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Structure and Properties of Interlayers in Polymer-Derived C/SiC Composites

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Abstract

The microstructural features of the interlayers between fibre and matrix are essential parameters governing the mechanical behaviour of ceramic/matrix composites. In particular, suitable carbon interlayers produced pyrolytically by chemical vapour deposition (CVD) may reduce the stress transfer from the matrix to the fibre resulting in the observed increase of the composite strength. Such matrix stresses are due to the shrinkage caused by the process technology during the production of composites via Si polymer pyrolysis. The layer parameters can be optimized by combining mechanical test procedures with microstructural (HVEM, HREM) and microchemical (EDXS, EELS) analyses.

Die mikrostrukturellen Besonderheiten der Grenzschichten zwischen Faser und Matrix sind wesentliche Steuerparameter des mechanischen Verhaltens keramischer Verbundwerkstoffe. Speziell können geeignete, pyrolytisch über chemische Dampfabscheidung (CVD) hergestellte Kohlenstoffzwischenschichten die Spannungsübertragung von der Matrix auf die Faser vemindern, was zum beobachteten Anwachsen der Kompositfestigkeit führt. Solche Matrixspannungen werden von den Schrumpfungen verursacht, die mit der Herstellung des Komposits durch Si-Polymer-Pyrolyse verbunden sind. Die Schichtparameter können optimiert werden durch Kombination mechanischer Testverfahren mit mikrostrukturellen (HVEM, HREM) und mikrochemischen (EDXS, EELS) Analysen.

La microstructure des couches présentes entre la fibre et la matrice est une composante essentielle de la tenue mécanique des composites à matrice céramique. En particulier, des couches de carbone produites par CVD pyrolitiquement peuvent réduire le transfert de contrainte de la matrice à la fibre, augmentant ainsi la résistance du composite. Ces contraintes proviennent du rétricessement dû à la pyrolyse d'un polymère à base de Si lors de la fabrication industrielle. On peut optimiser les caractéristiques de ces couches en combinant des tests mécaniques avec des analyses microstructurales (HVEM, HREM) et microchimiques (EDXS, EELS).

1 Introduction

As is well known, ceramic materials are unequalled for their abilities to sustain both high mechanical and high-temperature loadings if it is possible to overcome their inherent brittleness and to achieve a damage-tolerant quasi-ductile fracture behaviour. In monolithic materials such a behaviour has not yet been attained to the desired extent—in particular in the high-temperature range—despite improvements by means of transformation and micro-crack reinforcement and more homogeneous and finer structures. On the other hand, the possibilities offered by fibre reinforcement of ceramic materials have not yet been fully exploited. In these composite systems brittleness may be reduced considerably by activating a variety of energy-dissipating processes in the load and failure case.

This study deals with bidirectionally (2D–90°) reinforced C/SiC composites, the matrix of which has been produced by infiltration and pyrolysis of Si polymers.[1-3] After infiltration and cross-linking of the Si polymers the latter are transformed into a ceramic matrix material by pyrolysis in an inert gas atmosphere. Suitable Si polymers assuring a high ceramic yield and a reduced shrinkage in addition to a good processibility during pyrolysis are decisive for success. On the one hand, this procedure is economic, while on the other it allows the use of the production technology developed for fibre-reinforced polymers and makes it relatively easy to transfer the results achieved with samples to complex large-scale structures.

Nevertheless, it has the following disadvantage: in the production of composites the abovementioned shrinkage of the matrix, which is sometimes considerable (final porosity of 20 to 30%), occurs during the pyrolysis of polymers. It leads to internal stresses affecting the mechanical properties owing to the reduction of the interlaminar shear strength and the impaired friction behaviour during debonding and pullout processes. The porosity may be reduced by either reinfiltration cycles using suitable Si polymers and a chemical vapour infiltration (CVI) process, respectively, or by the use of basic materials of a higher ceramic yield. The polysilanes used contain Si and C in a weight ratio of approximately 3 : 2; the final product SiC, however, contains both elements in a weight ratio of 7 : 3, leading to a mass reduction of approximately 27% during the pyrolysis and to a volume loss of almost 80%, if the different densities are considered. This is the reason why SiC powder is added to the polysilane solution, i.e. the Si polymer content is reduced in such a way that the pyrolysed ceramic product only acts as a binding agent between the fibres and the SiC filler particles.

The strong internal stress resulting from the matrix shrinkage during pyrolysis cannot be reduced by uncoated fibres due to an insufficient sliding capability, so that composites with carbon-coated fibres are distinctly tougher and stronger than those with uncoated fibres. The strength increases by up to 70% with suitable interfaces, the ultimate elongation by approximately a fourfold amount. This study deals with the structure and function of such carbon coatings produced by chemical vapour deposition (CVD).

2 The Special Role of Interlayers

The properties of the interlayers or interlayer systems between fibre and matrix play a governing role in the composite behaviour since the energy dissipation and toughening mechanisms (crack shielding, crack deflection, multiple crack formation, crack branching, debonding and pullout of fibres), which become effective in the composites, are mainly located in these layers. In general, these interfaces have complex structures and may be formed by both fibre coating and transport or exchange reactions during the production of composites. Thus, there is a large number of decisive parameters resulting in a wide range of different complex interface structures. Thickness, internal subdivision, chemical composition and the particular microstructure of such layers influence the properties of the composite system in such a way that these values can also be considered as control parameters of the mechanical and thermal behaviour of the composite material (cf. e.g. Refs. 4–10). Furthermore, the interface protects the fibre against chemical and mechanical degradation during the production process and—if carbon fibres are used, as in this study—impedes the oxidation of the fibre during the high-temperature load.

As far as solid-state mechanics is concerned, a fibre/matrix interface can be described by means of two characteristic values, the specific interface energy Γ_i and the interface friction stress, τ, i.e. the shear stress in the fibre/matrix range transmitted by friction (see also Ref. 6). For an optimized composite material both values must fulfill application-specific requirements.

Γ_i is represented by the bonding between matrix and fibre which should be relatively weak in this case compared to systems with metallic or plastic matrices. If the fibre/matrix bonding is too strong, a matrix crack may lead to the entire failure of the composite owing to brittle fracture propagation similar to monolithic ceramics. This can mainly be attributed to the fact that the so-called initial debonding, i.e. the first (locally limited) debonding of the fibre from the matrix along the interface is not possible. This, consequently, also prevents the second step of debonding, the so-called progressive debonding, which would otherwise propagate during increased stresses owing to axial stress gradients between fibre and matrix.

