" FIBRE REINFORCED COMPOSITES FOR HiGH TEMPERATURES"

(A Comparative Study on C/C, C/SiC, SiC/SiC & SiC/Oxides)

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Abstract:

Carbon fibre reinforced carbon and especially graphite composites are the outstanding high temperature materials, not only from viewpoint of mechanical properties and thermal stability, but also from viewpoint of light weight and superior thermophysical properties.

The only disadvantage is the chemical instability in oxydizing environment above 350°. It is shown that this problem can be solved only partially by protection with SiC coatings.
Also a partial replacement of the carbon constituents, the fibres or the matrix, may solve the problem in limited manner only.

The total replacement of carbon by SiC solves the problem of chemical instability, but creates problems in physical and mechanical behaviour. SiC/SiC composites are far away to exhibit similar outstandig mechanical and thermophysical properties as carbon/carbon composites.

As further solution, a new fibre reinforced oxidic composite is presented. It consists of a ZrO_2 modified SiO_2 glass matrix with SiC fibres based on carbosilanes with promising properties for high temperatures and oxidizing atmosphere.

Introduction

Material scientists are used to differentiate between 3 main groups of man made materials, namely metals, non metallic inorganics and organic polymeres.These groups represent also the type of interatomic bonds, namely the metallic bond, the homopolar bond and the molecular bond and so their properties from viewpoint of the material scientist are sufficiently characterized.

The metallic bond, for which non localized electrons are characteristic, show the electrical and electron based thermal conductance. Because of the closest atomic packing and non directed bonds, the dislocation mobility is high and thus, plastic deformation becomes possible.

The non polar atomic bond is the strongest interatomic cohesion we know. Only phonon based thermal conductance is possible and dislocation mobility is so low, that these materials are extremely brittle.

The chemical bonds in polymers, interatomic also mostly non polar, are controlled by the cohesion of the molecules, which is weak and breaks by low activation energy already, causing plastic deformation, molecules elasticity but also thermal instability.

Mostly, it is forgotten, that the element carbon as a solid, does not fit into one of these three groups only.

It has very strong interatomic bonds, but also metallic ones in one geometrical direction and finaly some memory on polymer bonds and structures. It is proposed therefore, to demonstrate carbon as a forth basic group of man made materials in the center of the three others as shown in FIG.1 and it was already called as the most promising material for the future (1).

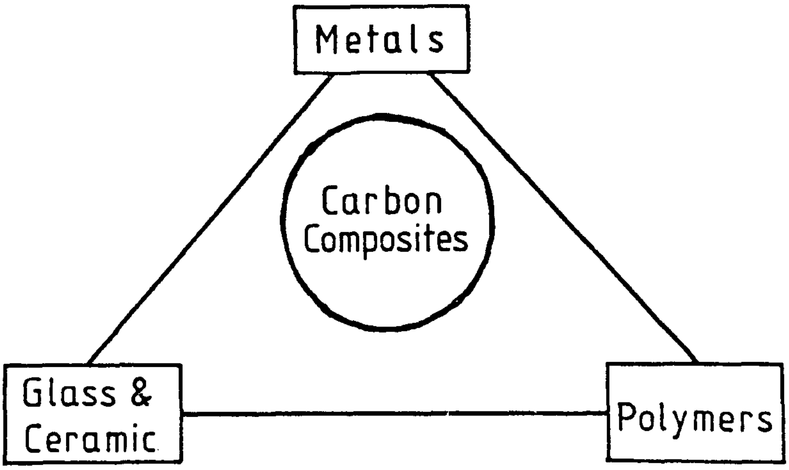


FIG.1: Position of carbon fibre composites within the various classical material groups

For high temperature materials, one needs solids with high melting or sublimation points. As FIG.2 shows, some metals, the so called refractory metals would be suitable, as the high melting points are caused by strong interatomic bonds and thus high Young's moduli and low thermal expansion behaviour.

Materials group	Examples	Upper application temperature °C	Oxidation resistance in air
HT polymers	Polyimides HT thermoplastics	350	no
Metals	Light metals (Al, Ti)	400 - 800	yes
	Iron metals	1000	yes
	Refractory metals	1500 - 2500	no
Glasses	Silicates	800	yes
	SiO_2	1200	
Hard metals	Si_3N_4, SiC	1400	yes
Intermetallics	Ni, Al	1300	yes
	Silicides	1600	yes
	Borides	1700	limited
Oxide Ceramic	Al_2O_3	1800	yes
	ZrO_2	2100	yes
Pure elemental carbon		2400	no

FIG.2: Matrix materials for high temperature composites

These refractory metals are heavy chemical elements and have therefore a bulk density higher than ten, for most structural application much too high. Furthermore, the metallic state of these elements is not compatible with oxydizing environment.

The non metallic inorganics, mostly oxides, are most suitable from the viewpoints of chemical behaviour, low bulk density and high melting points, but unsatisfying from viewpoint of fracture
behaviour because of their extreme brittleness.

The best compromise in mechanical and thermophysical behaviour between refractory metals and inorganics is the carbon material.
There remains the disadvantage of chemical incompatibility in oxidizing environment. The efforts, results and limits to overcome this oxidation problem, at present one of the mostly studied development activities, will be discussed in detail.

1.Part: CARBON, THE MIRACLE MATERIAL.

For understanding the mechanical behaviour of an elemental material as a solid, the interatomic distance is a good criterion. Low distance between two neighboring atoms indicates high binding strength, high Young's modulus, high melting point and low thermal expansion.

The element carbon in his graphite modification - which is thermodynamicly stable up to highest temperatures (below 4000 K) and not too high pressures (below 100 kilobars) - has an anisotropic crystalline structure with a very small interatomic distance of 0,142 nm in a- and b-direction, but with the large distance of 0,336 nm in c-direction.

Due to the directed sigma-bonds in a-/b- direction, the extremly high elastic number C_{11} of 1060 GPa is caused, whereas in c-direction with the non directed pi bonds, only the low elastic number C_{33} of 33 GPa is measured. Most impressive and characteristic for the extremly anisotropic graphite structure is the very low shear modulus C_{44} with 4,6 GPa only.

For the material scientist, the question arises, how and in what amount the high interatomic anisotropic binding forces can be translated into an either isotropic bulk material or into a material with controlled preferred orientation and thus desired anisotropy of the bulk properties.

Furthermore it is essential to know, how to apply in some cases the extremly low shear strength for technical purposes. More often however it is the task for the material scientist to avoid or inhibit this low shear resistance in modern structural materials.

The classical way for the application of synthetic graphite as a solid structural material is that in a polygranular bulk structure. In such cases one takes into account, that carbon and graphite does not melt nor sinter. A technology has to be applied, such as it is known in the ceramic industry, which starts from separated grains and powder and a binderphase, which holds the grains together. The resulting polygranular synthetic graphite materials are often described as polycrystalline graphite, which term is however uncorrect (2).

In such materials, the coke grains or better the granules, are distributed statistically in the binderphase. The grains themthelves constitute of more or less structurally imperfect or distorted anisotropic graphitic domains. The carbonaceous binderphase surrounds the grains. In such a way, the anisotropic domains in the binder phase are also statistically oriented and a bulk material with an overall isotropic crystalline structure results.

The absence of a preferred orientation can be measured best by the thermal bulk expansion behaviour of the material, as the anisotropy in crystal expansion coefficient in a-/b- direction

is around 0.5 x 10^{-6} /K, whereas in c-direction it is 28. x 10^{-6}/K.

The bulk expansion behaviour includes also the effect of the porosity, mainly anisotropy in poresize and - form distribution and is a better indication than the X- ray diffraction, which represents the arrangement of the crystalline domains only and not that of the pores. Furthermore the diffraction intensity is too sensitive for differences in the cristalline order of the various local parts of the bulk and the preferred orientation, which is based on the intensity ratio of the 002 diffraction line between different directions of the sample (3) can be influenced and the results on the overall preferred bulk orientation can be alterated.

The effect of the pores, especially the micro slit pores on the thermal bulk expansion and the bulk strength properties is the reason for the outstanding thermal shock behaviour of synthetic graphite bulk materials.

The thermal shock behaviour is given by
TW= strength x Thermal conductivity/ Youngs modulus x Thermal expansion,
if heat transfer is rate controlling and without the term of thermal conductivity, if it is not. In any case, the effect of the thermal expansion remains dominant, as the influence of the mechanical properties is more or less neutralized by the ratio of them.
The advantage of synthetic graphite is caused by the low termal bulk expansion in spite of the extremly high anisotropic expansion coefficient in c-direction.

The formation of the micropores in bulk samples of synthetic graphite works in the following manner:
An anisotropic domain in a coke grain with the high interlayer distance of around 0,35 nm in the disordered state after carbonization shrinks during subsequent high temperature graphitization treatment around 3000 K to interlayer distances

below 0,34 nm. This is shown in FIG 3 (4), based on measurements at room temperatur after cooling from the heat treatment temperature (HTT).

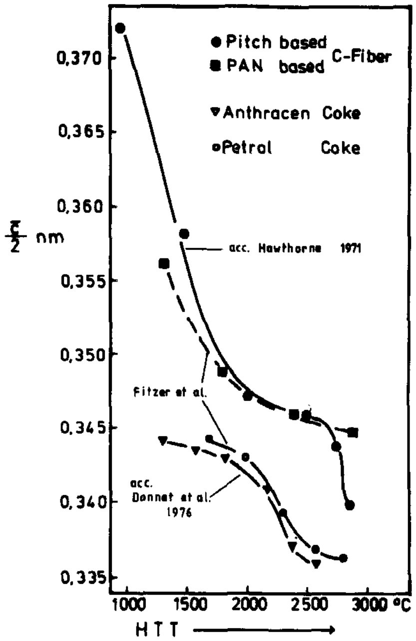


FIG. 3: Mean interlayer spacing as function of HTT (4)

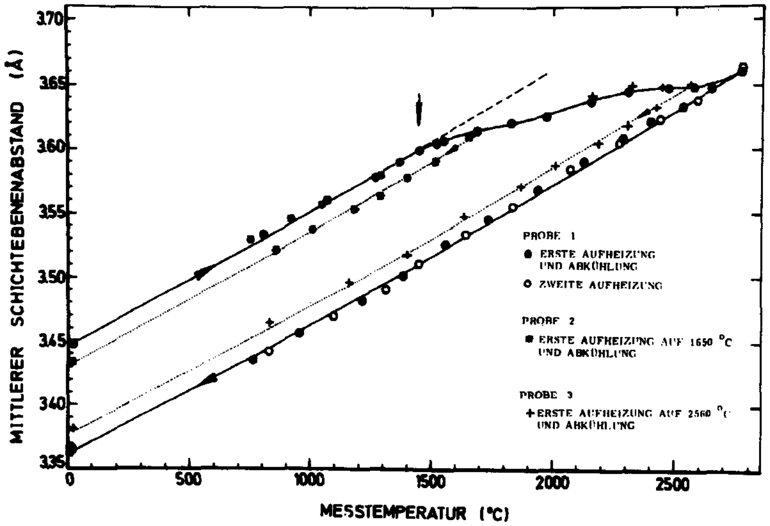


FIG.4: In-situ measurements on c/2-value as function of HTT (5)

The superposition of reversible thermal expansion (dilatation) and irreversible graphitization shrinkage can be seen best by in situ X ray diffraction measurements. One can also recognize in FIG 4 (5), that reversible expansion is independent of the degree of crystalline disorder.

