 coating. A general view of the fabric is shown in Fig. 4(a). Contraction cracks, fiber agglutinations and enrichments of the coating material can also be observed in the fabric.



(a)

(b)

Fig. 4. Secondary electron micrograph ((a) general view; (b) crossing point of fiber bundle) of the Nb_2O_5-coated SiC-fiber fabric.

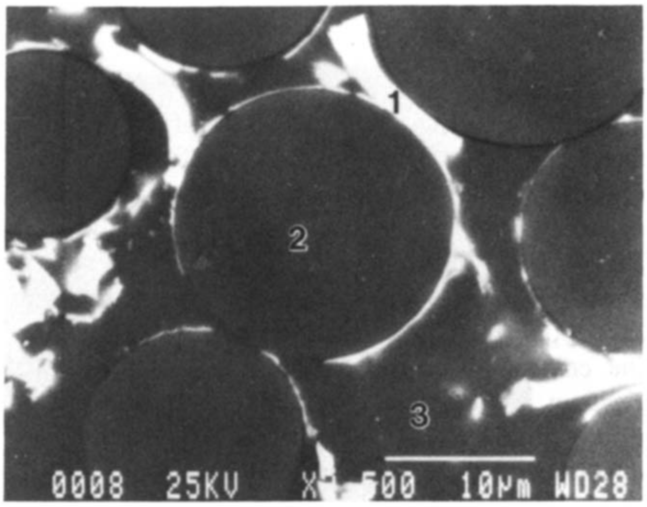


Fig. 5. Backscattered electron micrograph of the SiC-fiber (Nicalon)/borosilicate glass composite, for which a ZrO_2 sol–gel solution was used.

Furthermore, enrichments of several µm in thickness occur at the crossing points of the fiber bundles (Fig. 4(b)). According to HRAES, the layers on the individual fibers are about 50 nm thick. The top and the bottom of the fabric have to be distinguished. Due to gravity, an enrichment of the coating material takes place at the bottom during the process of drying. Consequently, a depletion is found to occur on the top side of the fabric. This is also observed for the other coatings.

3.4 Composites

When using a sol–gel solution in composite production, SiO_2 detection at the fiber–matrix interface is rendered more difficult. On the one hand, a SiO_2-rich matrix is used. On the other, SiO_2 may be released from the SiC-fiber (Nicalon) by oxidation during hot pressing and, hence, a C-rich layer is formed between the fiber and the matrix.[3,10–12] The Nb_2O_5-containing solution leads to the formation of rod-shaped NbC crystallites of about 40 nm × 100 nm in size at the interface. This was analyzed by HRAES investigation and is confirmed by other authors.[13,14] The microstructure of the composite, for the production of which a ZrO_2 sol–gel solution was used, is presented in Fig. 5.

Due to the higher atomic number contrast, ZrO_2 is represented by the bright phase in Fig. 5. As the layer thickness may vary between several 10 nm and 100 nm according to the findings obtained during fiber bundle coating, the inhomogeneity of the annular structures can be explained. The existence of ZrO_2 in the matrix can be attributed to the fact that the glass powder particles were also coated with ZrO_2. Comparison with other studies with zirconium content of the initial matrix[13] and in the

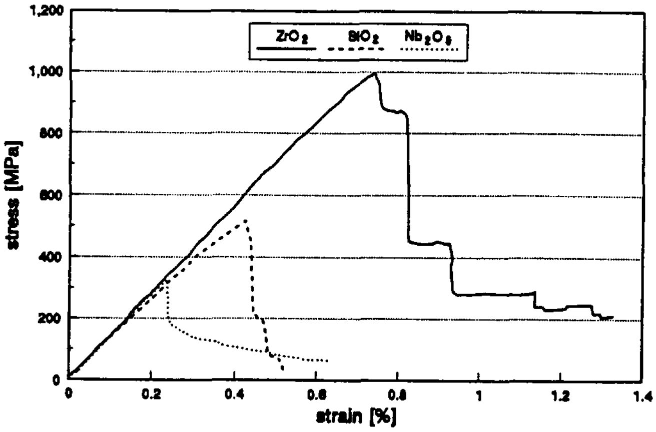


Fig. 6. Stress–strain curves of the SiC-fiber (Nicalon)/borosilicate glass composite produced with different sol–gel solutions.

matrix of the composite shows that the properties of the interface can be influenced by the method applied in this work.

The effect of the structural states resulting from the different sol–gel solutions on the mechanical properties was investigated by means of bending tests. Typical stress–strain curves of the three composites are shown in Fig. 6. The fiber volume fraction of the three composites is 45 vol.%. As is evident from the comparison of the three composites, the modification of the structure by the ZrO_2 sol–gel solution leads to a markedly increased bending strength and the fracture behavior is found to be more controlled.