If—on the other hand—a sufficiently weak bonding and suitable stresses allow the described debonding processes, the prerequisites of a damage-tolerant behaviour are fulfilled; the resulting actual fracture toughness and the strength of the composite are, however, also determined by the friction condition in the debonded zone of the fibre/matrix interface. That means that the pullout of the fibre from the matrix which is impeded by friction, and which is possible after fibre fracture and which may also occur on account of the statistic distribution of the fibre strength even outside the range of maximum axial tensions (i.e. not only limited to the crack plane), has to be optimized with regard to its energy dissipation effect by influencing the friction condition of the interface.

If the frictional shear stress is *too high*, it leads to brittle failure; if it is *too low*, the energy dissipation is not sufficient; and if it is *diminishing*, the propagation of progressive debonding is unstable, leading to a considerable reduction of toughness and strength. (For details of the micromechanics of fibre composites, see Refs 6 and 11–17.

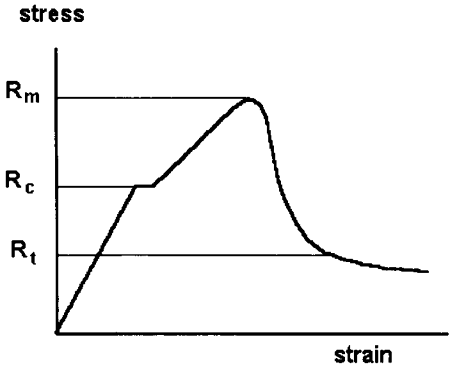


Fig. 1. The three strength parameters of ceramic continuous fibre composites (see text).

The particular role of the interface friction stress for all processes in damage-tolerant composite materials determining the characteristics becomes obvious by the fact that all characteristic strength parameters, i.e. the stationary critical matrix stress, R_c, the maximum stress (strength), R_m, and the residual strength (tail), R_t, depend on the interface friction stress.

The three strength parameters are explained in Fig. 1 by means of a stress–strain diagram typical of the examined material class (unidirectionally reinforced composites) for the tensile test. At R_c stationary crack propagation starts in the matrix in such a way that cracks, which may also interact with one or several fibres, propagate in a transverse direction to the fibre orientation. The fibres bridge the crack faces in order to suppress an increase of the crack tip stresses. From an energy balance[14–16] it follows that:

$$R_c = \left[\frac{6\tau\Gamma_m V_f^2 E_f E^2}{V_m E_m^2 r_f}\right]^{1/3}$$

where E stands for the modulus of elasticity of the composite which can be determined by means of the rule of mixture, V_f, V_m, E_f and E_m denote the volume percentages and moduli of elasticity of fibre and matrix, respectively, Γ_m stands for the specific surface energy of the matrix and r_f for the fibre radius.

The strength R_m, which is larger than the simple fibre bundle strength caused by the embedding of the fibres in matrix parts and the resulting transmittable shear stress τ, can be determined by an estimation[12] taking into account the Weibull parameters W_i of the fibre strength (σ_o, l_o, m):

$$R_m = V_f \cdot \left(\frac{2\sigma_0^m \tau l_0}{r_f(m+2)}\right)^{1/m+1} \frac{m+1}{m+2}$$

The frictional forces during the final fibre pullout determine the residual strength, yielding:[6,17]

$$R_t = V_f \frac{\sum(\tau, W_i, r_f)}{m+1} \Gamma\left(\frac{m+2}{m+1}\right)$$

with

$$\sum(\tau, W_i, r_f) = \left[\frac{l_0 \sigma_0^m \tau(m+1)}{r_f}\right]^{1/m+1}$$

(Γ denotes the gamma function).

The consideration shows that the three decisive parameters of the mechanical behaviour are controlled via interface characteristics, in particular by τ. In the case of a multilayer system or a layer sequence of several ranges of different degrees of graphitizing (see also Section 4) the mechanically weakest range is probably relevant for the macroscopic characteristics. For fibres with a rough surface, as e.g. the T 800 carbon fibres used, it is of particular importance to suppress a clamping between the fibre and matrix by the formation of suitable interlayers with a special texture influencing the debonding and sliding processes so that a favourable pullout behaviour may be achieved.

The coating of the fibres with graphitic layers of an orientation parallel to the interface should allow the control of the mechanical interface parameters. Owing to the microtexture of the turbostratically stacked hexagonal graphite basal planes a crack path may be expected within such a graphitic band, since the bonding in graphitic carbon is strongly anisotropic. *Within* the basal planes the C atoms are linked by strong σ-bonds on account of the planar trigonal sp^2 hybridization, whereas the distance of approximately 0·335 nm *between* the planes is too large for primary bondings. The electrons of the $2p_z$ orbitals form π-bondings and are delocalized in the basal planes. In addition to a minor contribution to the strong bonding within the basal planes they lead to a very weak bonding between the basal planes. This bonding behaviour results in a strong anisotropy: the K_{Ic} value, e.g. of pyrolytic carbon in plane orientation (crack introduction normal to the hexagonal basal planes), is approximately fifteen times the value of K_{Ic} for crack introduction parallel to the layers, on account of an extended delamination between the layers.[18] Experiments proved that the formation of a graphitic fibre/matrix interlayer, with a preferential orientation of the basal planes parallel to the interface, results in higher composite strengths and an improved toughness,[7–9] specially in considerably higher residual strength R_t.[10]

3 Process technology for fibre coating and production of composites

A general prerequisite to the optimum effect of fibre coating is the even deposition of all individual filaments (in this study it is 6000 per C fibre bundle). In combination with a procedure for the matrix formation guaranteeing the covering of the predeposited individual filaments with matrix material the optimum characteristics of the composite are to be achieved. The polymer pyrolysis already described guarantees that the maximum number of interfaces between fibre and matrix is attained by coating the individual filaments and by infiltration of the fibre bundle with the polymer slurry, assuring that all these interfaces contribute to an increased fracture toughness of the material. Contrary to this, it was observed that in materials, the matrix of which was produced by chemical vapour infiltration, the fibre bundles are covered with a shell of matrix material so that the inner part of the bundle is cut off from the precursor gas supply. Thus, the toughness of such materials is also based on the mechanical interaction of the filaments.