If we would consider an isolated anisotropic domain without any connection to the neighbouring material, like a graphite single crystal, a synthetic graphite domain will behave reversibly during cooling and reheating.
If however a realistic anisotropic domain in a coke after carbonization is considered, the parallel layers in the domain can not move free. They are locked on their edges by cross-linking or mechanical blocking by neighbour domains, which are oriented in other directions. The staples of layers in the domains, as do the single layers, will grow during graphitization by a solid state mechanism similar to grain groth and recrystallization. But such growth is limited because of sterical hindering by the other, neighbouring domains. Some blocking on the edges remains.
Only the inner parts of the grown parallel layers, which are not blocked on the edges, can shrink freely during graphitization and subsequent cooling. The hindered shrinkage causes frozen in stresses, which will split the domains between the staples of parallel layers because of the low binding forces of the graphite crystal in c-direction.

As a consequence, slit sized micro cracks are formed, the so called MROZOWSKY-cracks. During subsequent reheating, thermal bulk expansion is inhibited because of the closing of these micro cracks by which the reversible expansion in c direction is compensated.

This mechanism does not work completely in granular carbons. In the isotropic finegrained grades, a bulk expansion coefficient of

around 4 x 10^{-6}/K is measured in all directions, from which data a bulk volume expansion coefficient of 12 can be calculated.

For a pore free single crystal 29 x 10^{-6}/K would result what shows, that only half of the reversible expansion is compensated by this micro crack mechanism.

In coarse grained electrodes for UHP steel furnaces, this mechanism is supported by grains with preferred orientation in structure and grain form, the so called needle coke grains. A bulk volume expansion coefficient below 5 x 10^{-6}/K can be achieved.

Graphite is the only synthetic material with such anisotropic slit pore formation.This bulk structure is the key for understanding the excellent high temperature shock behaviour. Already before the age of fibre reinforced advanced composites, this outstanding advantageous behaviour of synthetic graphite materials was known and utilized.

An example is shown in FIG 5 (6), the leading edges, situated within the jet of the first big missiles (German AS 4 missile in world war II). They were fabricated from extruded graphite for electrochemical electrolysis.

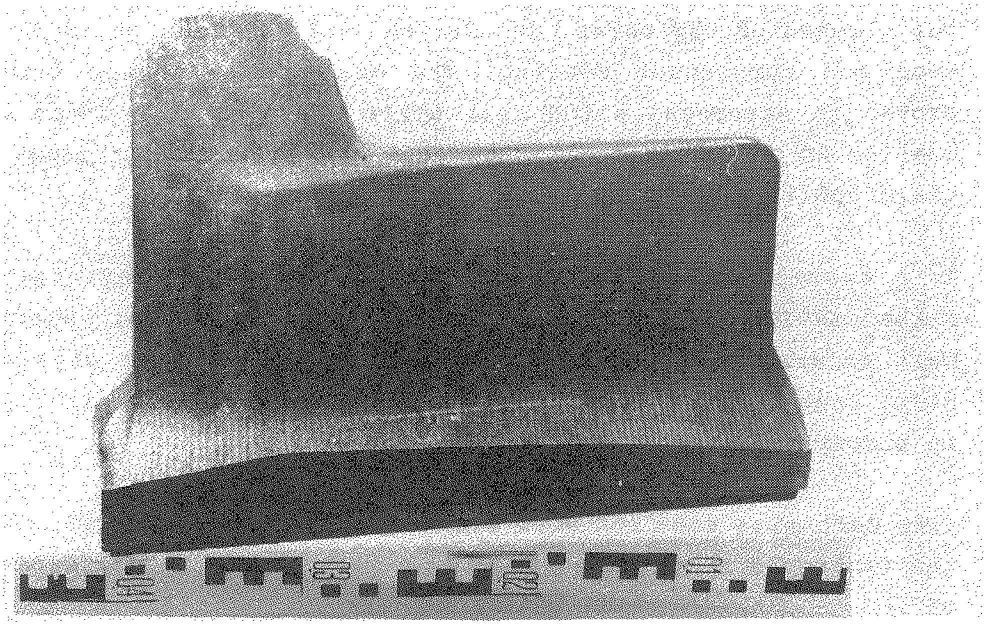


FIG.5: The fin of a World War II missile, made from fine-grain graphite (6)

In todays high performance carbon fibres and modern carbon/carbon composites, this effect is also utilized, but in a multiplied amount and under optimized design and fabrication control.

2.Part: CARBON/CARBON COMPOSITES,
the best utilization of the outstanding
high-temperature properties of elemental carbon.

Carbon/ Carbon composites are carbon reinforced carbons or graphites. They consist of a volume fraction between 40 and 60 % of carbon fibres and the rest consisting of carbon matrix material and pores. The matrix is structurally not uniform, as the interphase can differ from the structure of the matrix in the bulk. There are therefore 3 macroscopic phases, all consisting of elemental carbon, which can contribute in combination to the special structural and mechanical behaviour of the composite.

2.1 The carbon fibres.

The main characteristic of carbon fibres is their structural anisotropy. The parallel layer staples are oriented in direction of the fibre axis. By this structural arrangement, the directed sigma bonds in sp^2 hybridiziced carbon are in fibre direction and can be translated directly into the value of the Young's modulus of the fibre in tension. FIG 6 gives the well known correlation of preferred orientation measured by X ray with the Young's modulus in tension.

It must be pointed out, that newest UHM types, based on mesophase pitch, achieve 700 to 800 GPa, that is more than 70 % of the theoretical maximum value (see elastic C_{11} number).

For practical utilization of this enormous stiffness, UHM fibers must remain handable. This is achieved by a strength around 3000 MPa and a sizing, holding the monofilaments in the bundle of 3 K together temporarily.

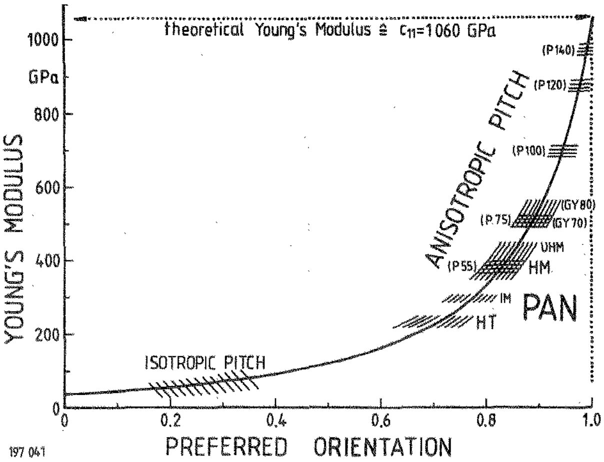


FIG.6: **YOUNG's modulus of various carbon fibres with respect to the preffered orientation of the fibre**

From viewpoint of the ultra structure, the parallel layer planes should deviate from defect free gaphite ordering. They need structural disorder, some missalignement, wrinkeling and crosslinking, what can be recognized by high resolution TEM (see FIG 7) and also in the Raman spectrum by the presence of the D line (see FIG 8).

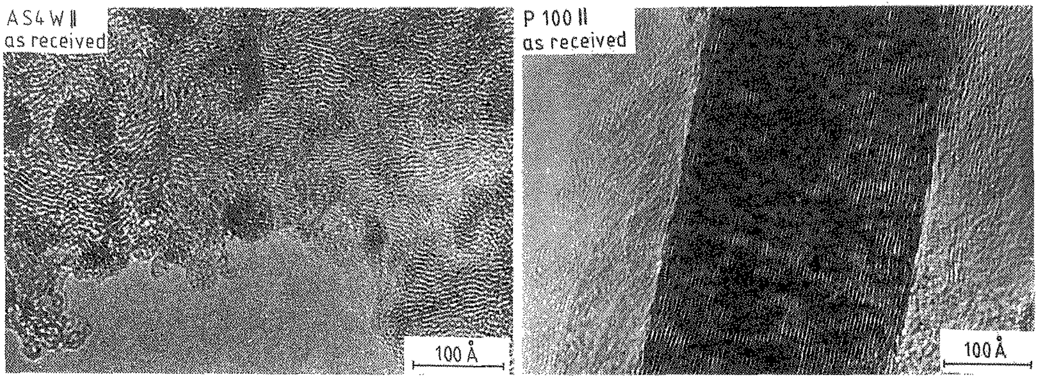


FIG.7: HRTEM-bright field image of carbon fibres
a) PAN based HT-type b) MPP based UHM-type

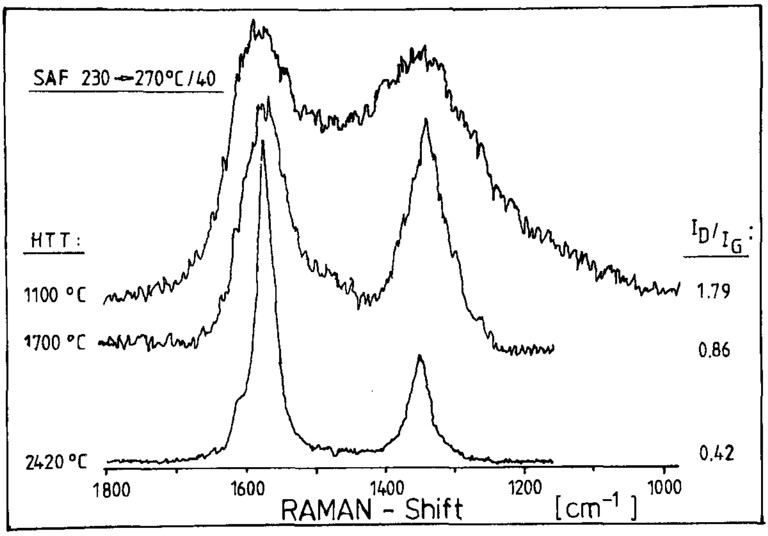


FIG.8: Raman-spectra of carbon fibres after different HTT

The PAN based HT types, the mostly used commercial carbon fibres, differ from HM types in the amount of structural disorder, what can be recognized easily in the HRTEM (FIG 7) and by Raman spectroscopy (FIG 8). In such a way, the low shear strength is inhibited nearly quantitavely, which is confirmed by the very high strength, in the order of 7000 MPa in newer commercial types.

