Composites for high temperatures

E. Fitzer

Institut für Chemische Technik, Universität Karlsruhe, 7500 Karlsruhe, FRG

Abstract – The paper will treat materials which are reinforced by fibres, so-called fibre reinforced composites. Such tailorable composites are considered as the most promising candidates in future materials development, especially for application at elevated and up to highest temperatures. The term high temperatures in the sense of the present paper is understood starting from the temperature range above the applicability of epoxies that means above 500 K up to more than 2500 K. The paper considers the fibre materials commercially available today, and in development on the one hand and the matrix materials suitable for combination with the various fibre types on the other. As compatible high temperature matrix materials for carbon fibres only to high temperature polymers and carbon itself can be used. All other high temperature matrix materials need diffusion and reaction barriers surrounding the carbon fibres. The status of preparation of diffusion barriers, their influence on the basic carbon fibre properties and the limitations in application temperature because of limited barrier function will be discussed. Special attention will be drawn to alternative fibres which can be used in metals, glasses, carbides and oxides due to their lower reactivity from the chemical viewpoint. Their disadvantage is a lower heat resistivity and most of them have also lower values for mechanical properties. Finally the possibility to develop fibre reinforced composites from brittle matrix with non-brittle reinforcement fibres is presented as an alternative challenge for high temperature material.

1. STATE AND HISTORY OF 'HIGH PERFORMANCE COMPOSITES'

Composites are materials composed of at least two different solids, which exist as separate phases in the final material. The kind and distribution of the different phases control the properties of the composites.

"Advanced composites" or so-called "high performance composites" are mostly based on reinforcement by continuous fibres. Rarely short fibres and whiskers are used for this purpose. The best reinforcement is obtained by the use of continuous fibres with a volume fraction above 50 usually 60 % and strictly controlled geometric arrangement of the fibres within the composite ("tailored material"). The special case of fibre arrangement in one direction is easy to understand and offers the possibility for precalculation of the strength and stiffness of the composites using the rule of mixture (ref.1). The disadvantage of such unidirectional reinforced (UD) composites is the strong dependence of the composite properties on the fibre direction. In practical application two dimensional reinforcement is applied with fibre arrangement in different directions. The reinforcement by short fibres or whiskers and isotropic distribution of the fibres lead to a reinforcement effect of 1/6 of the precalculated values using the rule of mixture, however in all directions (isotropic composites).

The enormeous progress in development of new materials during the last two decades is described as "Revolution in Materials" (ref.2) and is based on the reinforcement of high performance polymers mainly epoxy thermosetting resins with thin high modulus fibres, resulting in an ultra light composite material of high strength and stiffness and superior chemical and fatigue behaviour. First time it became realizable not only to substitute but also to surpass conventional metals by polymer materials in light weight application.

This paper is dedicated to Prof. Dr. Helmut Dörfel, BASF Ludwigshafen, on the occasion of his 60th birthday.

The story of this revolution started by the initiative of the US airforce to replace metals by boron fibres reinforced polymers in military aircrafts and missiles in the Sixties. In 1968 carbon industry demonstrated C-fibre properties similar to that of boron fibres, and in the beginning of the Seventies the Japanese and British process to fabricate carbon fibres economically from PAN has opened the practical application of carbon fibre reinforced polymers.
End of the Seventies PAN based carbon fibres were applied in military aircrafts. The most spectacular application was that in the space shuttle for the loading room doors. Only due to this material the space shuttle project was realizable at that time (ref.3).

In the Eighties, this new material was used in commercial aircrafts already. It is applied for the vertical stabilizer in the airbus A 310, at the moment the largest part of industrially produced carbon fibre reinforced composites. The present world wide use of carbon fibres is in the order of 5.000 to 10.000 tons per year with a strongly increasing tendency. The expected broad application in surface transportation such as railways and cars, in machinery, in pipelines and apparates, in sporting goods as well as in building materials was described in more detail last year here in Rome during the European Conference on Thermophysical Properties (ref.4). Most exciting for this material is the low energy need for raw material preparation in fabrication as compared with high energy consumption by conventional materials.

There is, however, one severe limitation for application of carbon fibre reinforced polymers, that is the limitation in temperature caused by the softening or thermal decomposition of the polymers. The high temperature resistivity of the carbon fibre is not used by far in combination with epoxy. For solving the future problems in aerospace and energy field, in industrialization in general and especially for high technology, composites for high temperatures are needed.

2. THE NEED FOR HIGH TEMPERATURE COMPOSITES

One can use the term "High Temperature" for the temperature range above that of the usual upper application temperatures of the respective material group. In the case of advanced composites the high temperature range is above 500 K, where carbon fibre reinforced epoxy can not be used anymore (ref.5).

One has to ask, however, what is the need for advanced fibre reinforced composite materials for application at high temperatures ? Can future technological requests not be satisfied by conventional material types for high temperatures such as metals and ceramics ? Let us consider as example the materials request of aerospace technology, not only because it demonstrates most impressively the need for light weight high temperature materials, but also because this field is most exciting for future world wide transportation and energy consumption and thus is a substantial precondition for the future technological age and the human civilization in general.

In supersonic aircrafts, for instance, the surface temperature can arise up to 500 °C, that is a temperature range where no today's resins for fibre reinforced composites can withstand. In the space shuttle with surface temperatures above 1000 °C during the period of entering the earth atmosphere, this heat attack problem was solved by the use of thermal insolation bricks. On the tipcone and in the edges of the wings, however, the temperatures arose up to 1500 °C. Here only carbon/carbon composites were applicable. The additional problem arising for this application is the attack by the oxygene in the atmosphere and carbon materials without surface coatings are not resistant against oxidation at those temperatures.

The most exciting future project is the Orient Express (ref.6) or the analogous British project HOTOL, flying vehicles which should start and land in air fields as commercial airplanes, but should travel in an altitude of 27 km, thus reducing the flight time from America to Asia to 3 hours only. In such vehicles surface temperatures up to 1800 °C are precalculated. The material problem is not solved by far. Obviously, one will use metals for the outer surface and for the tipcone and the edges carbon composites coated by ceramics.

The material requirements for the engines are similarly critical. In conventional water cooled engines the material temperatures do not exceed 150 °C and can be satisfied by conventional aluminium alloys. The additional request for lighter weight materials even opens here the chance for application of advanced composites for instance CFRPs for pistons and connecting rods.

The most critical technical high temperature problem since decades is the material requirement for the rotor in gas turbines. Gas temperatures as high as possible at least above 1200 °C are needed because of thermodynamic reason, and nickel based super alloys can not be used at temperatures above 1000 °C. Here again, high temperature strength, creep resistance and oxidation resistance are required. Some progress is achieved by single crystal blades, by internal cooling of the rotor blades and by high temperature oxidation resistant coatings on the nickel based alloys. Here arises an important field for new light weight materials.

3. REINFORCEMENT FIBRES FOR HIGH TEMPERATURES APPLICATION

The conventional reinforcement fibres for advanced composites – these are polyaramide fibres, glass fibres and carbon fibres – are compiled in Fig.1. Fig.2 shows the thermal decomposition of aramide fibres according to own testing. The organic fibres can not be used for temperatures above 250 °C.

The conventional E-glass fibres (boron silicates) loose strength above 200 °C already and soften in the temperature range of 500 °C. The recently developed Al_2O_3 rich silicates, the R-glass types, show improved strength at increasing temperatures, and softening is shifted to 200 °C higher temperatures. However, as all glass fibres also this type shows very low stiffness (see Fig.3) (ref.9).