The production procedure of the C/SiC composites under investigation by means of polymer pyrolysis proceeds as follows. Initially a continuous fibre bundle passes into a bath with Si polymer slurry. The fibre bundle impregnated in this way is then placed on a mandrel from which parts of unidirectional fibre orientation are removed after drying of the layup before being processed to laminates of defined fibre orientation. Hollow bodies can be produced directly on the mandrel. The laminates or hollow bodies are crosslinked under autoclave conditions, resulting in a strong, stable green body which can be brought to final dimensions and pyrolysed in an inert gas atmosphere at temperatures above 1000°C.

After pyrolysis the composite is impregnated with a further Si polymer under rough vacuum; the chemical crosslinking of the polymer is followed by a further pyrolysis. This cycle is carried out up to three times.

The porosity of the material is reduced to approximately 15% by reinfiltration, with the matrix strength being correspondingly increased, leading to a stronger bonding between fibre and matrix which has to be compensated by optimizing the interface (for details see Sections 4 and 5).

The coupling of polymer pyrolysis and fibre coating requires special layer structures which should not only assure the desired improvement of the fracture-mechanical properties but should also be adjusted to the production technique of the composite. The basic prerequisite is a homogeneous coating of large amounts of fibres (in the range of kilometers), all individual filaments of the fibre bundle have to be coated. Since these layers are to allow the sliding capability they have to act as a solid lubricant, i.e.—in the case of carbon or boron nitride—texturized layers are aimed at, with glide planes aligned in parallel to the fibre surface as far as possible. Thickness, homogenity and degree of texturization of that layer are decisive for the bonding and pullout behaviour. To avoid an impairment of the fibre strength the coating process must not affect the fibres chemically or mechanically. All these prerequisites have to be checked, which requires subtle analytical methods because of the similarity of layer and fibre (both mainly consisting of carbon) and due to the small layer thickness.

The coating procedure has to retain the further processibility of the fibre. In addition to a sufficient residual strength of the coated fibre already mentioned, this includes a minor increase of stiffness and a sufficient wetting capability with polymer slurry. Furthermore, the fibre coating has to resist the thermal and mechanical loads during the composite production and finally, the deposition procedure should allow a cost-effective and continuous work.

A special CVD procedure[19] which has been developed for this application by ABB, Heidelberg, fulfils these requirements. It also allows a multiple coating with different substances, e.g. the production of an additional SiC deposit on the C layer within one working process by connecting several deposition zones in series which are floated with the appropriate precursor gases. The facility used for this study consists of a feeding unit, a heating zone for the thermal removal of the fibre sizing, the deposition zone for C or SiC as well as a take-up unit. The entire facility is operated under vacuum. In order to separate the individual filaments to achieve an even deposition, the filament tension was varied periodically. For the C deposition acetylene or ethylene were used as reaction gases with argon or nitrogen as carrier gases at 1060 to 1080°C at a pressure of 60 to 100 hPa. The layer thickness was varied between 30 and 80 nm, in order to measure its influence on the mechanical properties of the composites. The measurement was carried out gravimetrically and monitored by electron microscopic procedures.

4 Mechanical Properties

All measurements of the mechanical properties of the composites produced with C-coated C fibres were carried out at room temperature.

4.1 Three-point bending strength

For the bending tests bidirectionally reinforced samples (2D–90°) of a length/thickness ratio of 15 were produced. Figure 2 shows the measured bending strength as a function of thickness of the fibre coating. Compared to that Fig. 3(a), (b) and (c) illustrates the corresponding fracture images, the recognizable pullout lengths of which were

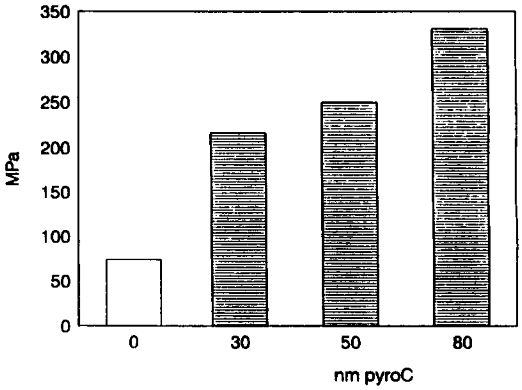


Fig. 2. Three-point bending strengths of 2D–90°C/SiC composites with pyrolytic C-coated T800 fibres.

used as a measure for the fracture toughness.

The strength of composites without fibre coating is approximately 80 MPa. Coating thicknesses of 30 to 50 nm lead to a clear increase of strength to 220 or 250 MPa; they are, however, not able to create a satisfactorily tough fracture behaviour. This is illustrated in the fracture area which is represented in Fig. 3(b), allowing the conclusion of a fracture course partially resembling a brittle fracture. Only a deposition of 80 nm of pyrolytic carbon combines a high bending strength of 320 MPa with a high fracture toughness, which corresponds to the strong fibre pullout represented in Fig. 3(c).

Therefore, the effect of the fibre coating can be interpreted as follows. In the case of lacking or insufficient coating the fibres are bonded to the surrounding matrix so strongly that the interface fracture energy is higher than the fracture energy of the fibres. Thus, debonding or pullout processes can not occur or only to a very limited extent,[11] and a macroscopic crack which will not be deflected into the fibre/matrix interface builds up a stress concentration at its tip, allowing its propagation through the material in a transverse direction to the fibre axis. The result is a mainly brittle fracture of the sample, and its strength is not higher than that of the matrix. In this case the composite strength depends on the quality of the fibre coating and is very low in the case of a lacking or insufficient interface as a consequence of (i) the internal stresses caused by shrinkage processes (see also Section 1) and (ii) the differences in the thermal expansion coefficients of fibre and matrix. As the deposition thickness of the fibres increases, however, these stresses may be reduced, which leads to an increase of the loading capacity of the matrix and thus to an increased composite strength. The fracture behaviour, however, remains brittle. Only with a layer thickness of approximately 80 nm is the friction between fibre and matrix reduced to such an extent that the toughening mechanisms (crack deflection, debonding and pullout processes) described in Section 3 depending on the interface gliding modulus can become effective. The measured high strength and toughness of such composites are a result of that.