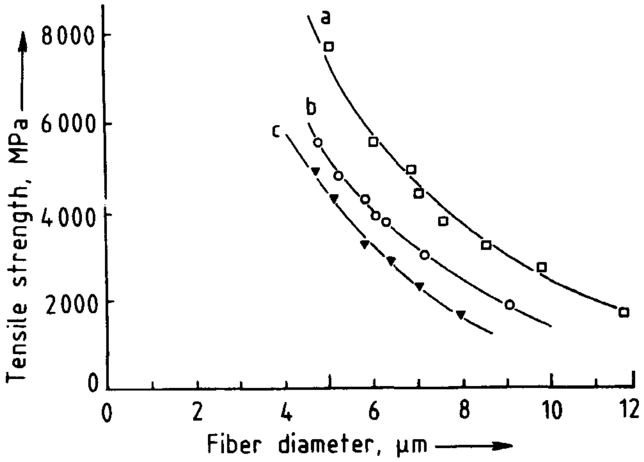


FIG.9: Tensile strength as function of the fibre diameter
a) AS4 (Hercules) b) T300 (Toray) c) M40 (Toray) (7)

As carbon fibres are brittle fracturing materials, the strength increases with smaller diameter, as demonstrated in FIG 9 (7).

Because of the high degree of preferred orientation, the thermal expansion in fibre direction does not differ from that of the graphite single crystal (around 0 to 0.5 x 10^{-6}/K). The thermal expansion perpendicular to the fibre direction, deviates from that of the graphite single crystal. It is difficult to measure, but is in the order of one third and below of the theoretical one (8, 9). We can recognize, that also in the carbon fibre, the unique mechanism of synthetic graphite works for compensation of the expansion. Same can be expected for the fibres in the carbon-carbon composite.

3.2 The MATRIX.

The carbon matrix is made from carbonized phenolics or from pitches or from pyrocarbon.
Lowest variability concerning the disorder in the crystalline structure of the carbon resulting from the carbonized precursor,
is in case of carbonized thermosets. These chars always result in a glassy like carbon matrix, at least in the bulk of the matrix.

Easiest way to modify structurally the matrix carbon is offered by usage of pitches as matrix carbon precursor. It can be modified to achieve structures from non graphitizing hard carbon to synthetic graphite. Consequently, carbon carbon composites with a pitch based matrix after passing a graphitization treatment should be named: carbon fibre reinforced graphite or carbon/graphite composites. This term however is only seldom used so far.

It can easily be understood, that carbon/graphite composites will offer the best chances for excellent thermal shock resistance of the composite because of the contribution of the matrix to the micro crack mechanism.

Theoretically, also pyrocarbon and pyrographite should offer a similar chance. But theoretically only, as the CVI (chemical vapour impregnation) parameters do not allow to deposite under conditions, at which the excellently graphitizing variety of pyrocarbon is formed.

2.3 THE INTERPHASE.

More exactly spoken, the interphase is an interphase aerea, with a thickness of some several tens of nm to microns. Good wetting of the dry fibre preform by the liquid carbon matrix precursor causes bad translation of the fibre strength properties into the composite after carbonisation. A very superficial explanation can be seen in the carbonization shrinkage of the matrix precursor, which causes a high internal stress level and even fibre damage during thermal heat treatment (10).

Best solution from strength considerations would be a highly heat treated pitch based HM fibre, what was demonstrated on model composites (10). This however is the most expensiv solution.
An other solution is the application of anti wetting agents on the fibres, recently published (11).
Each industrial producer will use his own method as a commercial secret.

In this paper, it should be pointed out, that as a result of the interphase, a third possibility is offered in the composite, to avoid thermal bulk expansion and thus thermal stresses during thermal shocks.
This ideal compensation of thermal expansion by micro slit pores is also used as crack stopping mechanism by deviation of crackpropagation, in such a perfection, never obtainable in fibre reinforced non carbon ceramic composites.

2.4 Properties of carbon/carbon and carbon/graphite composites.

In their structural composition and in fabrication technology, there are some similiarities between polycrystalline carbons and graphites and carbon/ carbon and carbon graphite composites respectively.

Fig 10 a gives a schematic explanation of the structures of both.

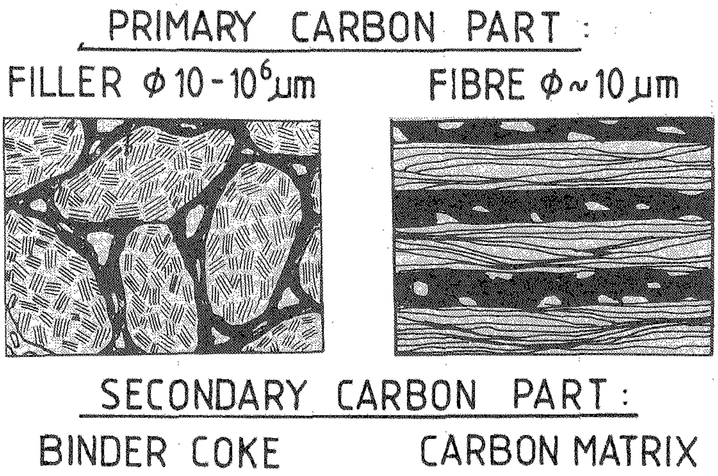


FIG.10a: The two-phase structure of synthetic polygranular graphites and C/C-composites

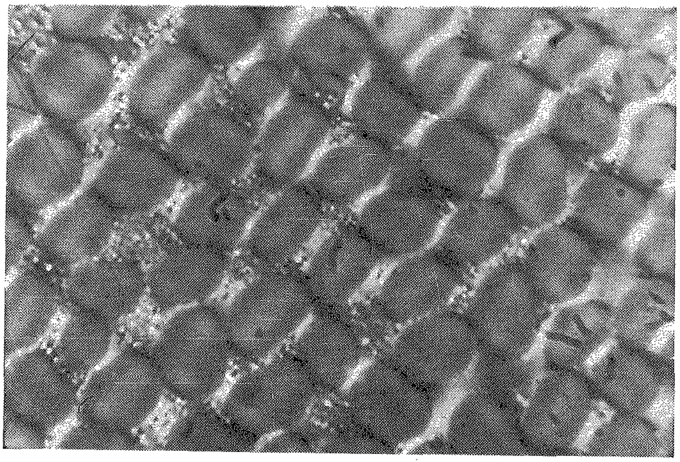


FIG.10b: Optical micrograph of the cross section of an UD-composite

In composites the fibres can be considered as filler and the matrix as binder, with the only decisive difference, that in polygranular carbons, only the binder is a continous phase and is the substituent controlling tensile and flexural strength, whereas in C/C composites, fibres and matrix, both are continuous phases and the fibres as the part with higher strength control tensile and flexural strength of the composite.
FIG 10 b is an optical micrograph of the cross section of an UD composite.

So far as the compressive strength is concerned, in polygranular carbons, it is controlled most by the type and granolimetry of the filler grains, and in minor amount only by the binder, whereas in composites mainly the amount of binder in form of the bulk density, which depends on the volume ratio between matrix and pores, is the controlling parameter.

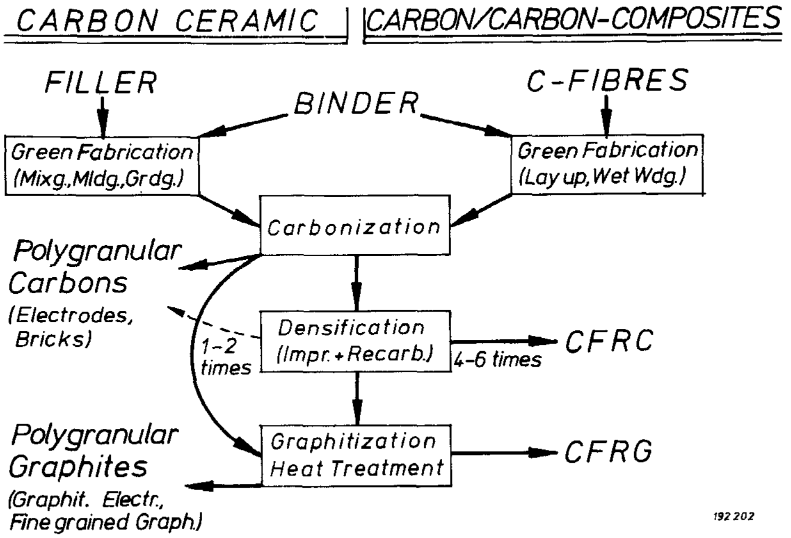


FIG.11: Comparison of production processes for synthetic polygranular graphites and C/C-composites

FIG.11 gives the schematic presentation of fabrication steps in both material types. One can recognize, that main difference consists in the number of densification cycles, which is much higher in case of composites.

This densification procedure for filling of the pores is needed for increasing the mechanical properties against compressive and flexural stresses.
Increase of the bulk density is also important from viewpoint of thermophysical properties, It can be performed not only by liquid impregnation and recarbonization, but also by gas phase impregnation at temperatures, which allow chemical deposition (CVI).

Not to forget, that the important fabrication parameter of final heattreatment (graphitization) is most important for the compressive strength in both analogeous material types.

The result of these differences in macroscopic bulk structure between granular graphite and C/C composites is presented by the short time flexural strength values, measured at temperatures up to 2500° (FIG 12). All carbon and graphite based materials exhibit beginning softening above temperatures above 2300° (see also FIG 15), but do never melt at normal or intermediate pressures.