So far as temperature resistance is concerned carbon is the ideal fibre material. The strength of the carbon fibre is remained until 2000 °C, the stiffness even increases with temperatures up to 2500 °C. The disadvantage of carbon fibres is the sensitivity against oxidation which reduces the strength after oxidation above 500 °C in air already (see Fig.4).
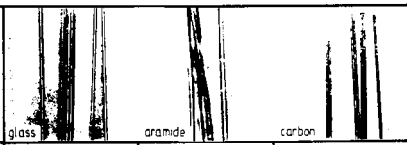
100 μm ⊢——⊣	glass	aramide	carbon
ρ [g/cm³]	2.5	1.45	1.8 (2.1)
σ_{Zug} [MPa]	2000–4000	3000	3000–5000 (2000)
E ‖ [GPa]	50–80	70–130	200–500 (700)

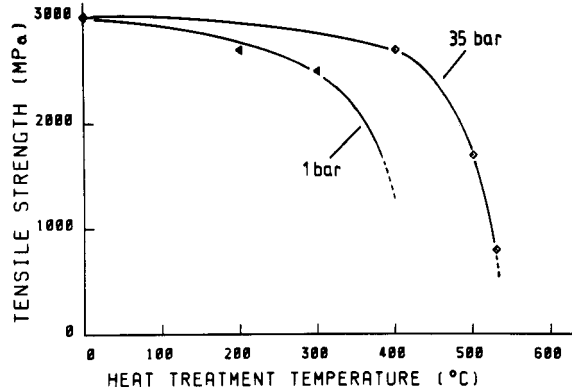Fig.1 : Fibres for high performance fibre reinforced polymers (FRP)

Fig.2 : Room temperature strength of polyaramide fibres after heat treatment in argon

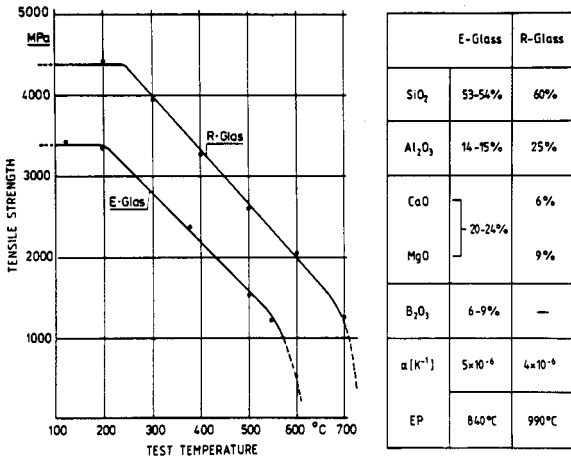|	E-Glass	R-Glass
SiO_2	53–54%	60%
Al_2O_3	14–15%	25%
CaO	20–24%	6%
MgO		9%
B_2O_3	6–9%	–
α [K⁻¹]	5×10⁻⁶	4×10⁻⁶
EP	840°C	990°C

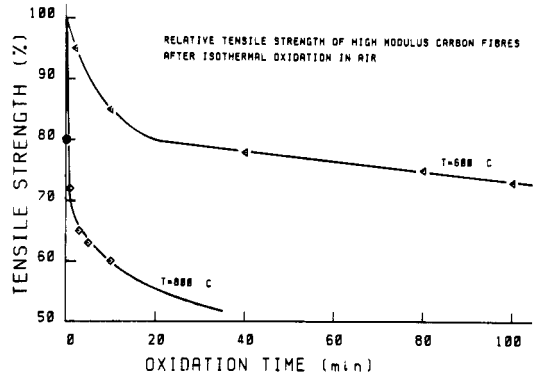Fig.3 : Strength of glass fibres measured at elevated temperatures

Fig.4 : Strength reduction in carbon fibres by oxidation

One has to ask what alternative fibres are available for high temperature application. In Table 1 the required properties and the degree of matching them by candidate fibres are compiled. Low density, one important precondition for light weight composites is most suitable for carbon fibres. Oxide fibres show densities above 3.0. Boron itself has a density of 2.5, but boron fibres are made by chemical vapour deposition on a tungsten substrate and therefore the average density is also in the area around 3.

Table 1 : Required properties of fibres to be used in high temperature composites and the degree of meeting them by candidate fibres

+ = good   0 = medium   − = bad

| Property	candidate fibre	B	SiC	Al$_2$O$_3$	Mullite	C
1) Density		2.5	3.2	3.9	3.4	2.2
1) Light weight of the fibre		0	−	−	−	+
2) Mechanical room temperature properties (strength, stiffness E, strain to failure		+	+	−	+	+
3) Temperature resistance short time during processing		−	0	0	+	+
long time during application		−	0	0	+	0
4) Oxidation resistance in air during application		−	+	+	−	−
5) Industrial economic producability of the fibre		−	−,+	0	+	.+
6) Handling of the fibre during fabrication of the composite		−	−,+	0	+	+
7) Compatibility with the matrix material and adhesion within the composite		−,+	−,+	+	−,+	−
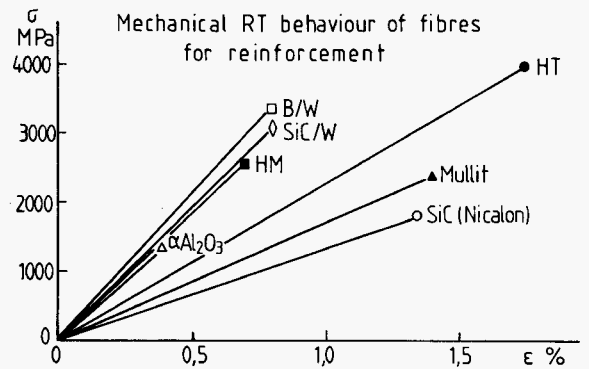
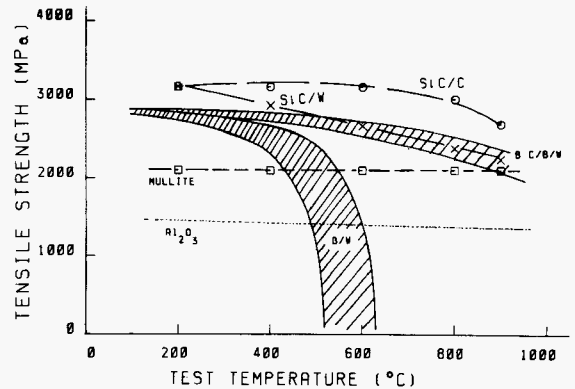Fig.5 : Mechanical RT behaviour of fibres for reinforcement

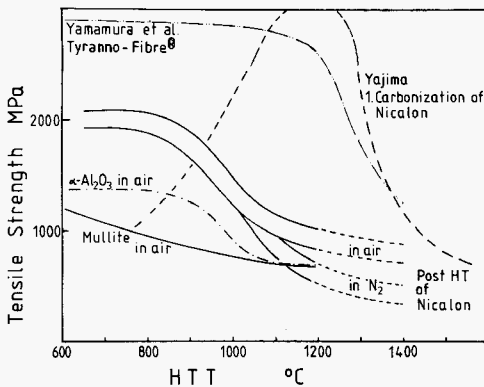Fig.6 : Strength of reinforcement fibres, in situ measured in air

Fig.7 : Temperature strength of thin oxide and carbide monofilaments after heat treatment
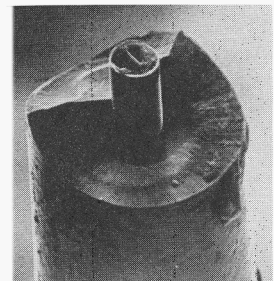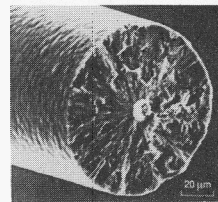

Fig.8 : SiC fibres fabricated by CVD: left side on tungsten substrate right side on carbon substrate

Fig.5 gives a compilation of the mechanical properties measured at room temperature. The stress-strain diagram shows highest stiffness for boron fibres. Boron fibres are also known as one of the best fibres for composites with high compressive resistance which specific property justifies their even limited application in polymers allowing high compressive stresses in spite of the high costs and the processing difficulties. However, one can recognize, that boron as well as silicon carbide fibres made by vapour deposition have very low strain to failure what indicates an extreme brittleness. All other future fibres such as aluminium oxides, mullite or silicon carbide fibres made from polycarbosilanes have much lower strength as the carbon fibres.