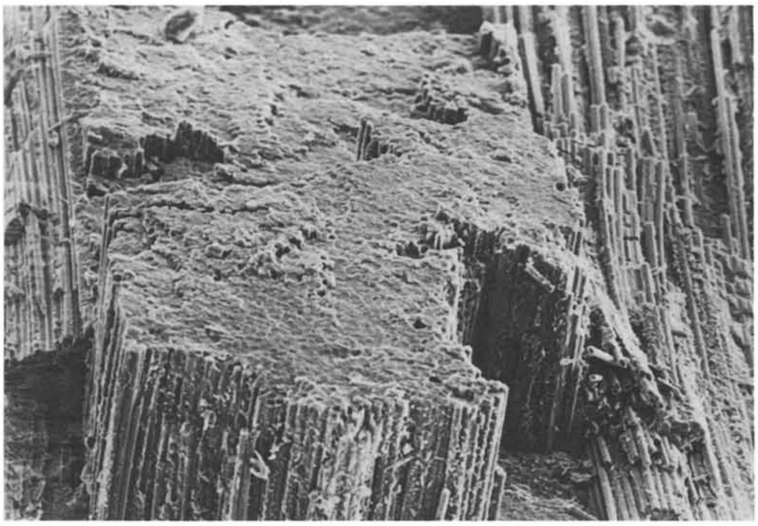
In summary, it can be concluded that in this case the fibre coating initially continuously reduces the internal stresses of the matrix and thus the degree of the brittle fracture behaviour of the composite.

4.2 Internal stress and tensile strength

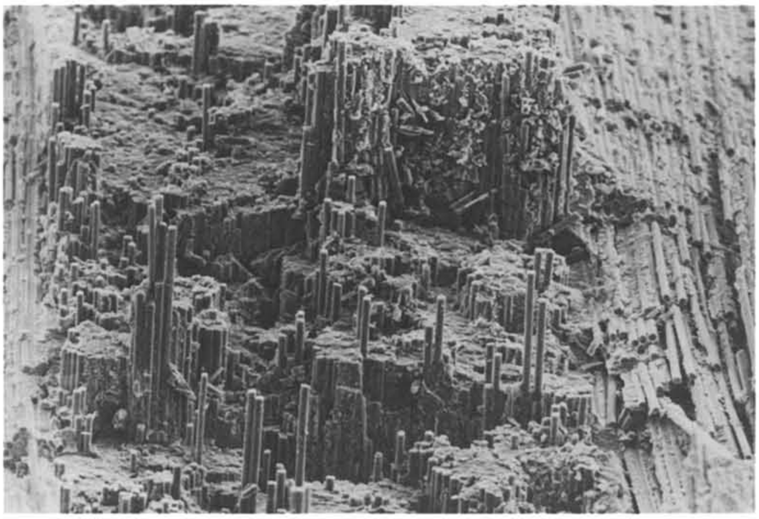
The tensile strength of an uncoated T 800 fibre (measuring length: 200 mm) was determined to be as high as 3 GPa. In contrast, a fibre coating with 80 nm pyrolytic carbon reduces the tensile strength to approximately 1·5 GPa. The residual strength depends on the coating conditions and the C layer thickness.[20] The maximum tensile strength achievable in a fibre/matrix composite material can be estimated. In a 2D–90° composite only 50% of the fibres are oriented in tensile direction, and the fibre volume percentage of the composites produced in this study is of the order of 50%. This means, referred to the loaded area of the tensile sample (neglecting the matrix), only 25% of that area will carry a load. Consequently, a tensile strength of the composite of 375 MPa could be expected, assuming an effective fibre length of 200 mm. As the effective fibre length in a composite is well below 200 mm, a tensile strength well above 400 MPa should result due to the higher fibre strength as a result of a lower number of flaws in the short fiber.

However, room-temperature tests of reinfiltrated C/SiC 2D–90° samples without fibre coating only yield maximum tensile strengths of 80 MPa and brittle fracture. In contrast, samples with a 80 nm thick pyrolytic C coating on the filament surfaces gave tensile strength values of up to 300 MPa and showed non-brittle fracture behaviour due to fibre pullout.

It appears that internal stresses developing at the fibre/matrix interface are the limiting factor for the tensile strength of the composite. These stresses can only partly be relaxed by the fibre coating. The pyrolytic conversion of the polymer to a ceramic is inevitably combined with a volume reduction. This volume reduction causes compressible stress on the fibres and tensile stress in the matrix as the fibres impede the shrinkage of the matrix. If these internal stresses exceed the matrix strength, matrix cracking will develop. This leads to a brick-wall structure of the matrix where compressive stress concentrations act on fibres where the matrix is uncracked and tensile stress on the fibers develop at the matrix cracks (Fig. 4). In particular, matrix cracks will develop in



(a)



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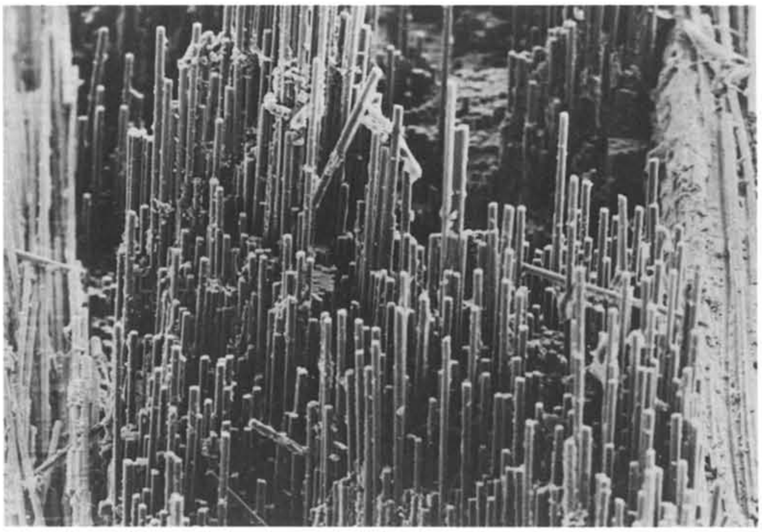

(c)

Fig. 3. Scanning electron microscope images of fracture areas at C/SiC composites. (a) Uncoated fibres; (b) 50 nm pyrolytic C (c) 75 nm pyrolytic C.

bidirectionally reinforced composites as the orthogonally oriented fibres of the individual laminate layers impede the matrix shrinkage of the neighbouring layers. Therefore, tensile stresses develop locally in fibres which are oriented perpendicular to a matrix crack.