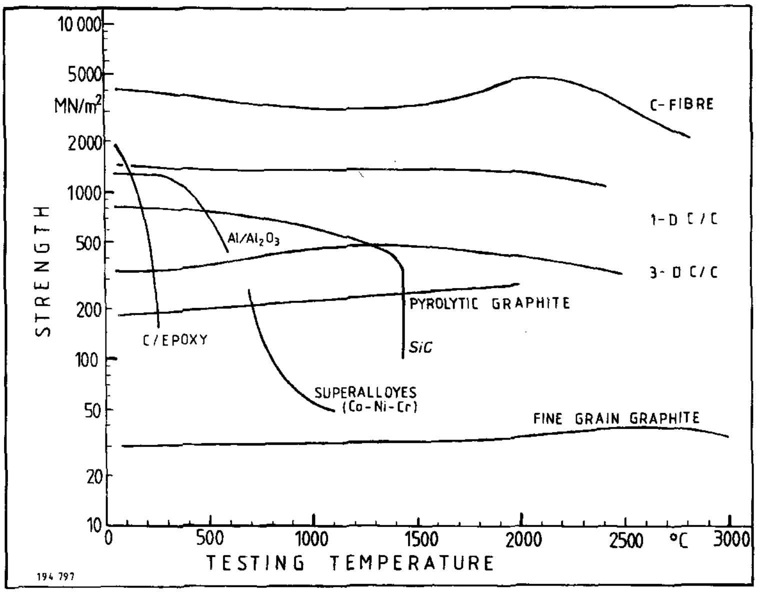


FIG.12: Short-term strength of carbon materials including CFRC compared with C/epoxy and metals

The superiority of the composites can easily be recognized, although both material groups, the convential granular carbons and the composites consist of the same elemental carbon. Fine grain graphite as the strongest of the polygranular materials was taken for this unequal comparison. Also the logarithmic scale should be noticed.

Not only the strength, but also the fracture behaviour of the composites is outstanding, if one considers the brittle nature of both constituents, the fibres as well as the carbonaceous matrix. The stress/ deformation behaviour is shown FIG 13.

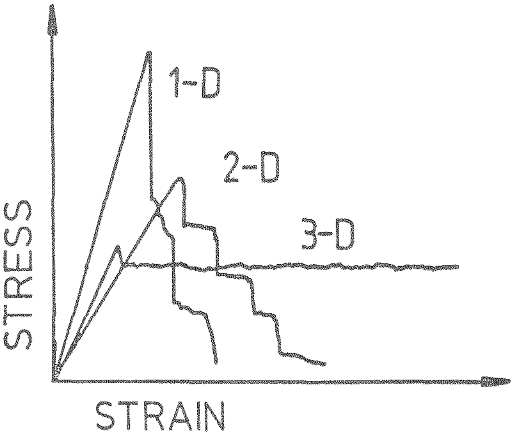


FIG.13: Pseudoplastic fracture behaviour of CFRC

A step like fracture indicates the formation of microcracks, by which crackpropagation is hindered. These microcracks are the same as discussed before. Often they are in a premature state only. Additionally, a limited pull out effect as shown in FIG 14 contributes to this favourable fracture behaviour.In such a way, a toughness is originated, which is unique for ceramic materials.

It was repeatedly demonstrated in former publications by us, that carbon carbon composites can even be nailed without brittle fracturing of the sample (1).

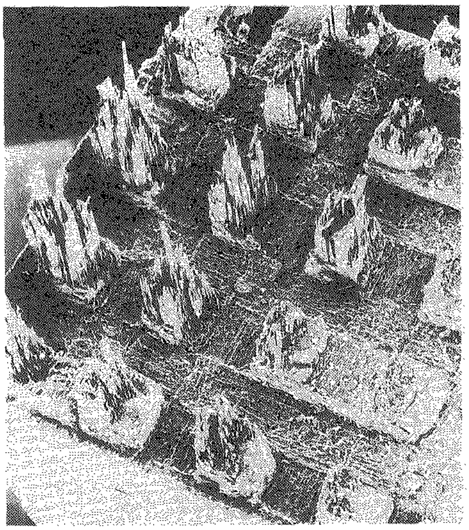


FIG.14: Fracture surface of 3D-CFRC

One will understand, that geometrical arrangement of the fibres, variation of the bulk density of the composite, selection of various types for the applied fibres and matrix precursors as well as the fabrication processes will contribute to a broad variety of carbon/ carbon and carbon/ graphite grades and properties.
It was reported recently by us (12), that UD composites with 70 Vol % HM fibres, a bulk stiffness at room temperatur of 500 GPa has been achieved, although the contribution of the fibre part to the composite was calculated to be only 300 GPa. This example demonstrates, that even the matrix carbon can be structurally arranged in such a way, that it contributes to the bulk stiffness in similar amount as the fibres do.

The limits in high temperature applications can be demonstrated by the creep behaviour as shown in FIG 15 (13). At 2000°, creep can be considered as negligible.

Also fatigue behaviour is a good indication of the applicability of this non metallic material for structural purposes, see FIG 16 (14).

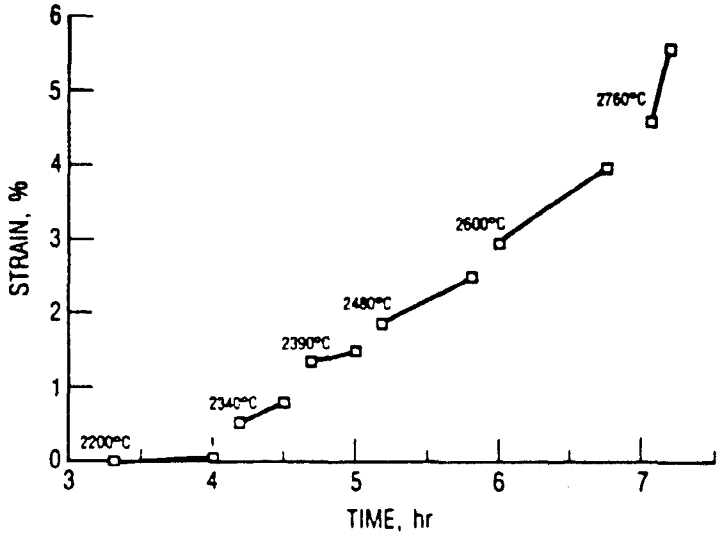


FIG.15: Creep behaviour of UD C/C-composite 2000 and 3000°C (13)

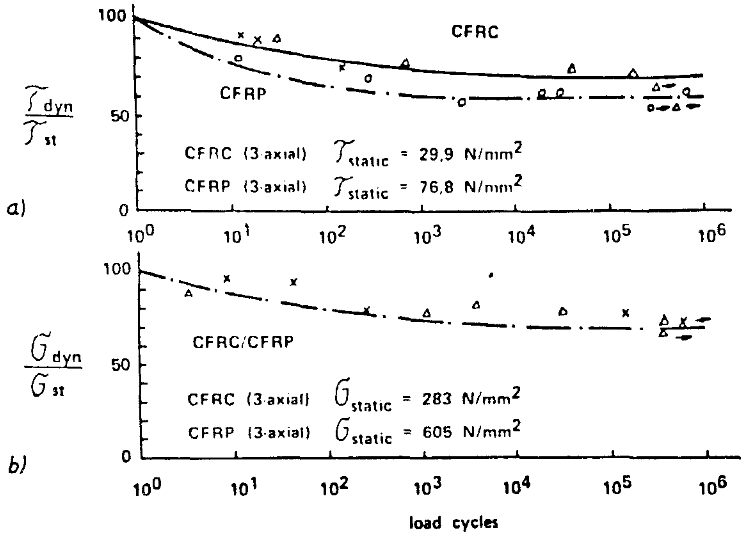


FIG.16: Fatigue behaviour of 3D CFRC and CFRP:
a) dynamic torsion test b) dynamic flexure test (14)

There is however the severe limitation for the application of carbon-carbon composites due to their sensibility to oxidation. This disadvantage is caused by the basic property of carbon in the elemental state, which forms volatile carbon oxides in air above 400°.

Fortunately carbon and graphite materials do not show any inflamability . For combustion an auxiliary high temperature flame is necessary.

3. Part: PROTECT OR REPLACE CARBON BY SiC.

In order to discuss the protection of carbon/carbon composites against oxidation, a distinction has to be made between oxidation in the intermediate temperature range between 500 and 600° and at temperatures above this range, as inhibition of the oxidative attack in the lower of these temperature ranges can be achieved by covering of the active sites in the carbon material. Such cover is performed by impregnation of the porous composite with inorganics, mostly boron oxides, phosphates and others. FIG 17 shows some results of such protection for 500° as weight change isotherms in air in comparison with a composite coated with a SiC protection layer, which is not so effective in this temperature range.

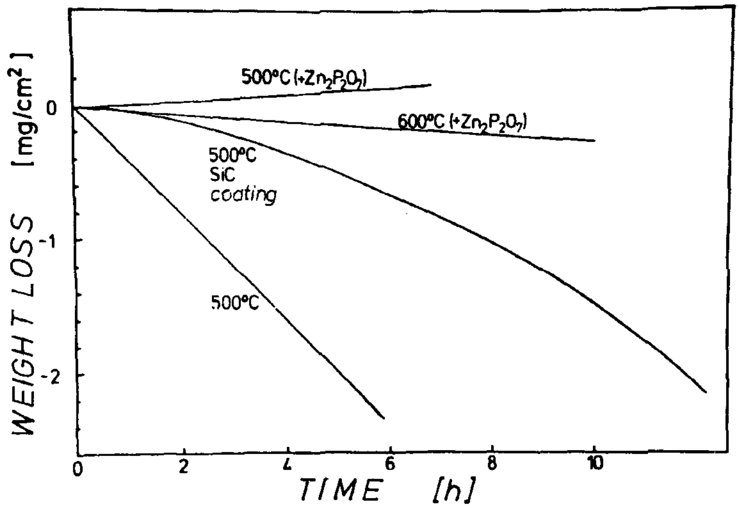


FIG.17: Weight-loss of UD C/C-composites by isothermal oxidation in air as affected by inhibitor or coating

For higher temperatures, coatings, consisting of oxides or such materials, which form protective oxide layers, have to be applied.

3.1 SiC protective layers and SiC impregnations.

SiC is one of the most applied coating materials for carbon and graphite. It forms a thin layer of SiO_2, which is the basis of protection.

For application of such protective coatings at high temperatures, the chemical compatibility is one of the most severe preconditions for the practical applicability, as solid/solid reactions can occure due to the mobility of the reaction partners at high temperatures. As known the mobility of atoms in the solids increases exponentially with the temperature.

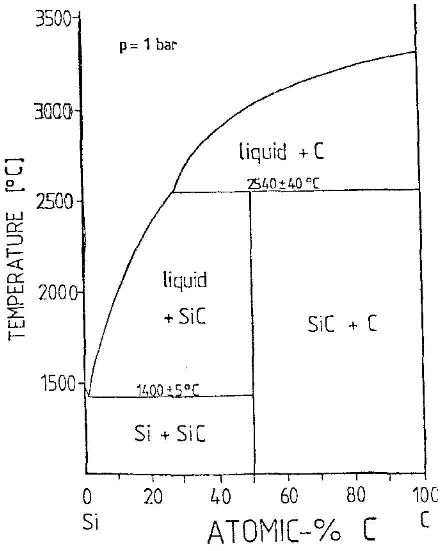


FIG.18: Phase diagram of Si with C

The compatibility of SiC with carbon can be expected from the binary system between silicon and carbon (FIG 18), from which it is seen that SiC is an equilibrium phase with carbon in solid state and shows nearly no solubility over the whole temperature range, neither for Si nor for C.