The room temperature data on mechanical properties do not give any indication on the behaviour at elevated and high temperatures. Fig.6 shows the tensile strength measured in situ at higher temperatures. One can recognize that all CVD fibres on tungsten substrates loose the strength because of recrystallization as well as chemical reaction with the substrate. Only silicon carbide fibres deposited on a carbon substrate behave better. As these tests were performed in air one can also see the sensitivity of these fibre materials against oxidation. Only the oxide fibres are stable, at least up to 1000 °C. There is an additional critical upper temperature even if applied at very short time only. It is the recrystallization temperature in the oxide fibres. Fig. 7 shows the room temperature strength measured after short oxidation in air. The oxidation resistant oxide fibres show, however, a strength
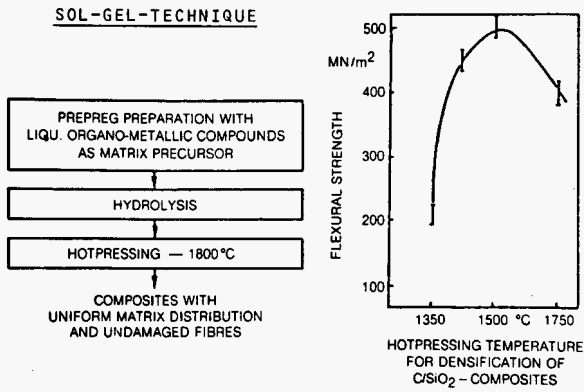
SOL-GEL-TECHNIQUE

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┌─────────────────────────────┐
│ PREPREG PREPARATION WITH    │
│ LIQU. ORGANO-METALLIC COMPOUNDS │
│ AS MATRIX PRECURSOR         │
└─────────────────────────────┘
              │
┌─────────────────────────────┐
│         HYDROLYSIS          │
└─────────────────────────────┘
              │
┌─────────────────────────────┐
│   HOTPRESSING — 1800°C      │
└─────────────────────────────┘
              │
      COMPOSITES WITH
   UNIFORM MATRIX DISTRIBUTION
     AND UNDAMAGED FIBRES
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Fig.9 : Flow sheet for fabrication of
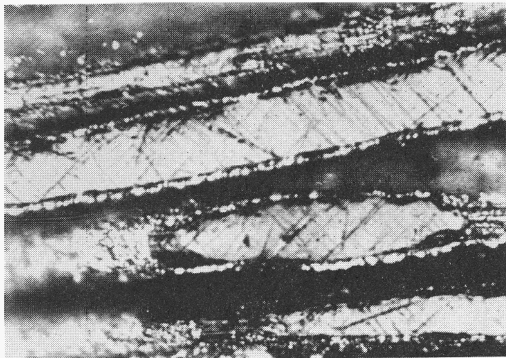carbon/oxide composites

Fig.10 : C-fibres with SiC-coating in
SiO_2 glass matrix

Table 2 : Matrix materials for high temperature
composites

Materials group	Examples	Upper application temperature °C	Oxidation resistance in air
HT polymers	Polyimides HT thermo-plastics	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

decrease if the recrystallization temperature around and below 100 °C has been passed. Recrystallization for NICALON [R] SiC- and for oxidic fibres starts in the 1000 °C area and levels out at 1400 °C when a protective coating on silicon carbide is formed. The results of YAJIMA (ref.11) who has developed these SiC fibres are included. A comparison with the behaviour of industrially produced and commercially available SiC fibres indicates that industrial fabrication obviously uses a carbonization temperature higher than that for which YAJIMA has measured the strength maximum.

The industrial producibility and the handling of the fibres during fabrication are in direct correlation with the fabrication methods. The fibres made by chemical vapour deposition (Fig.8) on tungsten or carbon substrate need a minimum diam.at about 100 μm. They are very brittle and the handling is difficult. They are monofilament fibres and cause very high production costs in the order of 500 Dollars/kg, against around 50 Dollars for today's carbon fibres. The handling of such thick and very brittle fibres causes often fracture of the mono-filaments during fabrication of the composites.

The oxide fibres are more flexible. Their thickness is comparable with that of carbon fibres. They are commercially available in yarns and rowings and can used for weaving to textiles.

An alternative for CVD-silicon carbide fibres is offered by polycarbosilane based fibres, and also by carbon fibres coated with silicon carbide which both are easy to handle. Fibres with SiC surface are needed for compatibility reasons in metals and oxide matrix (compare Fig.10).

Summarizing the conclusions on non-meltable alternative fibres, one can state, that especially from the viewpoint of industrial economic productability as well as from that of the handling only fibres made from precursor fibres by thermal decomposition like carbon fibre technology have a chance for industrialization. For the oxide fibres, melt spinning process – as can be applied for mullite – seems to be the most candidate method. It is similar to the most economic method for glass fibre fabrication.

4. MATRIX MATERIALS FOR HIGH TEMPERATURE COMPOSITES AND THEIR COMPATIBILITY WITH THE FIBRES

The material groups which can be considered as matrix materials for fibre reinforced composites for high temperatures are compiled in Table 2. The basic properties of these material

groups are known to the high temperature chemists. For the application as matrix materials, however, we have to consider additionally:

their density and the mechanical properties;

their thermophysical properties such as softening, thermal expansion, thermal conductivity;

their chemical behaviour in oxidizing atmosphere at high temperatures;

their fabricability and finally

their compatibility with the fibres during fabrication as well as during application.

Let us start with the important oxidation behaviour which is indicated in general in Table 2. This property decides on the applicability of the fibre in the different matrix materials in air. But even if non-oxidizing atmosphere is considered, like in the space for instance, there is severe danger by atomic oxygen at a very low partial pressure as it became known recently.

Let us continue now with the fabricability. The three upper material groups in the Table 2 (HT polymers, metals, glasses) are easier to fabricate because they are meltable and can be processed in liquid state, however only, if the fibres are highly resistant against the molten matrix. The processibility of the three lower material groups (the hard materials, the intermetallics and the high melting oxides) is more difficult and the applicability of composites with such a matrix depends strongly on the fabrication method.

Table 3 shows the principle methods how composites can be prepared. The melt method is the easiest one applicable for the resins, glasses and low melting metals. Similar but much more difficult is the sintering of the matrix starting from powders. Mostly high pressure at sinter temperatures (HIP) is needed. A modification is the use of a matrix powder precursor like in the sol/gel process which is explained in Fig.9 (ref.12). Reaction sintering is a well known method for fabrication of ceramic materials especially for the silicon ceramic (silicon carbide and silicon nitride). It can also be applied for preparation of composites.

Finally, one can prepare matrix by thermal decomposition of a liquid or a meltable matrix precursor like pitches of resins, and analogous to the fabrication method of artificial carbon materials. It can also be a gaseous precursor as in the so-called carbon vapour impregnation method, again applied for carbon/carbon composites and for silicon carbide composites.