In addition to the matrix cracking, the volume shrinkage causes a strong mechanical fibre/matrix bond which prevents a crack deflection or any other energy dissipation at the fibre/matrix interface and thus leads to an undisturbed path of a crack tip from the matrix into the fibre, resulting in a low strength of the composite material.

Internal stresses in ceramic matrix composites produced identically to those in this study have been determined by X-ray diffraction techniques.[21] According to the first results of these studies, the internal stresses depend on the combination of the fibre and matrix materials, the ceramic yield of the polymeric precursors as well as on the number of reinfiltration steps and the processing temperatures. In addition, the fibre orientation locally determines the magnitude and nature of the stress. In general, tensile stress was detected in the matrix parallel to the fibre orientation and compressive stress was measured perpendicular to the fibre axis. One example shows that an increase in pyrolysis temperature results in an increase of the internal stress by 80% as long as the pyrolysis reaction is ongoing, with peak values of ~280 MPa for 2D–90° C/SiC composites.

In addition, reinfiltration and subsequent pyrolysis increase the stress level by more than 200%. The internal tensile stresses approached peak values of 380 MPa in a threefold reinfiltrated 2D–90° C–SiC sample. Thermal treatment of the samples after pyrolysis is able to reduce the internal stresses considerably; in contrast, fibre coating yields a tensile stress reduction *in the matrix* of only 15%.[21] Of course, the internal matrix strain cannot be relaxed by a fibre/matrix interlayer, but an effective fibre coating will be able to reduce the *stress transfer from the matrix* to the fibre, resulting in the observed increase of the composite strength. Possibly, the microcracking of the fibre coating within the layer or at the fibre/coating/matrix interfaces, occasionally observed in these microanalytical studies can support this effect.

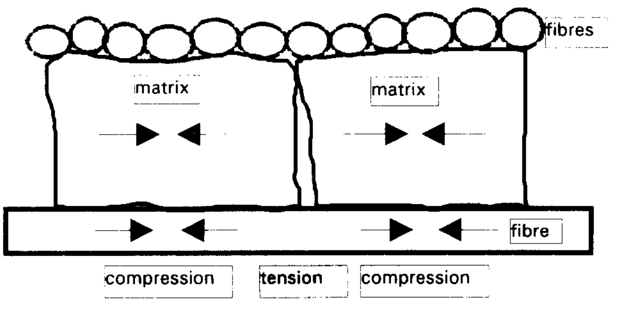

Fig. 4. Principle of stress development in a ceramic fibre/matrix composite due to matrix shrinkage during pyrolysis (see text). The high tensional forces on the fibre can be minimized by a fibre coating of suitable thickness.

4.3 Interlaminar shear strength (ILS)

In 2D–90° composites produced by lamination from unidirectional layers according to the polymer pyrolysis method, the ILS primarily depends on the matrix strength. In the case of a multidirectional fibre orientation the influence of the fibres should be more clearly noticeable. A fibre coating initially increases the ILS, since—as mentioned in Section 4.1—production-specific matrix stresses can be reduced. If the layer thickness is too high, its sliding effect dominates and the ILS is reduced. The measured results represented in Fig. 5 clearly show this effect: while the sample with uncoated fibres has an ILS of approximately 21 MPa, the ILS increases to 26 MPa for a fibre coating of 30 nm and decreases to 19 MPa at 80 nm.

5 Structure and Composition of the Fibre/Matrix Interlayer

The first aim of the electron microscopic investigations was to prove a successful fibre coating, since the determination of the layer thickness via the mass increase (compare to Section 3) is only an integral measuring procedure.

Furthermore, it was necessary to clarify the microstructure of the pyrolytical C layer as well as its microchemistry down to atomic dimensions, if possible, to understand its effect on the mechanical properties of the composites, in particular on the fibre debonding or pullout mechanisms increasing the toughness. Finally, the efficiency of the coating was to be proved by means of mechanically predamaged samples, i.e. crack propagation along the fibre/matrix interface, the exact path of the crack as a function of the layer microstructure being of particular importance.

The microstructural investigations at different structural levels including the imaging of atomic

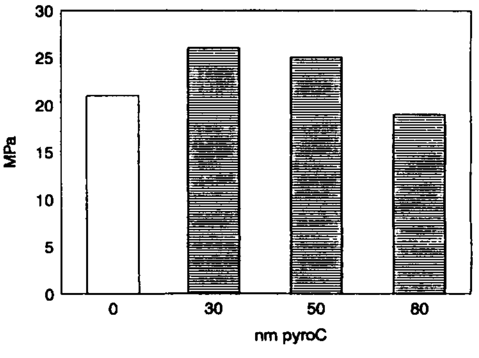

Fig. 5. Interlaminar shear strength of C/SiC composites as a function of layer thickness of pyrolytic C.

Fig. 6. HVEM image of the interlayer between fibre (bottom) and matrix (top).

planes were carried out using the transmission electron microscopy (TEM), in particular the high voltage (HVEM) and high resolution electron microscopy (HREM). Additionally microchemical analyses, partly down to the nanometer range, were carried out with the aid of different procedures of the analytical electron microscopy (EDXS, EELS) using a dedicated scanning transmission electron microscope (STEM), type VG HB 501 UX. The investigation and preparation techniques are described in Refs 22 and 23.

5.1 Microstructure

The microstructure investigations were carried out with 2D–90° composites whose fibres were coated with approximately 50 nm of pyrolytic carbon and which had a relatively good mechanical behaviour compared to uncoated samples (see Section 4). In the following microstructure phenomena which are typical of such systems will be presented.

Figure 6 gives an overview of a structure consisting of fibre cross-section (bottom right), interface range and matrix (top left). The matrix is strongly heterogeneous. Individual SiC crystallites with a darker contrast obviously resulting from the filling with SiC powder can be seen. They are surrounded by different matrix regions of pyrolytic origin acting as a binder between powder particles and fibres. At the same time structural separations or microcracks along grain boundaries as well as on tips and edges are visible which can probably be attributed to the volume shrinkage during pyrolysis.