The formation of an at least limited range for the formation of a solid solution is precondition for mass tranport and thus for the progress of the interlayer reactions in the coated solid.

More critical is the possibility of a chemical reaction between SiO_2 and SiC to volatile SiO. This reaction is known to occure below 1500° at low O_2 partial pressures only. Above this temperature limit SiC, can not be applied for long oxidation times in any case.

Basic information of short time protection of carbon/ carbon composites by SiC layers was given by NASA in connection with the US space shuttle development. The coating was prepared by a vapour deposition pack diffusion process. The disadvantages of unsufficient physical incompatibility of SiC layers on carbon substrates (mismatch of thermal expansion and thus crack formation in the protective coating), was overcome by a crack filling procedure with TEOS, which forms SiO_2 during pyrolysis.

An another approach to overcome the problems with missmatch of thermal expansion between SiC coating and carbon is the SiC formation not only on the surface, but also in the surface zone with open pores. This procedure can be performed by a CVI process with methylchlorosilanes and is widely used, but can be applied only, if a bulk structure with open pores achievable from the surface is present.
If the carbon-carbon composite has a dense bulk structure, the CVD treatment results in a thick SiC overlay coating with less effect on porefilling by SiC, as shown in FIG 19.

FIG 20 shows a turbine rotor, as published by SEP France (15) with a woven C-fibre bulk structure. If the open porosity is carefully optimized, a good CV impregnation result can be achieved, as shown by optical microscopy of the crossection.

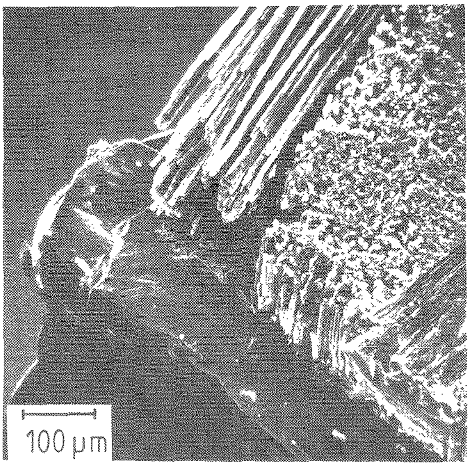


FIG.19: SiC coating on C/C-composite

The surface layer consists of pyrolytic graphite, which gives to the composite embritteled by the siliconizing a little more toughness.

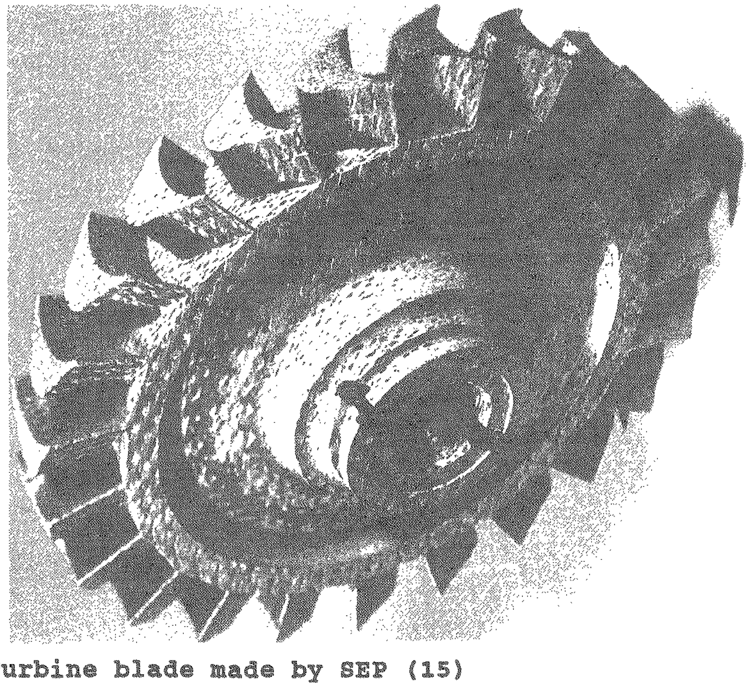


FIG.20: Turbine blade made by SEP (15)

There exists, however, an additional way to obtain excellent impregnation and pore filling; that is by chemical reaction with molten silicon and formation of SiC in a solid/liquid reaction.

Fig 21 (16) demonstrates the industrial application of this liquid-metal impregnation in case of a fine grained bearing shell.The surface layer transformed into a SiC pore filling substance is about 0,5 mm thick.

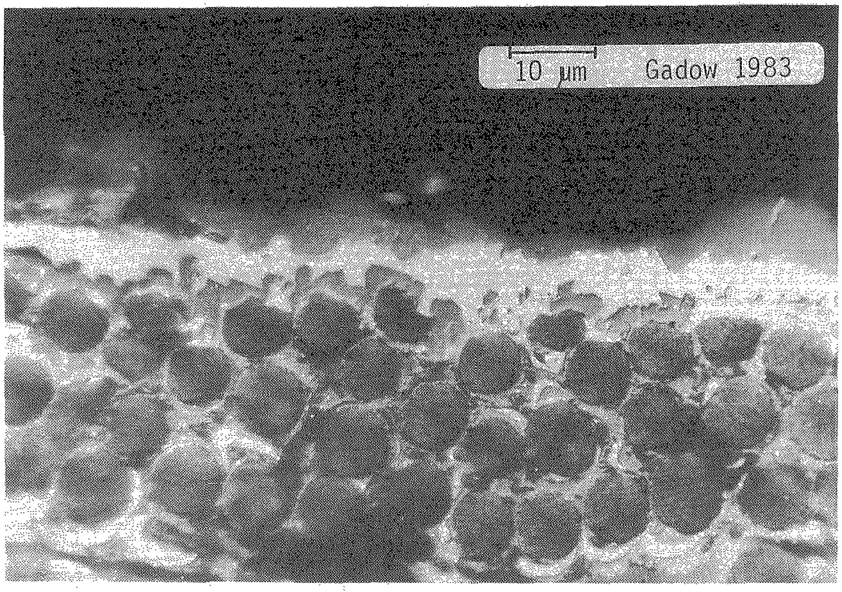


FIG.21: Carbon fibre reinforced SiC (16)

This SiC is formed very fast and under volume increase and is additionally selective against different kinds of structurally disordered carbons what has been studied in detail in Lit 16. A variety of reaction parameters are therefore available for the material scientist. The disadvantage of this method is the high brittleness of SiC formed in such a liquid reaction.

As an example, FIG 22 shows a carbon carbon surface zone, in which the fibres as well as the matrix are transformed into SiC and all pore entrances are filled due to the volume increase during the siliconizing procedure. The fracture surface shows complete brittle fracture without any pullout in the outer surface zone, however some toughness by the pullout below this surface zone, in which the carbon fibres are not yet transformed into SiC.

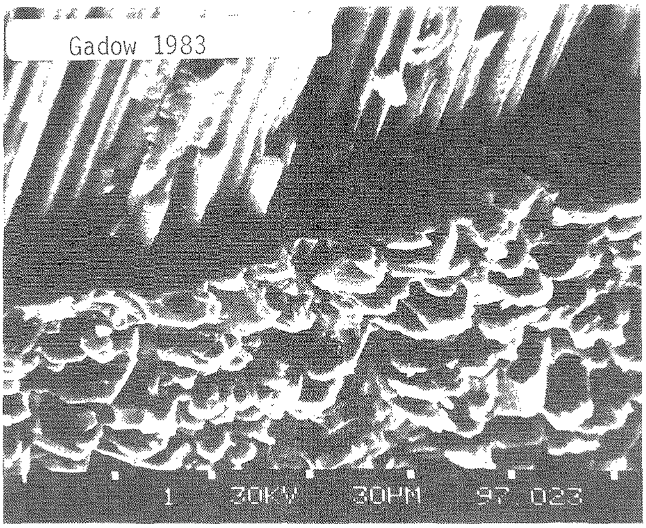


FIG.22: Totally siliconized surface layers with about 30 um thickness (16)

Recently, application of this method for bonded carbon clothes has been published (17). The author found as necessary preconditions and parameters for this process: high density and low porosity of the carbon-matrix, low viscosity of the silicon during the impregnation treatment, but a canal-system in the C/C composite as absolutely need for avoiding severe damage of the composite material. Nevertheless also in this application case, enormeous brittleness results.

A quantitative information on the embritteling by siliconizing is given in FIG 23. It shows stress strain curves of UD carbon/carbon composites, in which the matrix has been completely transformed into SiC, such a composite, where siliconizing was interrupted for completion and thus also with an only partial SiC matrix in the bulk and for comparison a C/C composite with a SiC surface layer only, furthermore a still porous C/C composite impragnated by polycarbosilane polymeres and pyrolysed to SiC porefilling and a commercial granular (reaction bonded) RBSiC. Most promising from this picture on fracture behaviour looks the SiC impregnation via polycarbosilanes.

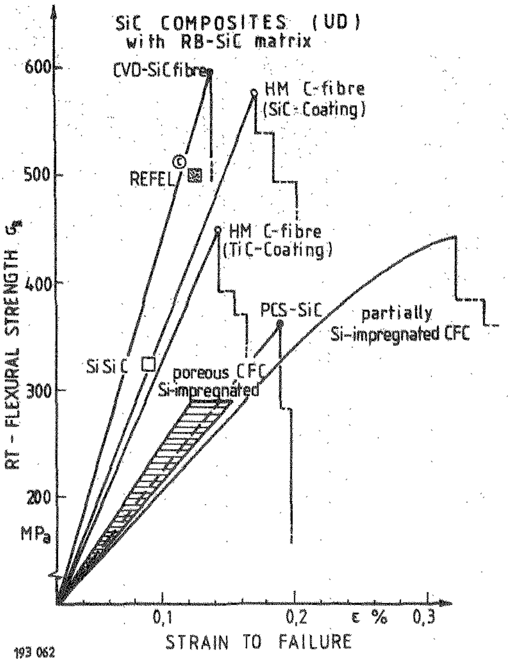


FIG.23: Mechanical properties of SiC-composites (UD) with RBSiC matrix; siliconized at 1800°C (3P bending test)

3.2 COMPOSITES WITH CARBOSILANE BASED SiC (18)

Carbosilanes are silicon organic compounds, in which -C-Si-C- sequences exist. The first polysilanes were produced in 1920 (19). Only in 1949 the white intractable and insoluble powder, which decomposes above 250° was characterized as a mixture of polydimethylsilane and dodecamethylcyclohexasilane (DMCHS), as shown in FIG 24 (20).