So far as the compatibility is concerned (Table 4) there is no problem to use carbon fibres and polymers in elemental carbon matrix, however in all other matrix materials carbon fibres will finally react at high temperatures with the matrix.

Table 3 : Fabrication processes for high temperature composites

Methods	Samples for application
Melting of the matrix or application of liquid or matrix precursor to be hardened	Applicable for C, B, SiC and oxide fibres in polymers, metals and glasses
Sinter process of the solid matrix powder (HP) or solidified, formerly liquid precursors (sol/gel)	C and SiC metal fibres hard metals, intermetallics C & Oxide filler in oxides
Reaction sintering of the matrix	SiC and C fibre in Si_3N_4 and SiC
Preparation of the matrix in situ by thermal decomposition of the matrix precursors	C-fibres in carbon C + SiC fibres in SiC and refractory oxides
CVD of the matrix formation in situ	C + SiC in SiC and C

Table 4 : Interactions between fibres and matrices

1) CHEMICAL	COMPATIBILITY, MAINLY AT HIGH TEMPERATURES DURING FABRICATION AND APPLICATION ADHESION
2) PHYSICAL	THERMAL EXPANSION AND INTERNAL STRESSES ADHESION
3) MECHANICAL	REINFORCING EFFECT AND FRACTURE BEHAVIOUR

AD 1)   CHEMICAL COMPATIBILITY

FIBRE	MATRIX	
C	C, POLYMERS, SiC	+ +
	METALS, OXIDES	-
SiC	SiC, C, POLYMERS	+ +
	OXIDES	+, 0
	METALS	0, -
OXIDES	OXIDES	+ +
	SiC	+
	METALS	+ -
	C	-

Therefore, carbon fibres need some coatings which can act as a reaction or a diffusion
barrier. As shown in Fig.10, silicon carbide barrier can be used for reinforcement of silicon
oxide glasses (ref.13). Alternative coating materials are titanium carbide, titanium nitride,
silicon nitride and others. These barriers can be deposited by chemical but also by physical
vapour deposition process.   I had the opportunity to report years ago already during one of
the previous IUPAC supported Conferences on High Temperature Materials at Toronto, Canada
(ref.14), that such coated carbon fibres can be applied for reinforcement of metals, glasses,
hard materials, oxides and other high temperature matrix materials. One has to consider,
however, the transport rates of the basic material from one side, and of the carbon from the
other through such coatings which limit the temperature and residence time of application at
high temperatures.

Silicon carbide fibres are chemically compatible with glasses and light metals at elevated
temperatures (below 400 °C). Their applicability in the chemical compatible high melting
intermetallics and oxides is limited because of the limited temperature resistance of these
fibres and the need of high application temperatures for the composites.

The boron fibres do react with metals, especially with aluminium. Also for this purpose coa-
tings have been developed (silicon carbide coatings as well as boron carbide coatings). At
the moment it seems that the use of boron fibres for reinforcement of aluminium passes a
renaissance because of the high stiffness and high compressive strength of such materials at
elevated temperatures and because of their thermal inertness.

There is no question, that oxide fibres are compatible with oxides, glasses but even also
with most intermetallics and metals because the rate of oxidation between solids is very low.
The suitability of oxide fibres is not yet tested comprehensively. Problems arise also in
fabrication of such composites at very high temperatures due to the recrystallization of the
fibres during this processing.

Besides of the chemical compatibility, the physical and the mechanical compatibility have to
be discussed (see Table 4).

The physical compatibility is mainly based on the difference in the thermal expansion in
fibre and matrix. In case of higher expansion coefficient for the matrix as for the fibre
during cooling from processing temperature, compression stress on the fibre is created, which
improves the fracture behaviour in general. The inverse case, e.g. in glass ceramics or SiO_2
glass the matrix can shrink away from the fibre during cooling. This process decreases adhesion
between fibre and matrix. The adhesion between fibre and matrix is precondition for stress
transfer in a composite. It can be of chemical or physical nature. For carbon fibres in poly-
mers it has been shown, that the chemical nature is most important. In fibre matrix couples
which are chemically incompatible at high temperatures, the chemical reaction tendency at
lower temperature can increase wetting during fabrication of the composite and can initiate
a chemical adhesion. It is known that for brittle composite materials limited adhesion can
improve the toughness and also the impact resistance (ref.15). This complicated and diffi-
cile interaction between fibre and matrix will be discussed later on special cases.

In principle we can state: brittle fibres can toughen brittle matrices (resins and ceramics),
brittle fibres, however, embrittle ductile metals.

5. FIBRE REINFORCED HIGH TEMPERATURE POLYMERS, GLASSES AND OXIDES

5.1 Carbon fibre reinforced high temperature resins

There are two classes of matrix polymers for high temperatures, the high temperature thermo-
setting resins, mainly the polyimides, and the high temperature thermoplastic resins, here
polysulphone and especially polyetheretherketon. The upper temperature limits for application
is above 250 up to 400 °C. It is believed that this is the upper temperature limit achievable
with organic polymers.

Problems arise with both polymer types if considered as matrix material, namely: brittleness
in case of thermosetting high temperature resins and processing difficulties during fabrica-
tion of composites with high temperature thermoplastics.

Fig.11 shows a relation of the strain to failure of the net resins against the impact be-
haviour. The high temperature thermosetting resins are placed in the left lower corner of
this diagram. Many efforts can be observed during last years to increase the toughness of the
high temperature thermosetting resins for instance by including some high temperature thermo-
plastics.

The high temperature thermoplastics are ideal as matrix from the viewpoint of the impact re-
sistance. They are placed in the right upper corner of the diagram (Fig.11). Concerning the
fabrication difficulties of such composites it is known that the polyetheretherketon is not so-
luble in a solvent, and the melt has such a high viscosity that it is difficult to distribute

the matrix material uniformly surround the C-fibre monofilament in a rowing. Nevertheless, all specialists see in the development of composites based on high temperature thermoplastics the most promising future solution.

As mentioned before, the brittleness of CFRPs can be reduced by a careful optimization of the interaction between fibre and matrix mainly the adhesion, which should match the requirement for each matrix combination (ref.15). The brittleness can be reduced by a reduction of the adhesion because the fracture energy is partly consumed by pull-out and by crack deviation. The reduced adhesion, however, reduces also the translation of the fibre properties into the composite (ref.16).

In contrary, the application of high strain fibres allows the best adhesion because the fracture energy is partly consumed by reversible elastic deformation of the fibre before fracture, although in such case a pull-out of the fibre is observed finally too. By such high strain carbon fibres the impact behaviour of a brittle material can considerably be improved as shown in Fig.12 (ref.17).
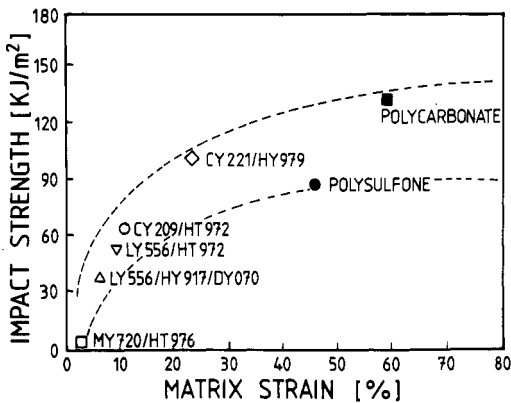
Fig.11 : Impact strength versus strain to
failure of net matrix polymers
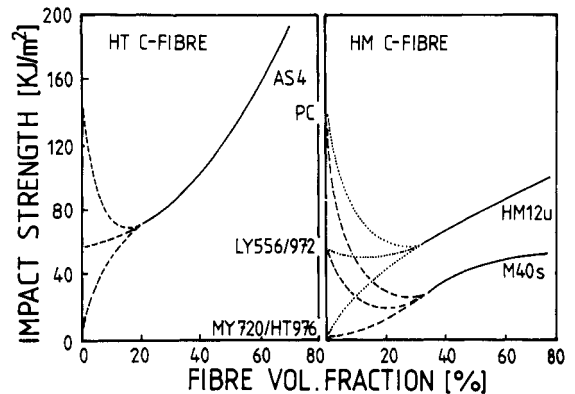
Fig.12 : Impact strength of UD CFRPs against
the fibre volume fraction

5.2 Carbon fibres in SiO$_2$-glass

The reinforcement of the very brittle SiO$_2$-glass by carbon fibres was described by us many years ago already (ref.18). At that time, there was no need for such composites. Today, however, these similar composites are developed by several research places mainly using the NICALON ^{R} - SiC fibres. The key to the solution of such fibre/matrix combination in our case was the coating on the fibres not only as protection against reaction between carbon and oxide but also as wetting and adhesion agent. Sol/gel technique with HP densification was applied (compare Fig.9).