In Fig. 7 the interlayer between fibre and matrix can be seen in an average magnification (bottom: range of fibre edge; top: matrix). The irregularly indented periphery typical of carbon fibres can be recognized. Carbon layers of different degrees of graphitization form the interlayer system. The fibre surface is characterized by an area with a thickness of 50 to 100 nm containing a distribution of pores of different sizes (1 to 20 nm), typical for the fibres used. Between the fibre surface and graphite layer this figure shows a crack path running parallel to the edge contour, indicating the weakest part in the composite and thus the

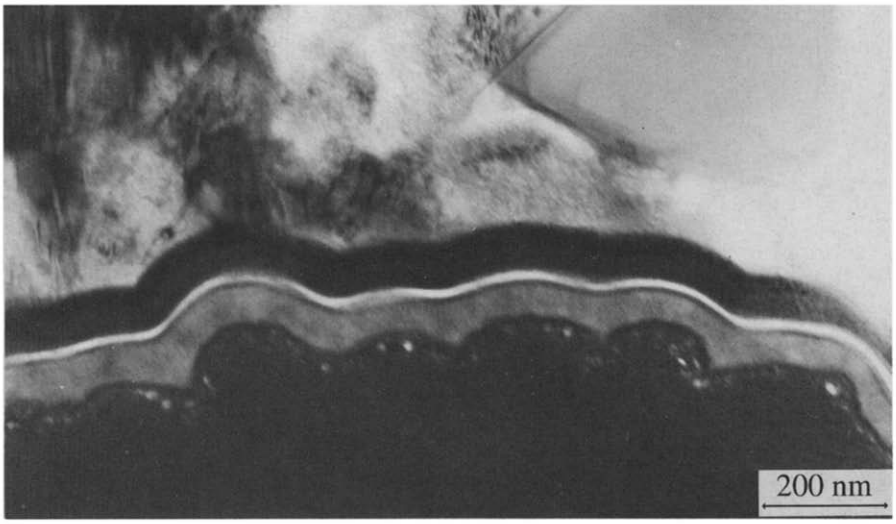

Fig. 7. Different regions of the fibre/matrix interlayer, separated by a crack path.

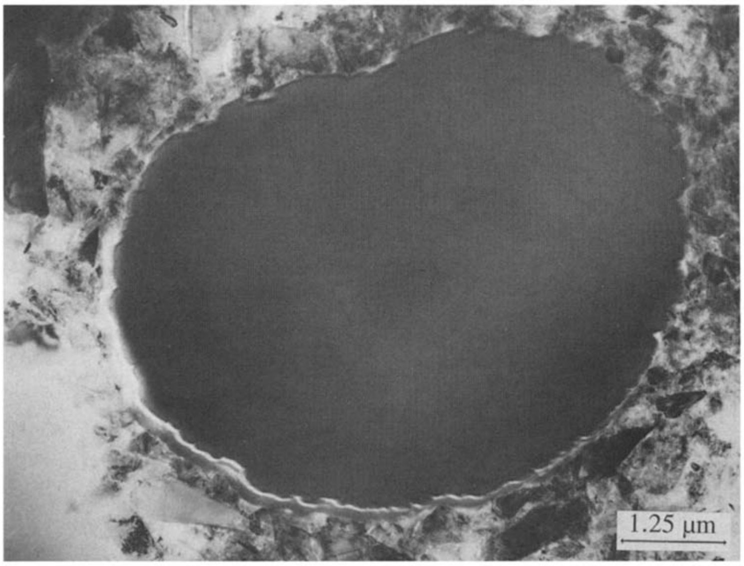

Fig. 8. Fibre cross-section with different interlayer formation.

place of debonding processes allowing the fibre pullout represented in Fig. 3, Section 4.

The entire cross-section of an individual fibre (see Fig. 8) reveals how reimpregnation is reflected in the structure. The individual fibre in the external range of the fibre bundle (centre of the bundle: at the top, outside the figure), was separated from the matrix on one side—probably due to an increased shrinkage of the more extended matrix ranges on the side averted from the bundle. The resulting space has obviously been filled during reimpregnation and can be seen as a dark band in the figure. Since the shrinkage cracks separating locally the fibre coating and the matrix initiate debonding processes, the peripheral fibres of a bundle should exhibit a debonding and sliding behaviour differing from that of the internal fibres.

Figure 9 is an HREM image of the interlayer structure showing the surroundings of a single bay of the fibre periphery (top right: matrix; bottom left: fibre). Near to the matrix and parallel to the interface graphitic regions with interesting contrast modifications similar to superstructures can be observed. The origin of these phenomena is revealed in the lattice plane imaging of Fig. 10 which represents the whole atomic plane resolved interface situation. In the diagonal the atomic planes within a graphitic layer are shown; nearly periodical arrangements of lighter and darker double stripes can be distinguished. At the bottom left the turbostratically arranged atomic planes of the neighbouring carbon fibre can be seen, which is cross-sectioned. Between the external fibre range and the graphite layer with superstructures there is (at the left of the diagonal) a further ribbon of graphite lattice planes with a width of approximately 15 nm which also has a clear orientation parallel to the interface but does not show superstructure contrasts. In the top right-hand part of the figure the fine structure of the adjacent, in this case nearly amorphous, SiC matrix can be seen. Debonding processes may easily occur along the graphite basal planes with a weak bonding or in a

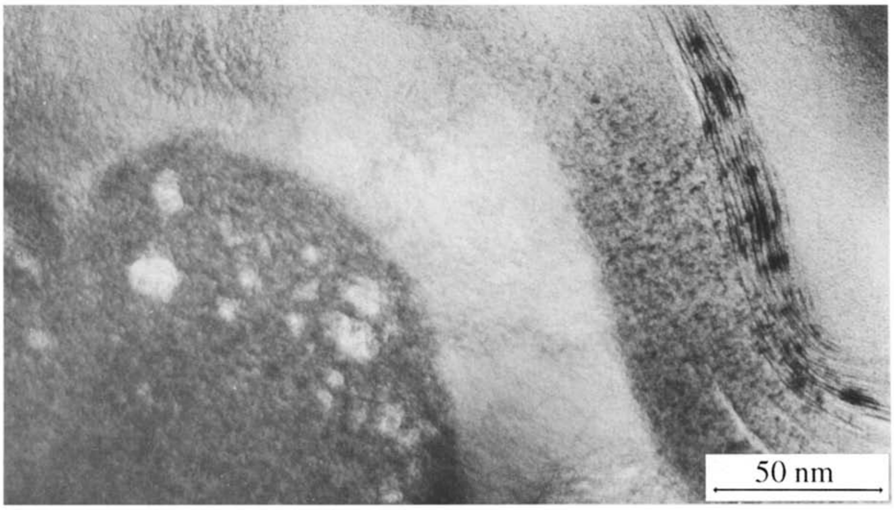

Fig. 9. Interlayer sequence surrounding a surface bay (bottom left) of the fibre.