The carbosilane chemistry was studied intensively in the fifties (21). The formation of SiC by pyrolysis of polydimethylsilane above 800° was described not before 1978 (22). Yayima the author discovered that a methylene group was inserted between two silicon atoms at 450°, if the reaction is performed in an autoclave.

The product, which was called Mark I by Yayima, is soluble in organic solvents and can also be meltspun to fibres, the production process for the commercial NICALON^{R} SiC fibres. The assumed chemical structure of Mark I is included in FiG 24.

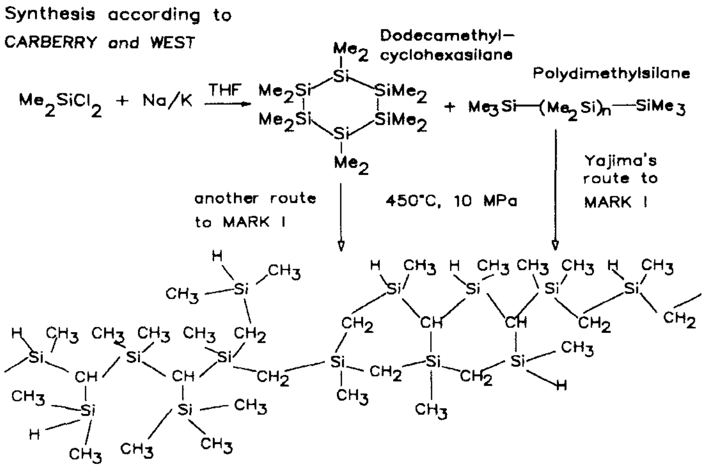


FIG.24: Polycarbosilanes (20)

We used in our own experiments a similar route to prepare the precursor polymer identically to Mark I, but with pure DMCHS as starting material. The objective of these work was the synthesis of matrix precursor for C/SiC composites.

For comparison, also polysilazanes can be used for the same purpose.
The polysilazane chemistry is based on the first papers of Andrianov 1963 (23) and Seyferth 1984 (24).
The polysilazanes are complex silicon organic polymers, in which carbon is partly substituted by nitrogene. The polysilazanes as used by us are liquid at room temperature. The assumed chemical structure is shown in FIG 25.

The polycarbosilazanes are synthetisized from methyl- and vinyl- substituted chlorosilanes as shown also in FIG 25.

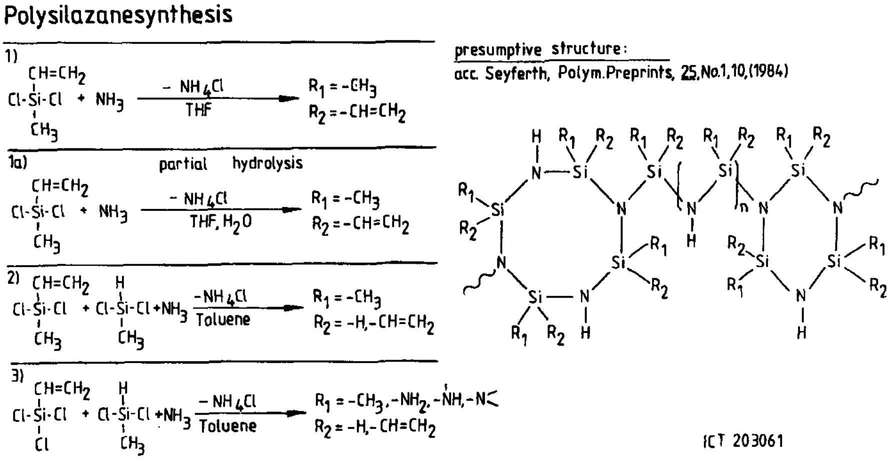


FIG.25: Polysilazanes

A more detailed description of our own synthesis work to achieve controlled viscosity are described in more detail in Lit 18.

The product with high viscosity gives after pyrolysis a ceramic residue up to 70 %. The residue consists of of SiC/Si_3N_4.

Both types of organo silicon polymeres were used as matrix precursor in composites with carbon fibres, with the attention to replace the carbon matrix in carbon/carbon composites by SiC and Si_3N_4 respectively.

Due to the availability of precursors in liquid form (the polysilane as solution only), same technology as for carbon/carbon composites fabrication according to the liqiuid impregnation process was applicable.

Instead of phenolics as first binder for the dry carbon fibres, we used polysilazanes of high viscosity. For the multiple impregnation steps we preferred the polysilazanes with optimized, low viscosity.

The results with a volume fraction of 50% of short HT type carbon fibres (T 300, 1mm length) are shown in FIG. 26 and 27.

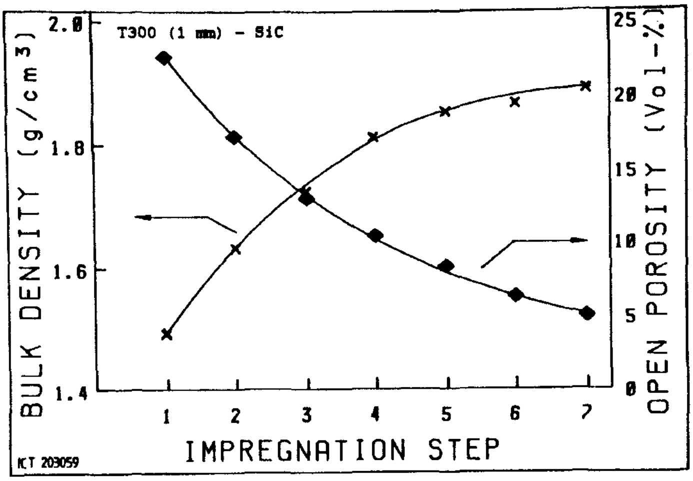


FIG.26: Density in dependence of impregnation steps

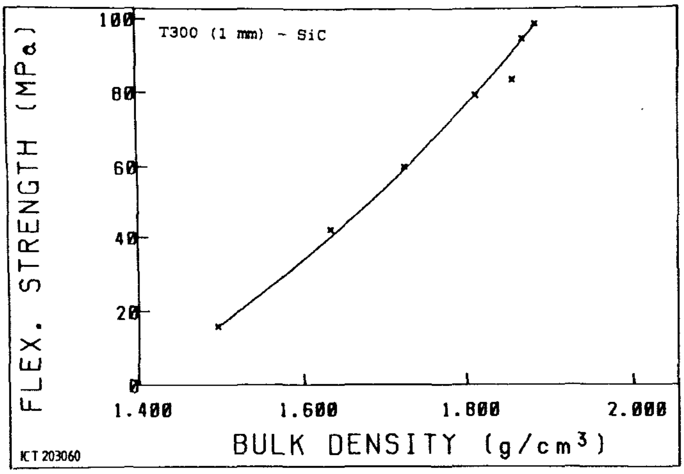


FIG.27: Flexural strength as function of the bulk density

In the composites with short carbon fibres, an open porosity of 5 % remained unfilled after 7 reimpregnation, pyrolysis cycles. The bulk density in the final state was 1.89 g/cm^2, the isotropic flexural strength 100 MPa.

UD composites with endless carbon fibres were prepared by the wet winding technique. HT type (Besfight HT-7) and HM Type (Torayca M 40), as well as both carbon fibre types with CVD SiC coating have been used in these comparative study.

Before pyrolysis to ceramic residue, a stabilization treatment in air is needed in order to transform the meltable polymer into crosslinked unmeltable resin. FIG 28 gives some explanations on the probable chemistry

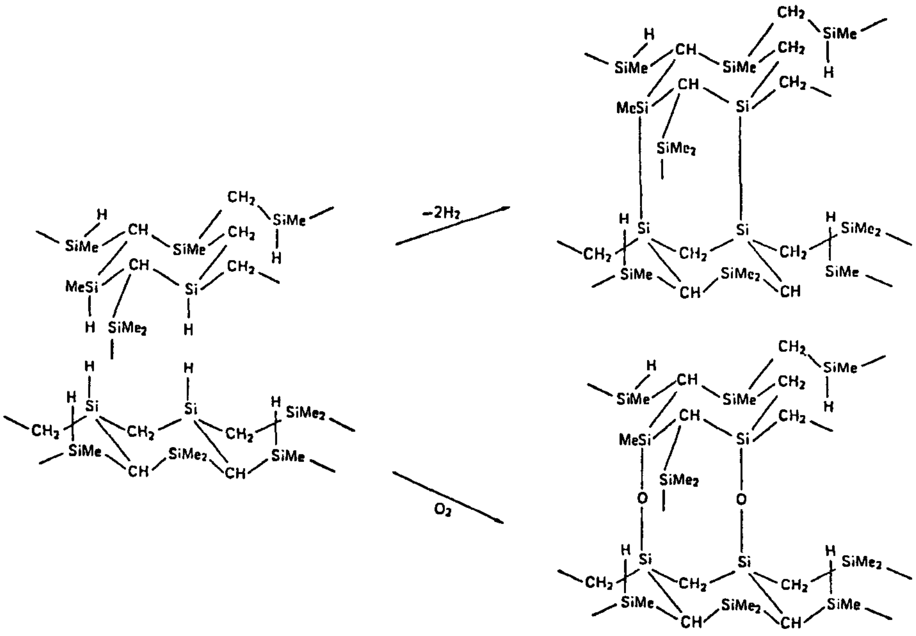


FIG.28: Molecular structures for both stabilization routes

It was found, that in the wet winding process, the polysilazanes are more suitable as matrix precursor for the first fabrication step. A flexural strength by 50 % better than with polycarbosilan type Mark 1 has been achieved. The results are shown in FIG 29.

After 6-9 impregnation cycles, and a final volume content of 50 % fibres, best bulk flexural strength values of 780 MPa have been achieved with uncoated HT carbon fibres.