The best coating on carbon fibre for reinforcement of SiO$_2$-glass was found to be a SiC coating prepared by chemical vapour deposition. Titanium nitride coatings have a smaller improving effect. Fig.13 shows the improvement of the flexural strength of UD reinforced composites and the influence of the fibre content (ref.19). Most important is the fracture behaviour, the well-known brittle fracture of non reinforced glass is shifted to a steplike fracture behaviour which is typical for fibre reinforced oxides.

5.3 Fibre reinforced glasses and oxides

SiC-fibre reinforced silicate glass and glass ceramic have gained practical importance during last years within the United States due to the availability of thin rowings made of silicon carbide fibres. The results on reinforcement and fracture behaviour are comparable with those using coated carbon fibres as described by us before.

The high temperature strength of 96 % silica reinforced with SiC yarn indicates an applicability up to the 1100 °C range (ref.20).

Also glass ceramics can be successfully reinforced by SiC. Literature on the effect of thick CVD SiC monofilaments on cordierite is available (ref.21). The toughening is indicated in room temperature tests not only by the increased strain to failure but also by steplike fracture.
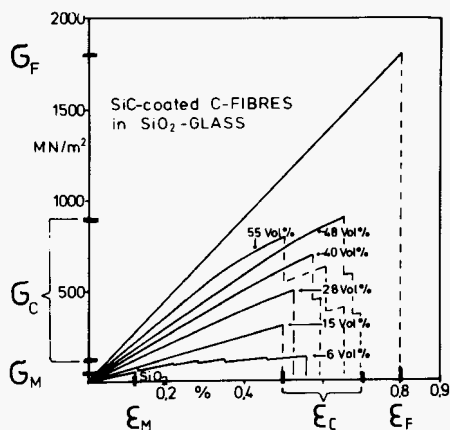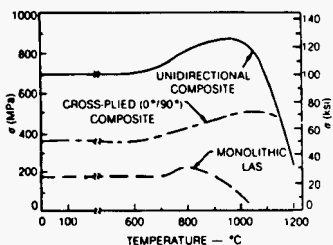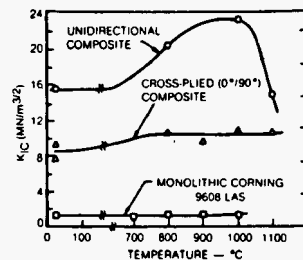
Fig.13 : Room temperature strength of C/SiO$_2$ glass composites

Three point flexural strength in argon of SiC reinforced LAS glass ceramic

Prenotched three point bend test determined fracture toughness in argon of SiC reinforced LAS glass ceramic

Fig.14: According to Prewo 1986

The strengthening and toughening effect by SiC yarn on lithium aluminium silicate is shown in Fig.14 (ref.22), measured up to temperatures of 1100 °C. Low adhesion in these samples at room temperature because of unfavourable physical compatibility (thermal expansion of the components) effects beneficially the toughness.

5.4 Fibre reinforced refractory oxides

The fabrication of fibre reinforced glasses and glass ceramic composites is easy to perform because of the meltability of the matrix. The problem of fibre reinforcement of refractory oxides is most difficult because of the extremely high sintering temperatures of the matrix and because high pressures during HP or HIP processes (high temperature pressure and high temperature isostatic pressure) will damage the fibres. The sol/gel technique as described before enables us to prepare composites with Al$_2$O$_3$ and with mullite as matrix. Al$_2$O$_3$ - fibres as well as carbon fibres coated by silicon carbide were applied by us. Silicon carbide rowings which were not available at that time can also be considered preferentially today. Some results on the room temperature properties of carbon fibre reinforced oxides are shown in Figs. 15 and 16 (ref.24). With Al$_2$O$_3$ matrix only a minor strengthening effect was found, however, the stress intensity factor is increased considerably. In case of carbon fibre reinforced mullite we achieved not only a toughening of the composite, but also an effective increase in flexural strength.

As conclusion from these results, one can expect that also short fibre additions to such refractory oxides will have a good toughening effect, even if no remarkable increase of strength itself is achievable. As well known, the main problem in application of refractory ceramics is their brittleness. Such a toughening effect has to be considered as important success, already.
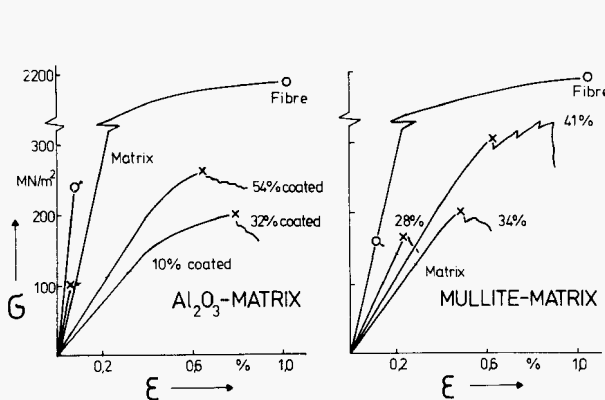
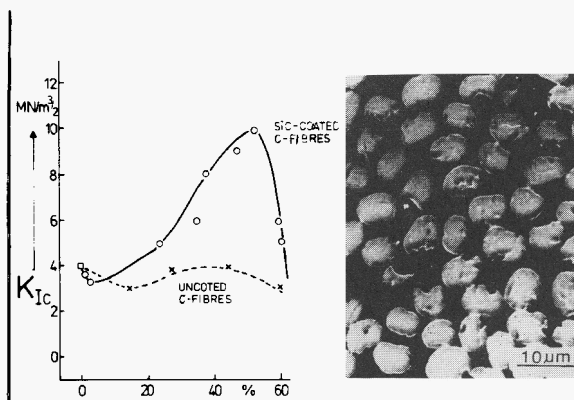Fig.15 : Stress/strain behaviour of sintered ceramics with C-fibres

Fig.16 : SiC coated carbon fibres in Al$_2$O$_3$ (hydrol. techn.)