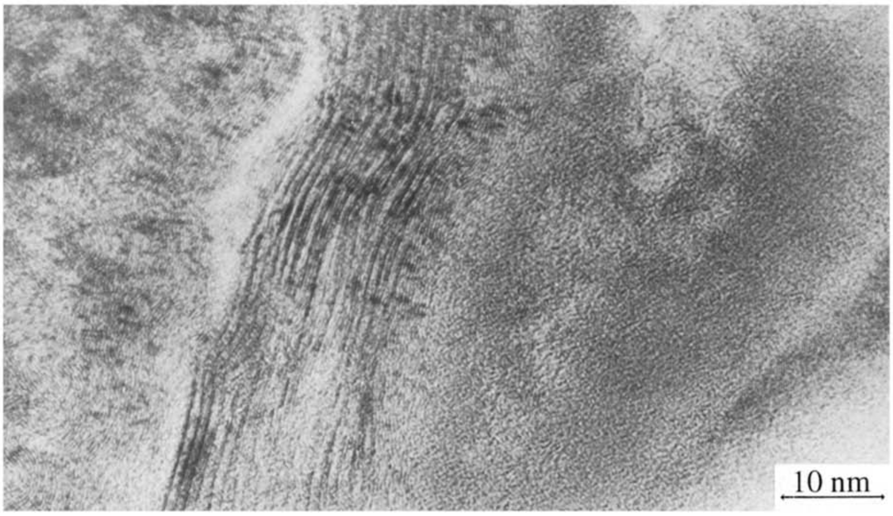

Fig. 10. HREM image showing the alignment of atomic planes of different graphitic regions in the interlayer (see text).

weaker transition zone at the fibre surface (see Fig. 7).

The characteristic double-stripe structure represented in Fig. 10 indicates the possible intercalation of foreign atoms between the graphite lattice planes which may lead to a corresponding change of interaction strength. Regular intercalations of foreign atoms in highly oriented pyrolytic graphite have been described, for example in Ref. 24, and are called graphite intercalation compounds. Intercalation atoms or groups of molecules may, starting from the edges of a graphite crystal, diffuse along the graphite basal planes arranged at relatively large distances (0·344 nm). The $2p_z$ orbitals of the nearest graphite atoms are influenced by chemisorption processes, resulting in the formation of intercalation compounds leading to superstructures. In the present study the nitrogen or silicon atoms detected by means of EELS or EDXS (see Section 5.2) may have penetrated as parts of groups of molecules into this interlayer by diffusion either during the pyrolytic deposition process of the graphite layer or later during the composite production. It can be assumed that intercalations of groups of foreign atoms or molecules have an influence on the mechanical and chemical properties as well as, of course, on electronic and optical characteristics. In particular the degree of graphitization or the sliding or frictional behaviour between the graphite basal planes could change, which would influence the pullout behaviour and thus the macroscopic strength and toughness of the composite material.

5.2 Microchemistry

The results of the analytical investigations are related to the composition of the interface range between fibre and matrix as presented in Fig. 10.

Figure 11 shows a series of EEL spectra in the energy range between 200 and 700 eV taken at a one million-fold magnification in the spot mode of the electron probe with a diameter of 1 nm. The points of analysis are marked with **a** to **e** in the bright-field STEM image inserted. Bright–dark

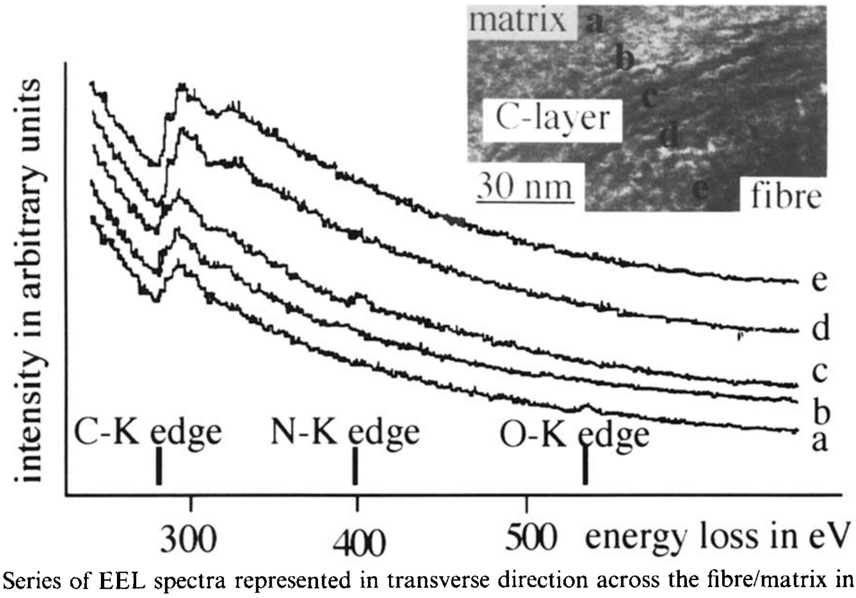

Fig. 11. Series of EEL spectra represented in transverse direction across the fibre/matrix interlayer.

contrast modulations are visible in the graphite layer grown pyrolytically. The spectrum taken from the amorphous polymer-derived matrix reveals an O–K edge in addition to the C–K edge. Oxygen from the polymer precursor has obviously been implanted in the amorphous matrix, possibly in the form of SiO_x or SiO_yC_z. In addition to the elements to be expected according to the material composition nitrogen could be detected as light element impurity in the interface range, in particular within the graphitic fibre coating, which indicates that nitrogen was introduced in the CVD coating process. Silicon also occurs in the interlayer, which has probably diffused during the matrix formation. The percentage of elements within the fibre coating was determined as follows: approximately 45 at.% carbon, 26 at.% nitrogen and 29 at.% silicon. The relatively high concentrations of nitrogen and silicon within the graphite layer indicate an intercalation of foreign atoms as compounds, probably in the form of Si_xN_y or $Si_xC_yN_z$ in the turbostratic carbon (see the foregoing section).