4 Summary

The coating of reinforcing components by means of the sol–gel technique provides a decreasing layer quality with an increasing complexity of fiber architecture (mono-filament–bundle–fabric). The following problems are found to occur:

- —contraction cracks of the fiber coating;
- —enrichment of coating material between the fibers due to capillary forces and fiber agglutinations resulting in the peeling-off of the surface layer during further handling;
- —enrichment of coating material at the crossing points of the fiber bundles and segregation effects during the drying of the coated fabrics.

These problems are independent of the layer thickness. As far as the composite is concerned, however, the results show that the microstructure of the composites and particularly of the fiber–matrix interface can be influenced considerably by the coating. With the individual components (fiber, matrix, sol–gel solution) being selected accordingly, this becomes manifest by an increased bending strength and a better controlled fracture behavior of the composites.

References

1. Langley, N. R. & Li, C. T., Effect of interfacial diffusion barriers on thermal stability of ceramics fibres. *Mat. Sci. Res.*, **21** (1986) 401.
2. Hsueh, C.-H., Becher, P. F. & Angelini, P., Effects of interfacial films on thermal stress in whisker-reinforced ceramics. *J. Am. Ceram. Soc.*, **71**(11) (1988) 929.
3. Brennan, J. J., Interfacial characteristics of glass-ceramic matrix/SiC fiber composites. *Journal de Physique, Colloque C5, Supplement No.* 10, **49** (1988) 791.
4. Wahl, G., Chemische Abscheidung aus der Gasphase. In *Proceedings Verbundwerk*, ed. S. Schnabel, R. Gadow & J. Kriegesmann, 1988, pp. 29.00–29.40.
5. Pannhorst, W., Spallek, M., Brückner, R., Hegeler, H., Reich, C., Grathwohl, G., Meier, B. & Spelman, D., Fiber-reinforced glasses and glass ceramics fabricated by a novel process. *Ceram. Eng. Sci. Proc.*, **11**(7–8) (1990) 947.
6. Spallek, M., Pannhorst, W., Hegeler, H., Reich, C. & Brückner, R., Neue Hochtemperatur-Verbundwerkstoffe: Faserverstärkte Gläser und Glaskeramiken. *VDI-Berichte*, No. 734 (1989) 245.
7. Popp, G., Böder, H. & Gruber, K., Ermittlung mechanischer Kenndaten von kohlefaserverstärktem Kohlenstoff (CFC) mit dem Biege- und Zugversuch. *Z. Werkstofftechnik*, **16** (1985) 252.
8. Davis, L. E., MacDonald, N. C., Palmberg, P. W., Riach, G. E. & Weber, R. E., *Handbook of Auger Electron Spectroscopy*, 2nd Edn. Physical Electronics Industries, Eden Prairie, MN, 1976.
9. Meier, B. & Grathwohl, G., Microanalytical investigation of fibre-reinforced ceramic materials. *Anal. Chem.*, **333** (1989) 388.
10. Grathwohl, G., Hähnel, A., Meier, B., Pippel, E., Richter, G. & Woltersdorf, J., Fibre-reinforced SiC-matrix composites: microstructure, interfaces and mechanical properties. *J. Eur. Ceram. Soc.*, **10** (1992).
11. Meier, B., Spelman, D. & Grathwohl, G., Microstructure, interfaces and mechanical properties of fibre reinforced glasses. In *Fourth European Conference on Composite Materials*, Stuttgart, ed. J. Füller, G. Grüninger, K. Schulte, A. R. Bunsell & A. Massiah. Elsevier Applied Science, London and New York, 1990, pp. 475.
12. Cooper, R. F. & Chyung, K., Structure and chemistry of fibre–matrix interfaces in silicon carbide fibre-reinforced glass-ceramic composites: an electron microscopy study. *J. Mat. Sci.*, **22** (1987) 3148.
13. Mazerolles, L., Michel, D., Ulmer, L., Pastol, J. L., Parlier, M. & Ritti, M. H., Interfaces in SiC fiber-reinforced glass-ceramic composites. *Journal de Physique, Colloque C1, Supplement No. 1*, **51** (1990) 879.
14. Bischoff, E., Rühle, M., Sbaizero, O. & Evans, A. G., Microstructural studies of the interfacial zone of a SiC-fibre-reinforced lithium aluminium silicate glass-ceramic. *J. Am. Ceram. Soc.*, **72**(5) (1989) 741.