6. FIBRE REINFORCEMENT OF METALS, INTERMETALLICS AND CARBIDES

6.1 Fibre reinforced aluminium

More than 10 years ago, boron fibre reinforced aluminium was used as stiffening beams for the US Space Shuttle. At the same time, we performed a basic study on the reinforcement of aluminium. We used CVD fabricated boron fibres on a tungsten substrate with various coatings (SiC coatings and B_4C coating) as well as silicon carbide coated carbon fibres for comparison. The composites for these basic studies were prepared by a melt process. A cross section of such a composite is shown in Fig.17 (ref.25). The results of the reinforcement tested at increasing temperatures up to 600 °C are shown in Fig.18 (ref.26). One can easily recognize, that both coatings on boron fibres behave similar. The strength of the composite with alloy Al 6061 as matrix decreases considerably at temperatures above 300 °C. In a later study (ref.27,28) we developed possibilities of technical fabrication processes using boron fibre aluminium sheets as prepregs and different fabrication methods like the foil filament, the diffusion brazing or the liquid infiltration processes. It turned out, that at that time the silicon carbide coatings on the boron fibres are more reactive with the aluminium as the B_4C surfaces and therefore the fabrication process becames more difficult to control. In any case, the application of the thick, brittle boron fibres as monofilaments introduces fabrication problems. Finally we turned to carbon fibre yarns as reinforcement and we used SiC coatings on the carbon fibres and very thin surface layers of silver as wetting agent. Fig.19 (ref.29) shows the results of strength measurements on UD-composites at increasing temperatures. As can be recognized, the strength increases by a reinforcement up to 1250 MPa and decreases at temperatures above 400 °C only. One can conclude, that carbon fibre yarns are more preferable for reinforcement of aluminium than boron fibres, and one can expect that silicon carbide fibre yarns will behave similar (ref.10,29). Obviously however, Al_2O_3 fibres would be a good substitute for all other reinforcement fibres for aluminium in spite of their lower strength because of their superior chemical compatibility.

In any case, each fibre reinforcement of aluminium causes an embrittlement of the ductile metal which is in general a disadvantage for fibre reinforcement of metals.
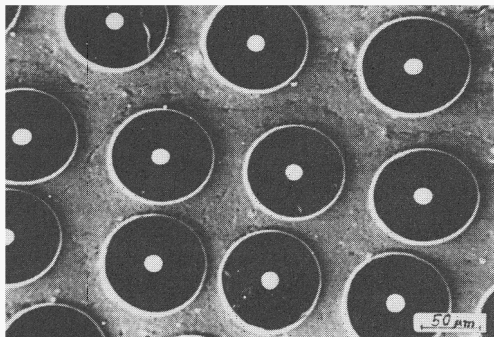

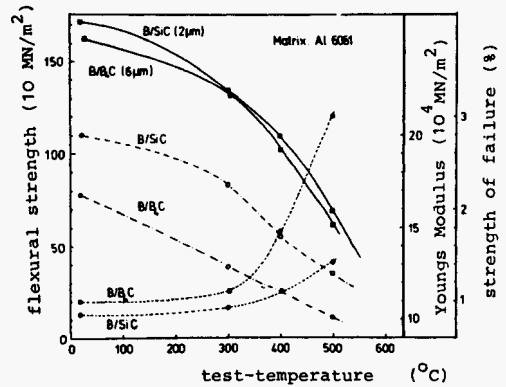Fig.17 : Aluminium reinforced by CVD B-fibres

Fig.18 : Mechanical properties of B/B_4C- and B/SiC fibre-reinforced aluminium as a function of the test-temperature
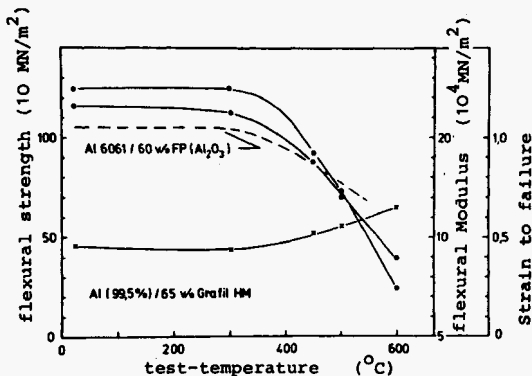

Fig.19: Mechanical properties of C-fibre reinforced aluminium as a function of the test- temperature
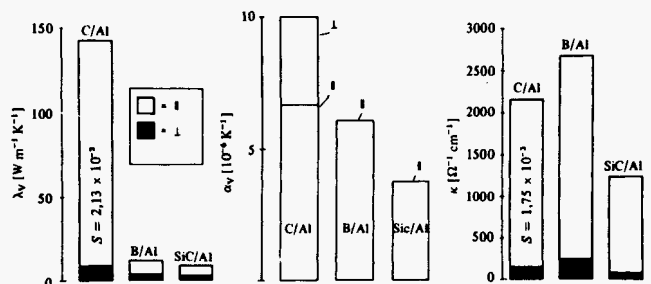

Fig.20: Thermophysical properties and electrical conductivity of fibre reinforced aluminium

The effect of reinforcement of aluminium by the various fibre types (boron, silicon carbide, carbon) on the thermophysical properties and on the electrical conductivity is shown in Fig.20 (ref.30) in dependence of the reinforcement direction of UD-composites. One can see, that fibre reinforced aluminium measured in fibre direction can not be considered simply as consisting of a group of parallel resistores.

Concerning the thermal conductivity of fibre reinforced aluminium, carbon fibres are much more advantageous than boron and silicon carbide fibres. The thermal expansion of aluminium composites is considerably reduced by the fibre reinforcement what indicates that some internal stresses have been created at room temperature during cooling from the melting processes.

6.2 Fibre reinforced intermetallics

In modern material science intermetallics such as nickel-aluminides, silicides or borides are strongly considered as a future structural material. The reinforcement by aluminium oxide fibres is promising, there do not exist any descriptions in literature so far.

The intermetallic molybdenum disilicide ($MoSi_2$) is a compound with best oxidation resistance at higher temperatures, that means nearly up to 1700 °C. Because of its brittleness, however, it has found for instance a limited technical application in heating element for oxidizing atmosphere so far.

We tried to apply a very unusual reinforcement method, namely to reinforce this extremely brittle matrix by a high ductile fibre (ref.31). We used niobium wires for reinforcement because these wires have a low reactivity with silicide and are practically chemical compatible even at highest temperatures. Figs. 21 and 22 give the results on the strength increase as obtained by various volume fractions of niobium up to 40 %. One clearly can recognize the toughening as well as the strength increase.

The explanation for this behaviour can be seen from Fig.23. In spite of the brittle fracture of the surrounding matrix, the reinforcing fibres show only a plastic deformation.
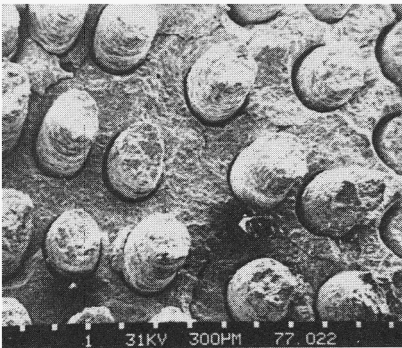

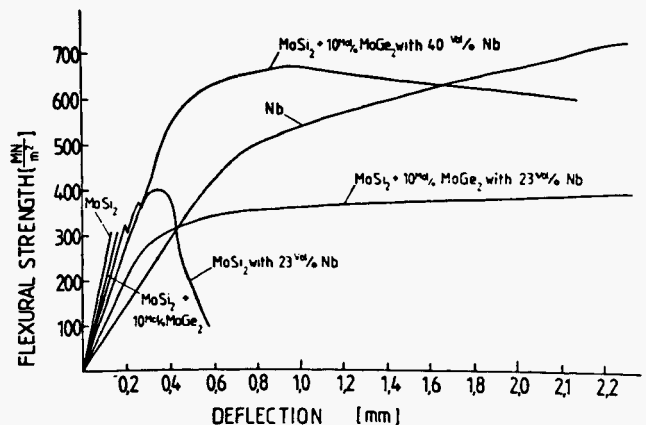Fig.21: Fracture surface of the Nb wire reinforced $MoSi_2$