The element distribution in the interlayer is, in summary, represented by means of a line profile (Fig. 12), which has been taken in an adequate fibre/matrix range via EDXS in transverse direction over the interface structure. The EDXS measurements confirm the results achieved by means of EELS. A nitrogen accumulation can clearly be recognized within the graphitic fibre coating. Furthermore, a minor concentration of nitrogen occurs in the adjoining surface regions of the fibre possibly due to the specific characteristics of the fibre composition (approximately 6 at.% of nitrogen can occur in a T300 fibre[25]). The profile of the Si signal from the matrix (right) via the interlayer into the fibre reveals that silicon has diffused towards the fibre. In the range of the C coating a plateau has been formed which indicates an accumulation of silicon and the compound formation. On the matrix side of the interlayer an oxygen accumulation can be seen.

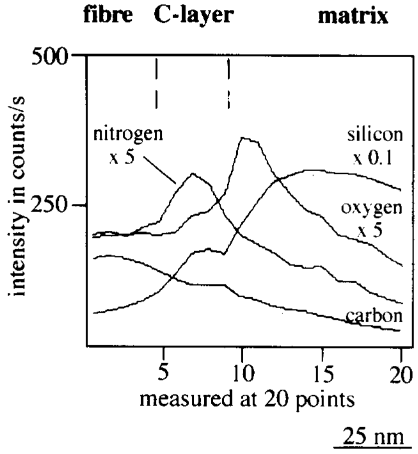

Fig. 12. Element distribution in the fibre/matrix interlayer (EDXS line profile).

The element distribution images of Fig. 13 clearly demonstrate the chemical composition of the interlayer provided by EDXS line profiles. Due to the relatively low fluorescence yield of the X-radiation of light elements, the signal/noise ratio of the corresponding mappings is relatively low compared to that of silicon. Nevertheless, a

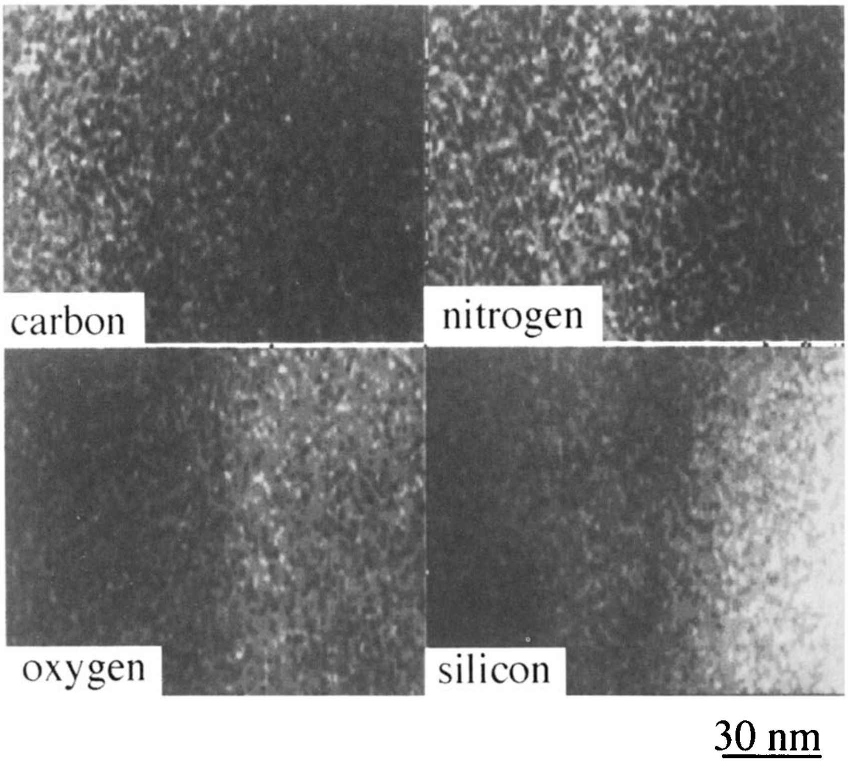

Fig. 13. EDXS element distribution images (carbon, nitrogen, oxygen, silicon).

local accumulation of nitrogen and silicon can be detected within the graphitic layer. At the side of the matrix there is a 20 nm wide zone rich in oxygen compared to the inner part of the matrix (see partial image bottom left). At the same time it seems to be poor in silicon. The reason for the reduced silicon content (see also Fig. 12) is probably the diffusion of silicon towards the fibre.

6 Summary

The purpose of this study was to investigate the relationship between the fibre/matrix sliding–friction conditions and the macroscopic properties of polymer-derived C/SiC composites reinforced bidirectionally. The study confirmed that the desired increase of strength and fracture toughness can only be attained by the introduction of a sliding interlayer of sufficient thickness between fibre and matrix, produced by fibre coating. A pyrolytic carbon-rich layer having a thickness of 80 nm was the best compromise between the improvement of fracture-mechanical properties of the composite and the residual strength of the fibre as well as its processibility in the method applied for the production of the composites (fibre infiltration and polymer pyrolysis). The carbon deposition by means of CVD coated all individual filaments within a fibre bundle. The three-point bending strength was improved by a factor of 4 to a value of 320 MPa by means of an interlayer of pyrolytic carbon having a thickness of 80 nm. At the same time an improvement of the fracture toughness was observed and the tensile strength was increased to 300 MPa by the C coating.

The two-dimensional architecture of the reinforcing fibres effects that a fibre coating has only a minor influence on the interlaminar shear strength, and with a layer thickness of 80 nm even a slight decrease can be noted.

The TEM investigations (HVEM, HREM) after mechanical tests revealed the microstructure of the composite material, especially of the interlayers, proved the successful coating of the fibres and detected the microcrack-initiating effect of the sliding interlayer. The microstructure of the composite is characterized by the embedding of C-coated fibres in a matrix consisting of SiC particles (filler material) and the amorphous basic material resulting from the pyrolysis of Si polymers. Between the fibre surface and the deposited graphite layer microcracks occurred indicating that there are the weakest points in the composite and thus the places of debonding processes.

The HREM interlayer analysis revealed that the atomic basal planes of the graphitic regions are mostly aligned parallel to the fibre surface, which is an optimum condition for the desired sliding effect.

Nitrogen, silicon and oxygen atoms were detected in the graphitic interlayers by means of EELS and EDXS, which obviously are inserted during the fibre coating or the production of the composite.

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