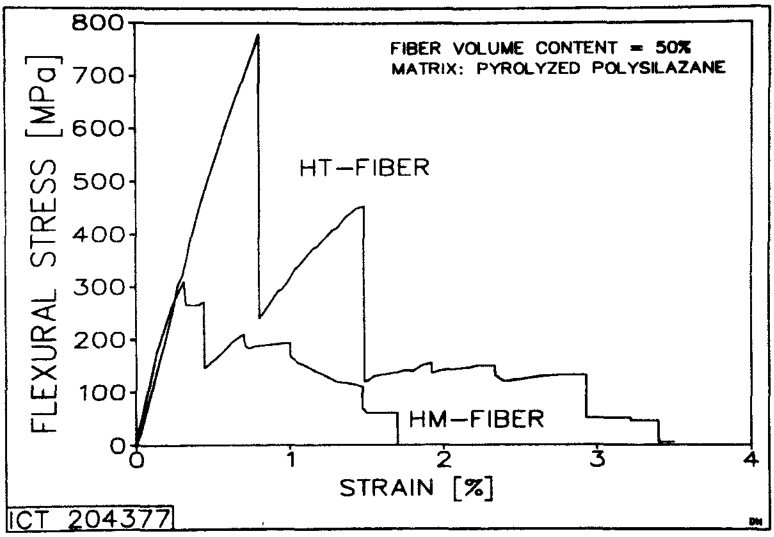


FIG.29: Stress/strain diagram

A rough calculation of the translation of the fibre properties into the composite gives only 25 % according to the role of mixture and a strength value of 4000 MPa for the fibres and 100 MPa for the matrix. The matrix strength value is taken from the results with short fibres above.

The fabrication of the UD composites is not yet optimized, however one can recognize already, that substitution of the carbon matrix in a carbon/carbon composite by polysilico organic based SiC/Si_3N_4 matrix reduces the translation of the fibre strength properties into the composite to a quater only. This is the best case.

If we consider HT fibres with CVD SiC coatings for improvement of the wetting and adhesion, even only bulk strength values below 200 MPa were achieved, corresponding to less than 5 % translation of the fibre strength into the composite, see FIG 30.

With HM type fibres, these first results are not so clear, because with uncoated HM carbon fibres, a bulk strength of 300 MPa, with SiC coated ones values between 200 and 500 MPa have been achieved.

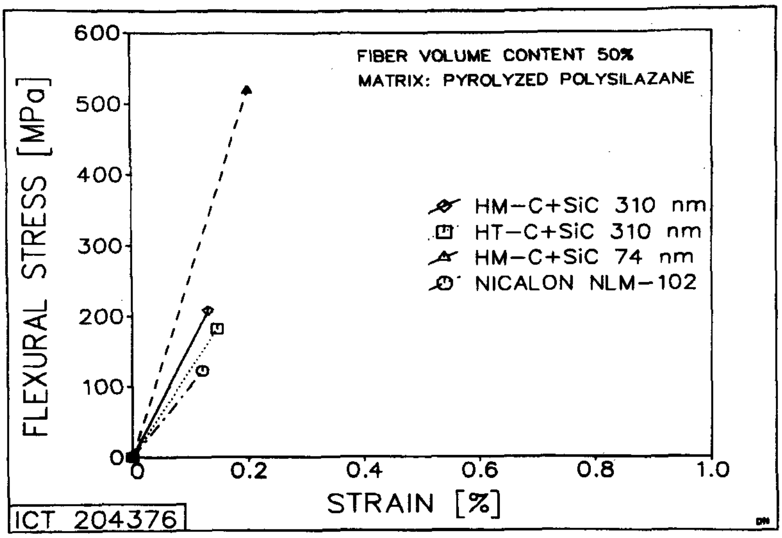


FIG.30: Stress/strain diagram

Let us consider the best value of 500 MPa and a fibre strength of 3000 MPa, then a translation yield of 30 % would result. Nevertheless, SiC matrix can not substitute carbon matrix. SiC matrix is isotropic and has isotropically distributed and not slit shaped pores. There is no mechanism for inhibition of fracture propagation in the matrix itself.

Only the mechanism for crack stopping in the interphase by loose adhesion, pullout and similar effects works, similar as in pure glasses and oxides.

Most impressive is the fracture behaviour, as to be recognizable in FIG 29. With uncoated carbonfibres and bad wetting and low adhesion, a steplike fracture is to be observed in any case, thus offering a limited toughness of the composite. In siliconized carbon/carbon composites this steplike fracture behaviour of carbon/ carbon composited diminishes rapidly by the progressive embrittlement.

Nevertheless, the silico organic based SiC seems to exhibit less brittleness than that from liquid reaction of silicon melt with carbon.

The polymer based SiC is amorphous as shown in FIG 31 up to 1200°. Only after heattreatment at 1400°, the diffraction lines of beta SiC can be identified.
Commercial SiC fibres have similar crystallization behaviour, which is however combined with a rapid decrease in strength.

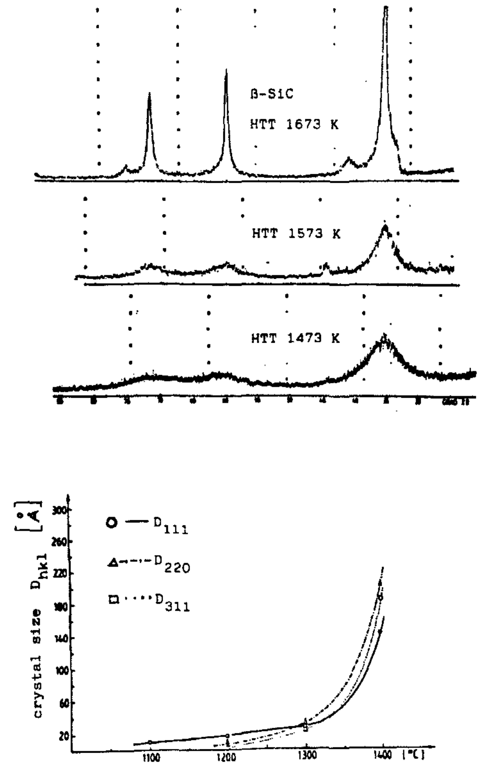


FIG.31: X-ray diffraction on carbosilane based SiC after different HTT in inert atmosphere

Concerning the improvement of the oxidation resistance, no quantitative results are available so far. What we can expect is, that the oxidation damage will be reduced gradually by the partial replacement of carbon, but the oxidation problem will remain unsolved without protectiv overlay coatings.

There remains the question, if all carbon parts can be replaced by SiC.

The problem of oxidation damage would be solved completely, question only for what a price concerning strength and brittleness.

In FIG 29, an all SiC composite was included already, for which commercial NICALON^R SiC fibres and a polymer based SiC/Si_3N_4 matrix have been used. The achieved flexural bulk strength was 130 MPa. According to the rule of mixture, and taking into account a fibre strength of 1000 MPa only because of the heat treatment damage and due to the handling, also 25 % translation of the fibre strength into the composite would result. But complete brittle fracture is observed. The problem could be solved, by improved fibre strength and some inhibition of adhesion, for instance by coatings.

4. Part: SiC FIBRE REINFORCED OXIDES (25)

The world wide efforts, to create all ceramic composites have shown only limited success. There are no high strength oxide fibres in the commercial market with better properties than the commercial SiC fibre types based on silico organic polymers as described before. However, also the strength of these SiC fibres is by far below that of advanced carbon fibres.

There are studies in the literature to apply coated carbon fibres to reinforce oxides, for instance SiO_2 glass matrix with SiC fibres (26). Some results are reproduced in FIG 32.

One has to be aware that such composites need again overlay coatings against burning out of the C-fibres, when applied in oxydizing environment.

There are reports in the literature on SiC fibre reinforced cordierite (27). These fibre reinforced oxide composites show very impressively the toughening effect by the continous fibres (FIG 33).

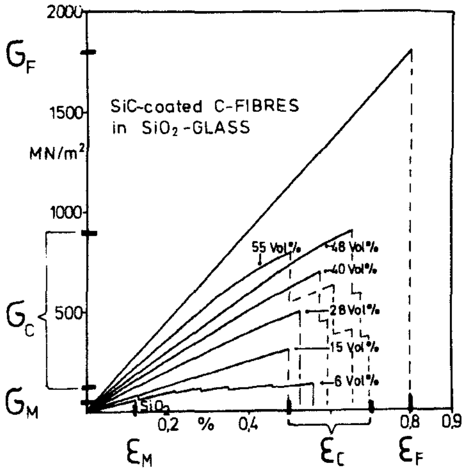
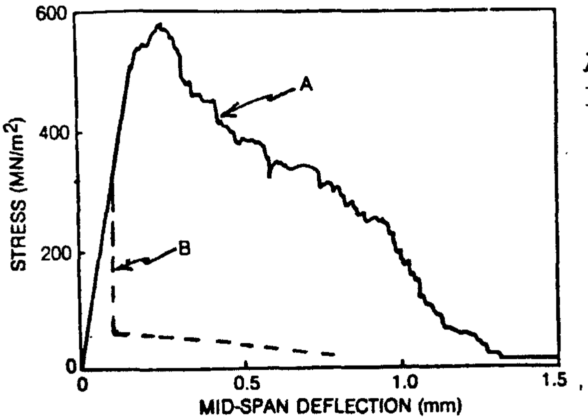


FIG.32: Stress/strain behavior of SiO_2/glass composites (26)



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for SiC large diameter fiber reinforced cordierite

FIG.33: Typical catastophic and step-like fracture of ceramic composites (27)

However the high temperature application problem has not been solved by such matrix systems based on crystallized glasses.

There is a further way, to improve high temperature resistent oxide ceramic, that is more by toughening as by reinforcement of the strength. Best studied is the toughening of Al_2O_3 ceramic by SiC whiskers.

Unfortunately, the SiC whiskers are not only very expensive, but also an acute danger for the health (28), and many countries, for instance Germany, have stopped all research support for such whisker toughening processes.

A more careful research on reinforcement of SiO_2 glass with SiC fibres was reported recently by us. The main effort in this study was the matching of the thermal expansion behaviour of the matrix with that of the commercial SiC fibres. We expected that all internal stresses within the composite created during thermal shock attack can be avoided in spite of the low thermal conductivity of the matrix oxide. The high temperatur stability should be conserved or even improved by such a modification.

We succeeded with ZrO_2 modification of SiO_2 glass.The increase of thermal expansion is shown in FIG 34.
The preparation of the modified SiO_2 glass was performed with the sol gele technique. Modification by ZrO_2 was achieved in the sol precursor already the silico organic SiO_2 as sol precursor.