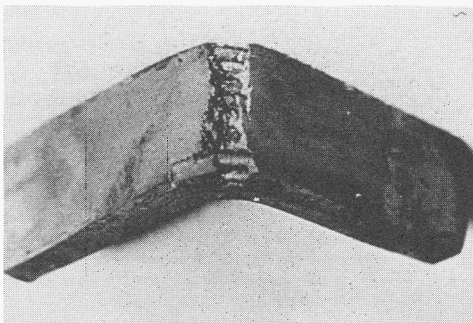Fig.22: Stress strain behaviour of composites of intermetallics

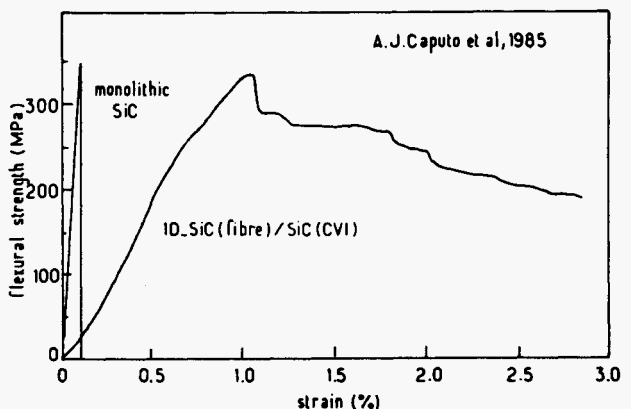Fig.23: $Nb/MoSi_2$-fracture after bending test at room temperature

Fig.24: Stress strain diagram of fibre reinforced SiC in comparison with that of monolithic SiC

This principle of reinforcement reminds to the reinforcement of concrete by steel. In this connection the replacement of steel reinforcement in prestretched concrete by glass should be mentioned. POLYSTAL [R] of BAYER exists of glass fibre bundles protected by polymer surrounding. The high strength of such thin glass fibre tows is used for reinforcement of concrete and is in practical test as load carrying material for a traffic bridge at Cologne since one year (ref.32).

Such principles of reinforcement of very brittle materials by ductile reinforcing elements but without a homogeneous distribution of the reinforcement fibres can be a new way for fabrication and application of high temperature composites.

6.3 Fibre reinforced silicon carbide

Silicon carbide and also silicon nitride are most interesting high temperature materials which are extremely resistant against oxidation at temperatures above 1000 °C, that means above the application limits of nickel based super alloys and can be used up to working temperatures of 1450 °C in air.

They can be reinforced by silicon carbide fibres or by silicon carbide whiskers but also by silicon carbide coated carbon fibres. The main problem of such composites is their fabrication as silicon carbide and silicon nitride are very difficult to sinter by powder metallurgical methods and if, than only under high pressure. Silicon carbide fibres in surrounding powder, however, do not tolerate high pressure during fabrication of composites.

The technical fabrication of non reinforced silicon carbide and nitride is performed by reaction sintering. One can consider to apply this method also to fabricate composites. Reaction sintering means in situ reaction of a carbon precursor matrix by molten or vapourized silicon or by nitrification of a metallic silicon. If transferred to fabrication of composites, the reaction sintering method is difficult to perform because SiC carbide and C-fibres are sensitive against reaction with molten silicon or against nitrification.

There is another method which can be applied to fabricate silicon carbide fibre reinforced composites, that is that of chemical vapour deposition or chemical vapour impregnation, the same method as applied in fabrication of carbon/carbon composites (see later).

Fig.24 shows from literature (ref.33) the comparison of a 1D SiC fibre / SiC matrix composite with a monolythic silicon carbide. In principle no increase of strength is achieved, but an enormeous improvement of the toughness (increase of the strain to failure).

Fig.25 shows the high temperature strength (short time test) of fibre reinforced composites compared with that of non-reinforced silicon carbide materials as published by us and supplemented by other authors (ref.34). An improvement of strength is found, but the advantage in improved toughness seems to be even more important. Fig.26 shows results of the stress intensity factor in dependence of testing temperature (ref.35).

Preparation of silicon carbide composites by vapour deposition is in any case a very costly procedure. Results of basic studies on the applicability of the reaction sintering for fabrication of composites can be seen from Fig.27. Here again, more beneficial effect is the increased toughness (strain to failure). The carbon precursor modification was the reaction parameter used to influence the final properties of the composites. This precursor forms the carbon bridges between the fibres which are siliconized during reaction sintering. One has to
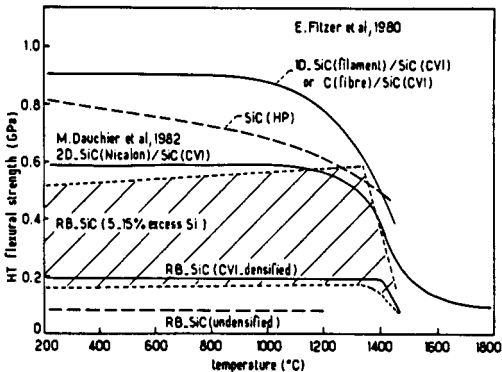

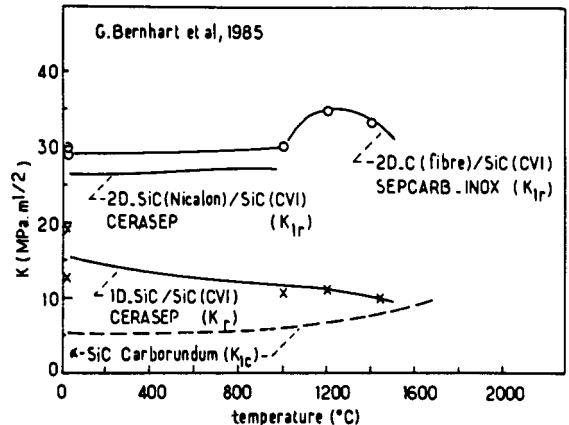Fig.25: High temperature flexural strength of SiC-based ceramics

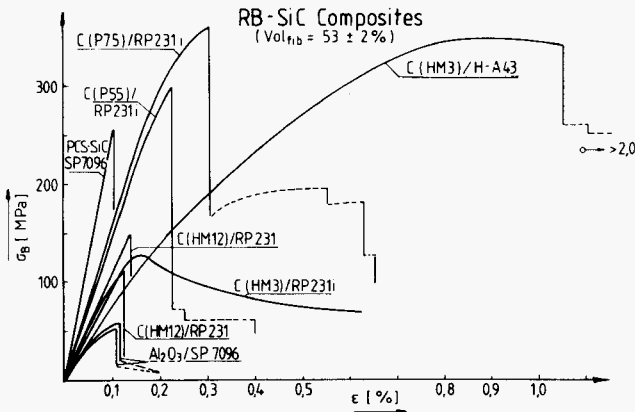Fig.26: Stress intensity factor of fibre reinforced SiC

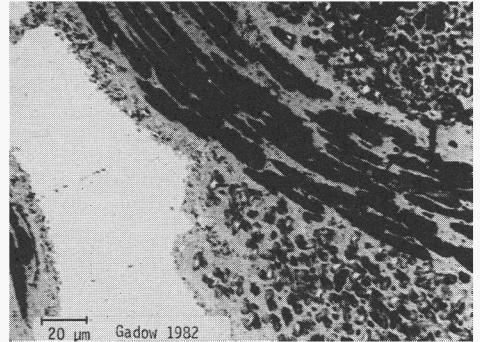Fig.27: Stress strain diagram of RB silicon
carbide composites

Fig.28: Impregnation of carbon/carbon
with silicon melt

consider that by reaction sintering (siliconizing with molten silicon) the carbon binder increases in volume. Structure and porosity of these carbon bridges to be siliconized have a decisive effect on the final mechanical properties of the silicon carbide fibres reinforced silicon carbide composite. Fig.28 gives an idea how reaction sintered fibre reinforced silicon carbide looks like. It can be expected, that the fabrication method by reaction sintering can offer an industrial way to produce economically such interesting materials, not only with continuous (endless) fibres but also for application of whiskers in reinforced silicon carbide (ref. 38).

