Transparent fiber reinforced glass composites

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Abstract: The paper deals with transparent composites on the basis of a glass matrix and nanocrystalline oxidic (Nextel) fibers. In order to hinder or prevent the reaction between the fibers and the matrix glass and – in consequence – to influence the mechanical behaviour of the composite, the fibers are definedly coated. BN, TiO_2 or a double layer of both were applied. BN-layers allow sliding between the fibers and surrounding matrix glass. It is of greatest importance to choose ccompatible fiber and matrix glasses; especially the thermal expansion coefficient and the refractive index must correspond. The composites were hot pressed. In case of processing in vacuum there is the possibility of BN-decomposition and of appearance of atomic lead in lead oxide containing matrix glass, which turns the colour of the composite grey. The protection of the BN- by a TiO_2-layer and hot pressing in oxidic atmosphere prevet this effect. Moreover one can avoid small bubles by increasing pressure during hot pressing or vacuum at low temperatures and pressures at high temperatures.

Keywords: glass-matrix composites, transmittance, damage tolerance, coating layer, hot pressing

1. Introduction

It is very well known, that the reinforcement of glass with different components like fibers, whiskers or platelets leads to enhancement of fracture toughness, strength and thermal shock resistance compared to monolithic sheet glass. Some composites have already been produced on an industrial scale and commercialised [1]. In most cases the reinforcing fibers were carbon or carbon-coated SiC-fibers. Black composites resulted.

In the past there were undertaken some efforts to make glass composites transparent for the visible light using transparent fibers and adapting the optical properties of the components [2]. The disadvantage of these composites is their brittleness. Up to now a practicable solution which meets the complex optical and mechanical demands has not been found. Each chemical interaction of the components leads to brittle fracture. But such an interaction could improve the optical properties.

In order to produce optically transparent and at the same time damage tolerant glass composites, one has to optimise contradicting parameters:

- The improvement of fracture toughness by crack deflection, fiber debonding and fiber pull-out can only be achieved by a force- or shape-bonded interface between fiber and matrix.
- In opposite the optical transmittance requires as low as possible disturbing interfaces, and practically identical refractive indexes of all components.

While differences of thermal expansion coefficients of the components always impair the optical transmittance, they can positively influence the mechanical properties. An insufficiently controlled technology resulting in irregularly distributed fibers, bubbles and other heterogeneities impairs both the mechanical and optical properties.

Therefore the starting point for achieving good mechanical and optical properties of the composite is the adaptation of the mechanical and optical properties of the components as well as a suitable interface between fiber and matrix provided by fiber coating. Furthermore the fiber composition has to guarantee its softening at much higher temperatures as for the matrix glass. Nevertheless the strongly distinguished compositions of matrix and fibers should have nearly the same thermal expansion coefficient.

The fiber coating should meet the following requirements:

1. Prevent chemical interactions between fiber and matrix by diffusion or reaction and allow fiber sliding.
2. Optical transmittance in the visible wavelength range
3. Thermally and environmentally stable, also under oxidizing conditions.

Because the thickness of the coating layers is far from the wavelength of the visible light their refractive index is not so critical. Earlier investigations have proven the efficiency of double coating concepts [3, 4].

2. Materials

For the investigations presented here the following components were used (Table 1).

As seen, the refractive indexes correspond relatively well, the thermal expansion coefficients only in case of the glass denoted 8650. However, this glass contains high amount of lead oxide what prevents the hot pressing in vacuum. From the point of view of the thermal expansion coefficient the next suitable glass could be the glass N-SK 4. However, its high transformation temperature requires high processing temperatures.

Table 1. Properties of the used composite components [5]

property	dimens.	glass F 4	glass N-SK 4	glass 8650	fiber Nextel 440
refractive index		1.617	1.613	1.61	1.616
therm. exp. coeff.	$10^{-6}K^{-1}$	9.1	7.4	5.1	5.3
transform. temp.	°C	439	658	475	=
E-modulus	GPa	56	84	58	190
bending strength	MPa	70	57	50	=
tensile strength	GPa	-	-	-	2.07
fiber diameter	µm	=	=	=	10 - 12

The Nextel 440-fibers (mass-%: 28 SiO_2, 70 Al_2O_3, 2 B_2O_3) are nanocrystalline up to 1100 °C [6] and contain γ-Al_2O_3-crystals.