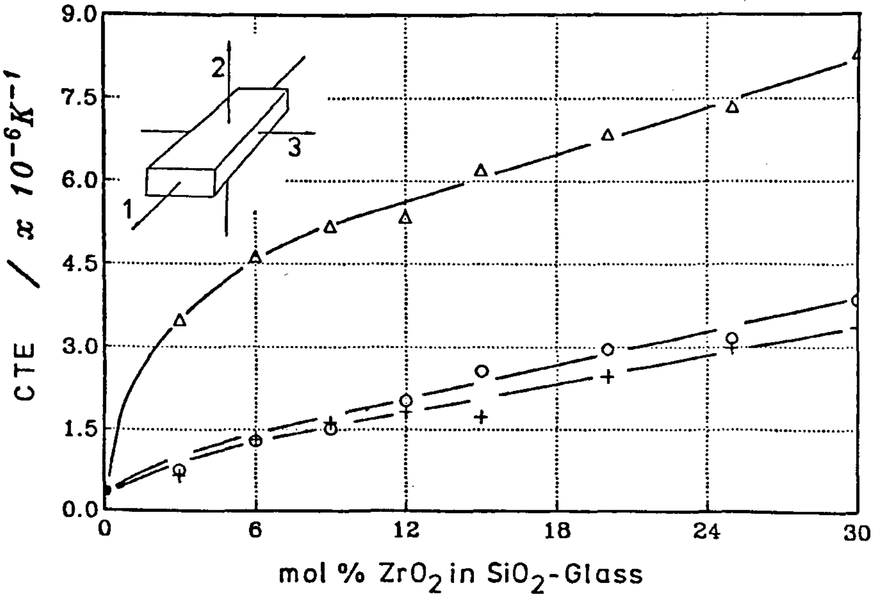

FIG.34: Anisotropic thermal expansion of hot molded SiO_2/glass as function of ZrO_2-content

Further important process steps were the fabrication of UD prepregs and the final application of these prepregs to form pore free laminates by high pressure treatment.

The FIGS 35 and 36 give some informations on the high pressure process step.

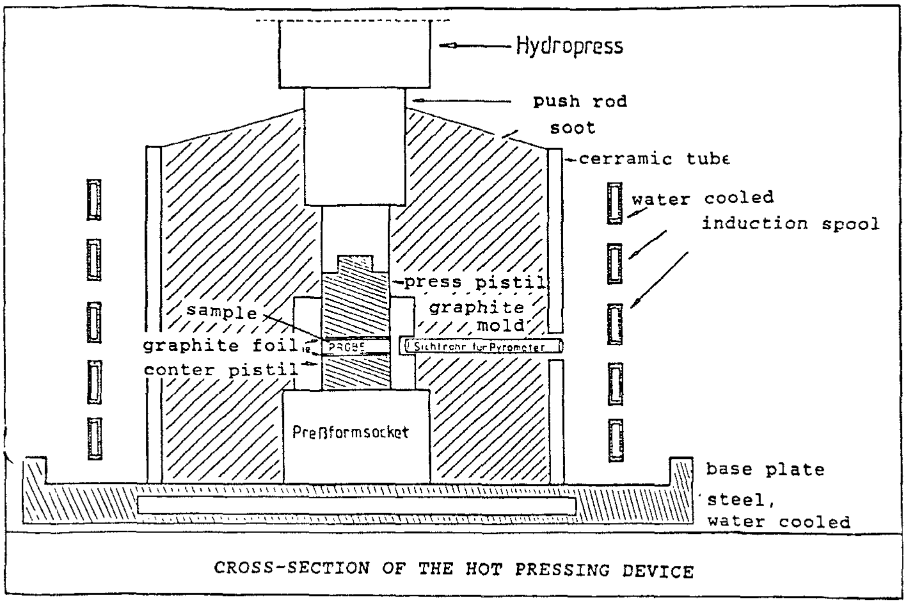

FIG.35: Cross section of inductive heated hot pressing device

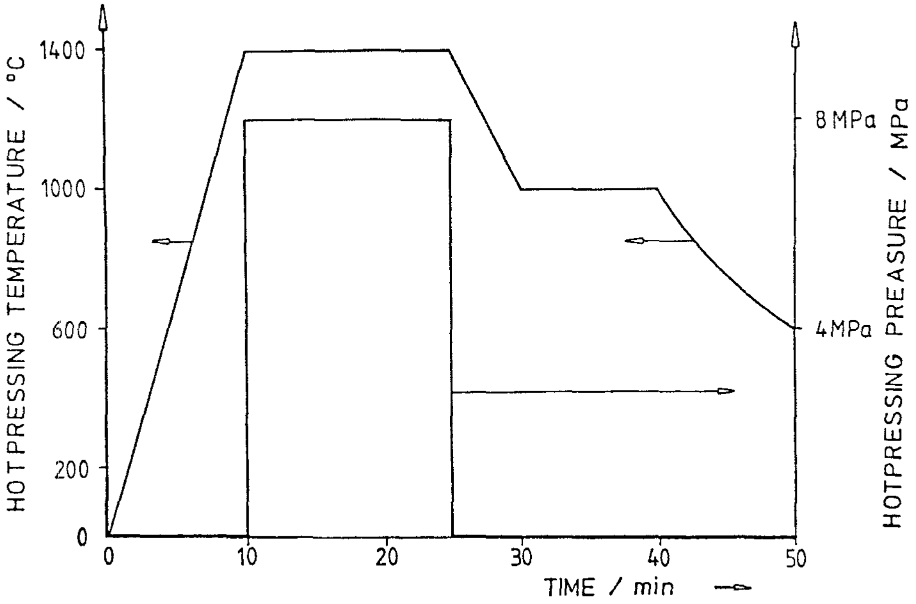

FIG.36: Modelling of the hotpressing parameters

Results are shown in FIG 37 with the stress strain behaviour of UD and 2D composites. Maximum strength of 400 MPa have been achieved.

According to the rule of mixture and assuming a fibre strength of 1000 MPa,a fibre content of 50 vol % and a strenth of the matrix of 50 MPA (see Fig 32), a translation of fibre strength in the order of 75 % can be estimated. This is a good result, although the absolute strength values are quite moderate, if one compares with carbon fibre composites.

The usage of carbon fibre in this oxide matrix brought the very low strength of 250 MPa. We can conclude, that the isotropic thermal expansion is a main reason for the good reinforcement result of the ZrO_2 modified SiO_2 glass.

High temperature strength was tested up to 1200°. Best behaviour show Nicalon^{R} fibres without surface treatment (FIG 37) .

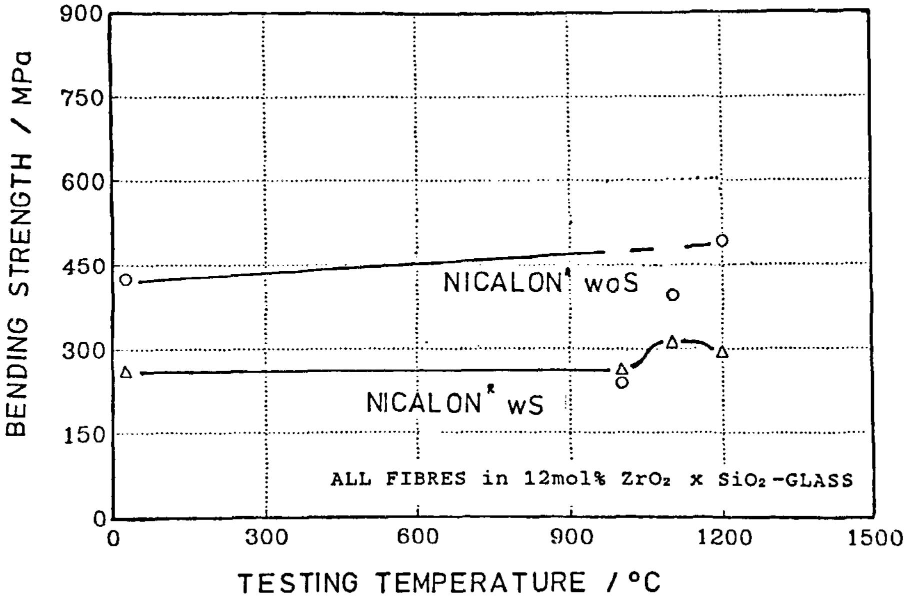

FIG.37: High temperature strength of the reinforced glasses

Summarizing Conclusions

Elemental carbon is an outstanding material because of its position between metals and nonmetallic inorganics and additionally due to some similiarities with the behaviour of polymers.
The explanation of this singularity of carbon is given by the exceptional anisotropy of the crystalline structure of graphite with sigma bonds in the basal lattice planes and a very weak metallic bond between the layers.
Best utilization of this given structural fact for technical materials is in the form of carbon fibres with the superior specific strength and stiffness values.

Elemental carbon in fibre form is also basis of the best high temperatures material we have available, the carbon/carbon composites. The unique mechanical properties, especially the toughness, the stability at highest temperatures and its thermal shock resistance make carbon/carbon composites to an unique solution of the material problems for high temperature application.
However the incompatibility with oxidizing environment excludes many technical applications.

The chances to inhibite oxidative damage of this high temperature material par excellence with the help of the oxidation resistance of SiC is discussed in most detail.
Overlay coatings may help limited time only. The riscs of SiC overlay coatings and also of the partial substitution of the carbon matrix by SiC are neither a mean for longtime oxidation resistance nor a chance to conserve the unique mechanical and thermal properties of carbon carbon composites.

Best solution from chemical viewpoint is the carbon free all-SiC or -oxide composite. The possibilities to achieve mechanical properties similar to those of carbon/carbons are discussed in more detail.

Matrix SiC based on silico organic precursors is less brittle than that from the reaction of carbons with liquid silicon. Polymeres as basis for the SiC matrix offer the possibility to transfer the fabrication technology, as applied for carbon/carbon composites to composites with SiC matrix. It is shown that in SiC matrix composites, best composite properties are achieved with carbon fibres only. This result may indicate, that the anisotropy in the fibre is important for the toughness of the composite.

In contrary to this conclusion, the results presented for the new high temperature composite with ZrO_2 modified SiO_2 matrix, reinforced by the isotropic SiC fibres show, that the compatibility of thermal expansion between fibre and matrix is an even more important precondition for the complete translation of the fibre properties into the composite as bulk property in case of brittle matrix materials.

The well known experience with brittle composite materials, that incomplete adhesion between fibre and matrix contributes to the toughness of the composite, is confirmed by all results of this comparative study.

The exceptional toughness of carbon/carbon composites could be achieved only however, if slit formed microporosity like in synthetic graphite will be synthetizable in other matrices.

So far, only limited progress in development of oxidation resistant composites concerning the application in temperature level and time, as well the mechanical and thermophysical bulk properties has been obtained so far. It will be necessary, to continue critical analysis of all possible material combinations for application in future high temperature composites to fulfill the requests of already todays high tech engineering.

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