7. CARBON FIBRES IN CARBON MATRIX—THE IDEAL COMBINATION FOR APPLICATIONS AT HIGHEST TEMPERATURES

Carbon/carbon composites or more precisely carbon fibre reinforced carbon composites are the high temperature materials par excellence. The specific strength measured at temperatures up to 3000 K is shown in Fig.29 (ref.37). Fig. 30 shows a cross section of a UD composite with 60 v% of carbon fibres combined with a carbon matrix. By high temperature heat treatment above 2500 °C a very ductile synthetic graphite matrix is performed.
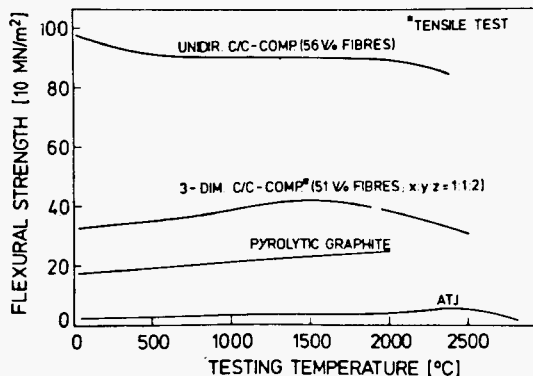

Fig.29: High temperature strength of CFRC
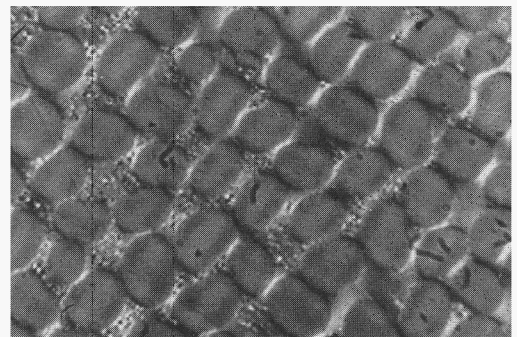pyrolytic graphite and ATJ fine
grained graphite

Fig.30: Cross section of UD reinforced
C-fibre/C-matrix composites with
60 v% C-fibres

It has been shown with SiC and other brittle composites already that two methods can be applied for fabrication of such composites, the CVD (CVI) and the liquid impregnation method. In the first one the carbon matrix is built up by gas phase deposition, in the second one by carbonization of a liquid matrix precursor and repeated impregnation, recarbonization steps. Comprehensive literature on the subject was presented recently (ref.38).

Carbon/carbon composites are reinforced in three or more directions. In such a way, a nearly isotropic reinforcement can be achieved. The absolute strength values exceed those of conventional polygranular carbon and graphite materials by the factor 10. The stress strain curvatures are characterized by a step-like fracture behaviour, as shown in Fig.31 (ref.38). Post heat treatment at highest temperatures has an distinct toughening effect.
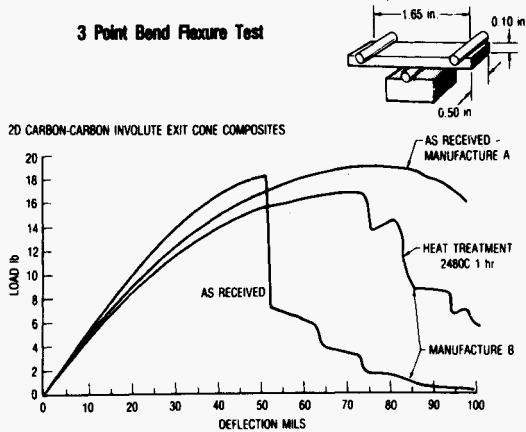
Fig.31: Fracture behaviour of C/C-composites
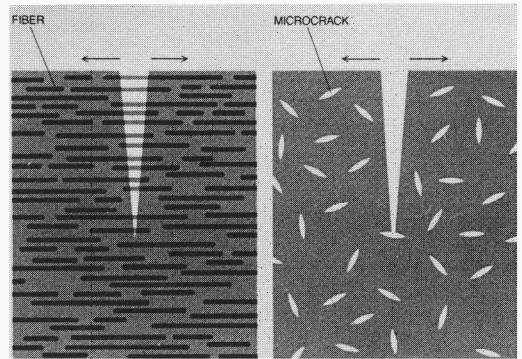measured by 3-point bend flexure test

Fig.32: Toughening effect in brittle materials
by fibres (left) and slit pores (right)

The explanation for this superior mechanical behaviour is to be seen in the presence of slit pores in the whole structure. Cracks starting from everywhere are very soon stopped or deviated by the pores, and fracture energy is consumed in such a way (see Fig.32) (ref.39).

Astonishing is also the high fatigue behaviour. After more than some millions cycles still 70 to 80 % of the original modulus and strength are conserved.

Combinations of this interesting mechanical behaviour with a very low thermal expansion and the extremely high thermal conductivity offers a material with high thermal shock resistance.

The only severe disadvantage is the sensitivity against oxidation at temperatures above 600 °C. In the temperature range up to 800 °C the oxidation rate can be reduced by inhibitors like phosphates, borates, silicates as indicated in Fig.33 (ref.40). At higher temperature only coatings offer a protection.

Silicon carbide coatings have been applied for carbon/carbon composites for the space shuttle (pack cementation and impregnation with hydrolized silicate esters) (ref.37). However, even this protection is limited in time and temperature and the efforts in numerous research centers all over the world are concentrated on development of a better protection against oxidation.

One way is impregnation with silicon carbide or oxides. It has been proved, however, that the exchange of carbon matrix by such brittle binder materials reduces the superior toughness and such composites become brittle. The challenge to develop high temperature materials with very good oxidation resistance seems to be in a transfer of the ideal internal structure of carbon/carbon composites with slit pores and fibre reinforcement (compare Fig.32) to refractory oxides, silicon carbide, silicon nitride or intermetallics.

It is hoped to have shown that no materials commercially available so far or in development can fulfill the request of most advanced design proposals of the engineer. But one can recognize from this paper that there are several ways to approach the ultimate requirements.
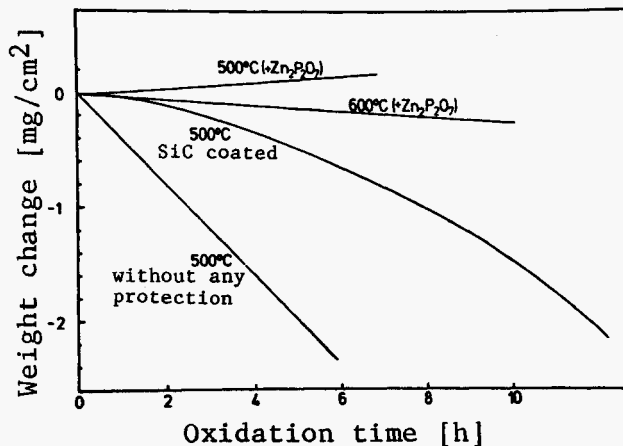

Fig. 33: Effect of inhibitors and coatings
on the isothermic oxidation of
C/C composites (50 vol. % Mod.I
C-fibres, 4 times pitch
impregnated, 1400 °C final HTT)

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