With respect to the common coating concepts in fiber reinforced-brittle matrix-composites, a non-oxide boron nitride (BN) layer (that has the same lubricant nature like pyrolytic carbon) and an oxidic titania (TiO_2) layer were tested, together with a BN/TiO_2 double coating.

3. Experimental procedure

CVD-coating of the Nextel 440-fiber was carried out at the TU Chemnitz, Dept. of Physical Chemistry. It was carried out with 40 or 100 nm BN-, 40 or 100 nm TiO_2- and combined layers continuously under atmospheric pressure in a vertical hot wall reactor. Before coating the fibers were thermally desized (3 h/500 °C). The deposition of BN was carried out by reaction of boric acid-trimethylate and ammonia at 900 °C. TiO_2 was received by thermal decomposition of isopropyl-orthotitanate in the presence of oxygen at 450 °C [7, 8].

The composites were prepared by the slurry method described in [9]. Previously the matrix glass was pulverized (d_{90} < 70 µm). All composites presented have an unidirectional fiber reinforcement. The hot pressing was carried out under vacuum for the F 4- and N-SK 4-matrix glasses, and in air for the 8650-matrix glass. The maximum pressure (5 MPa) was held also during the cooling phase between the maximum and the transformation temperature. The maximum hot pressing temperature depends on the softening behaviour of the matrix glass. The N-SK 4-glass was hot-pressed at 850 °C, the F 4- and 8650-matrix glasses at 750 °C . The fiber tensile strength [10] and the 3-point flexural strength [11] of the composites were measured using an INSTRON 4467 equipment. The optical transmission curves of the composites in the wavelength range of visible light were measured with an UV-VIS-NIR spectrometer Shimadzu UVPC 3201. The surface topography of the desized and coated fibers before and after 5 hours treatment at elevated temperatures (annealing) was examined by an atomic force microscope type TMX 2000 Explorer SPM from TopoMetrix in contact mode under atmospheric condition. The structure of the composites could be visualized with a SEM CamScan 44 from Cambridge Instruments.

4. Results and discussion

4.1 Single fiber strength

The single fiber-tensile strength-test after fiber annealing at the temperature close to the hot pressing temperature indicates if the joining process will damage the fiber or not. The diagram (Fig. 1) compares the tensile strength of the desized fiber and of the fibers coated with 40 nm BN or 40 nm TiO_2 or both 40 nm BN/40 nm TiO_2 before and after annealing at 750 °C (the shown results are a small selection from a great amount of measurements at different temperatures and for varying layer thickness).

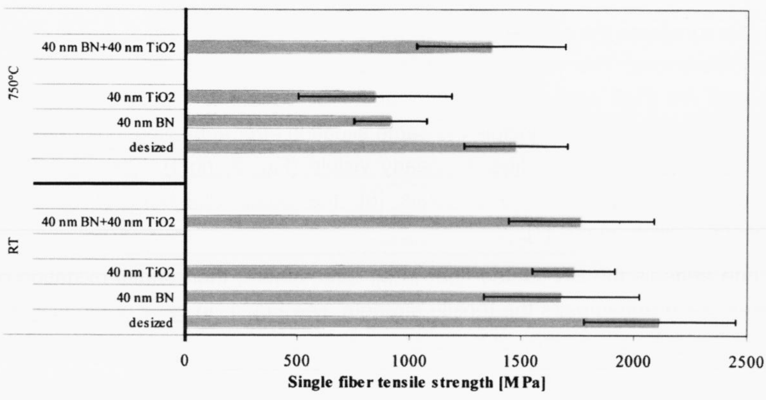

Fig. 1: Tensile strength of different coated fibers before and after annealing for 5 hours at 750 °C; the black stretches indicate the scatter of experimental results.

Desizing at 500 °C does not influence the room temperature mechanical properties of Nextel 440-fibers (see Table 1). . However the coating at increased temperatures decreases somewhat the mean values of the tensile strength, but the differences are not significant. Also the deposition temperature of 900 °C for BN seems to be nearly without influence on the strength at room temperature.

Different values have been measured after annealing at 750 °C. The tensile strength decreases significantly in all cases and shows very small values compared to the original fibers. Note that the loss of strength of the double coated fibers is not as dramatic as for the single coated ones. Nevertheless all coated fibers could be used as the reinforcement of glass matrices.

Fig. 2 shows the surface of double coated fibers before and after annealing.

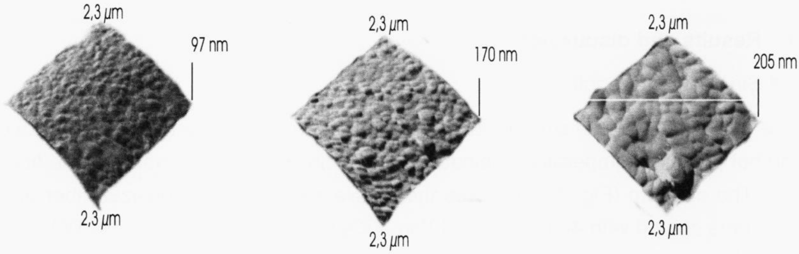

Fig. 2: AFM-micrographs of a desized fiber (left), the double coated fibers before (middle) and after (right) annealing at 750 °C/5 hours

If one compares the picture (middle) with the one of the desized fiber (left) there are no differences. The very fine γ-Al_2O_3-crystals of the fiber itself are copied. The several nm thick double layer of BN and TiO_2 does not influence the topography significantly. This is in principle the same situation after annealing, but the beginning of crystal growth in the fiber is clearly visible (Fig. 2, right). The inner BN-layer consists of turbostratic nanocrystals [8], the outer TiO_2-layer of homogenous nanocrystalline anatas [7].

If one anneals the BN-coated fiber in air atmosphere, then partial oxidation of BN takes place and impairs the tensile strength, see Fig. 1. In case of the single TiO_2-layer the grain boundaries of the anatas nano crystals act like flaws and reduce the strength in a similar matter, see once more Fig. 1. The double coated fiber has nearly the same tensile strength as the desized one.

4.2 Mechanical properties of the composites

In previous investigations [12] the only aim was to develop a damage tolerant glass composite. Because the optical transmittance was not important, Duran™ from Schott could be used as the matrix glass with an optical mismatch to the Nextel 440 fiber and lower thermal expansion coefficient. This may promote the fiber pull-out under load. The sliding layer was carbon and accordingly light absorbing. Fig. 3 demonstrates typical results for the most fiber reinforced materials. For comparison the stress-strain curve of the as-received composite is shown, together with the curves after a heat treatment at 500 °C for 200 and 500 h. It is clearly visible the damage tolerant behaviour, bending strength and fracture strain are much higher as for Duran™ (bending strength = 80 MPa). The fracture toughness was calculated to be 8.6 MPa · $m^{1/2}$, the work of fracture is 45 ± 10 N/m [6]. The fracture surfaces show characteristic fiber pull-out.

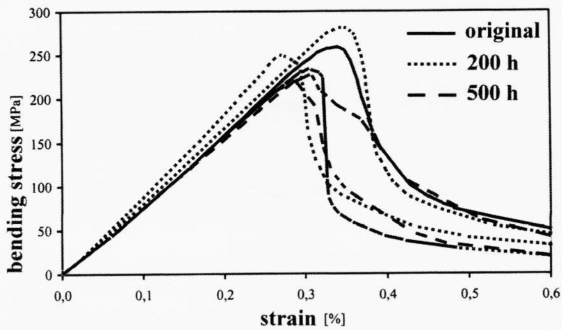

Fig. 3: Stress-strain curves of the Nextel 440/C/Duran™ composite as received and after annealing at 500 °C for 200 or 500 h [6]; in each case the best and the worst curve is shown.

The situation changes if the thermal expansion coefficient of the matrix glass is higher than that of the fiber, like in case of the N-SK 4 or F 4 glass matrix, see Table 1. During the cooling of the hot pressed composites, the fibers are compressed by the surrounding matrix glass. It is true that fibers are coated with a functioning sliding layer, but this does not act like in a composite with adapted or lower thermal expansion coefficient of the matrix glass. Fig. 4 demonstrates the results for

- the pure hot pressed matrix-glass N-SK 4

- a composite containing 8 % FVC (fiber-volume content) desized Nextel 440-fibers
- some composites with differently coated fibers and 15 … 17 % FVC.

The pure matrix glass, the composite containing desized fibers and the (not shown here) composite containing TiO_2-coated fibers show brittle fracture. The bending strength of these probes is as low as usual for glass sheets or even worse. In some cases the interactions between the not coated fibers and matrix lead to formation of micro cracks in the matrix perpendicular to the fiber direction. In opposite the composites with BN-single coating or BN/TiO_2 double coating showed:

- an increasing specific work of fracture up to 2000 N/m
- a bending strength of more than 300 MPa up to 360 MPa and
- a fracture toughness up to 6 MPa · $m^{1/2}$.

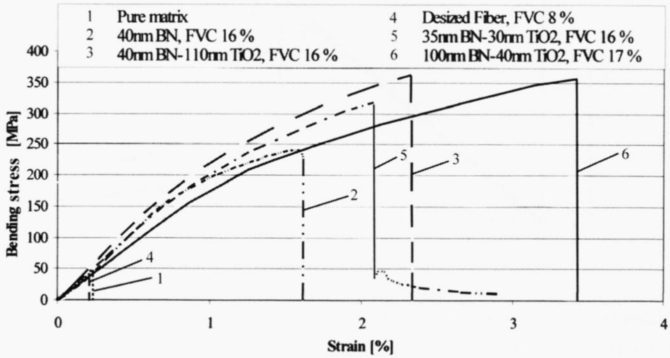

Fig. 4: Bending curves of Nextel 440-fibers/N-SK 4-matrix composites with different interfaces

While the bending strength of the composites with double coated fibers does not depend so strongly on the thickness of the BN- or TiO_2-layer, a thick BN-layer which causes a good sliding increases the work of fracture dramatically, compare curves 5 and 6.

The shape of the stress-strain curves of the composites 2, 3, 5 and 6, shown in Fig. 4, differs from all previously reported curves. At low strains the curves are straight lines and at higher strains they become root like. This results from an overlapping of sliding and fiber clamping. Finally these composites break suddenly, but at much higher stress and strain values as pure, not reinforced glass. The fracture areas show the fiber pull-out, but at the same time the brittle matrix fracture, see Fig. 5.

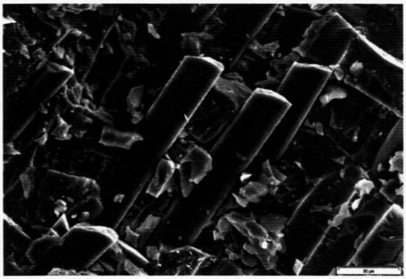

Fig. 5: Fiber pull-out and matrix fracture in Nextel 440/BN/TiO_2/N-SK 4 composites

With application of the matrix glass 8650 with a thermal expansion adapted to the Nextel 440-fibers, the problems of clamping disappear. As the glass contains lead oxide, which is sensitive against vacuum or reducing atmosphere, the hot pressing must be carried out at oxidizing atmosphere in order to prevent formation of atomic lead and oxygen, which causese grey colour and bubbles. The remaining small bubbles influence the mechanical properties. The shape of the stress-strain curves is similar to those shown in Fig. 3.

In order to prevent or to diminish the negative influence of the entrapped gases, the pressure during hot pressing was increased. As a resulting all mechanical properties improved. A combination of evacuation of the probes at room temperature for removing gases between the powder grains and than hot pressing in air requires a new equipment for the following experiments.

4.3 Optical properties of the composites

The optical properties of the composites with various (see Table 1) matrix glasses differ considerably. Because of the bad adaptation of the thermal expansion coefficient in the composite with the F 4-glass matrix, inner thermal stresses prevent good optical transmission. Also in case of the N-SK 4-matrix glass the results were not satisfactory. These materials are translucent. Fig. 6 shows the results for different N-SK 4-containing materials.

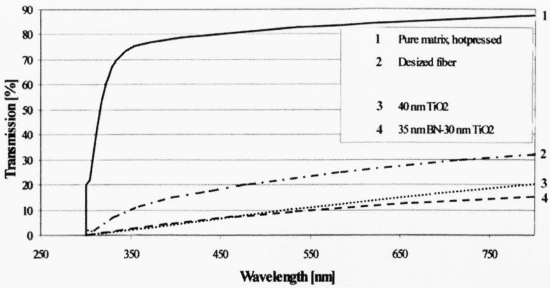

Fig. 6: Transmission spectra of hot pressed N-SK 4-glass (curve 1), its composites with ≈ 15 % FVC (curves 2, 3 und 4)

The curve 1 of the hot pressed pure matrix glass shows already the influence of enclosed small bubbles or former grain boundaries of the glass powder.

The transmission of the composite with desized Nextel 440-fibers (curve 2) is markedly lower. Even though chemical reactions take place in this case between fiber and matrix (this softens the optical effect of grain boundaries) and the refractive indexes correspond, the thermal stress is the reason for this behaviour.

Using coated fibers, the single TiO_2-layer (curve 3) gives the best results. The sample with the double coating is also translucent. In case of the single BN-layer the transmission was only 4 %. Here a coating degradation in the course of hot pressing might occur, see Fig. 7. This effect can be avoided by the TiO_2 protection.

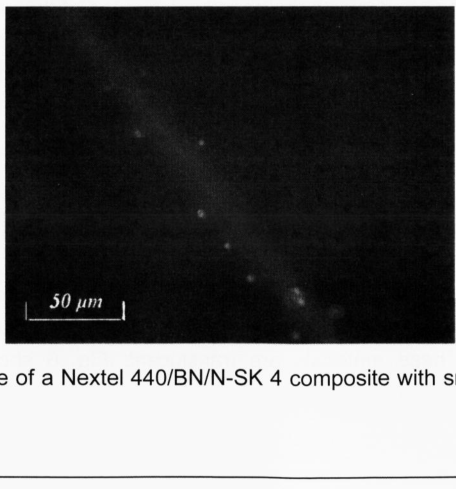

Fig. 7: SEM-picture of a Nextel 440/BN/N-SK 4 composite with small bubbles at the fiber surface [13]

The matrix glass 8650 (the composite hot pressed in air) would solve the optical problems. The first composites hot-pressed at a pressure of 1 MPa were translucent. The increase of the pressure up to 5 MPa does not only improve the mechanical properties but also the optical, see. Figure 8. The bubbles were compressed. That they are not disappeared completely show the transmission curve, see Fig. 8, with an increasing tendency from the NUV up to the NIR.

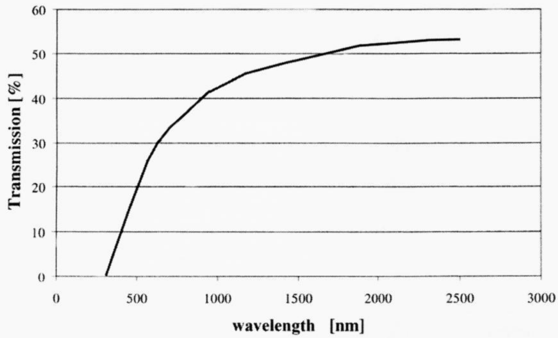

Fig. 8: Transmission curve of a Nextel 440/BN/TiO_2/8650 composite, containing 10 % FVC (multidirectional)

The transmission in the VIS is now as before not so high as expected, but relatively good in the NIR. The composite is transparent without tint. The single fibers are not visible. The position of the endless filaments is not unidirectional, but random.

5. Summary

It was the aim of the research to develop a damage tolerant, optical transparent glass composite. Because of former good experiences the Nextel 440 fiber was used for reinforcement. In order to guarantee fiber pull-out and to minimize optical losses, the fibers were coated with BN, TiO_2 and BN/TiO_2. The matrix glasses had nearly the same refractive indexes as the fiber and distinguished in thermal expansion coefficients. The mechanical properties varyed strongly in dependence on the expansion mismatch. Fiber pull-out and clamping were observed. Bending strengths of 360 MPa and a fracture toughness up to 6 MPa $\cdot$ $m^{1/2}$ were measured. The research confirms the possibility to produce a transparent, damage tolerant composite on the basis of Nextel 440-fibers and the Schott-glass 8650. The composite has an optical transmission of nearly 30 % in the VIS and of 50 % in the NIR. Because it is a lead oxide containing material, an oxidizing atmosphere has to

be used during the processing. There is a great potential to optimise the mechanical and optical properties in dependence on the process parameters.

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6. References

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