SOME FUNDAMENTAL ASPECTS
OF THE STRUCTURAL APPLICATION
OF CERAMIC COMPOSITE MATERIALS

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The Seventh Congress
of the
International Council of the
Aeronautical Sciences

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Abstract

Most of the traditional problems connected with the use of ceramics as structural materials for advanced technology, like brittleness and poor thermal shock resistance, can be solved by reinforcing ceramic materials by strong refractory fibres. Ceramic composites can thus be designed and made that show strong improvements in the properties and can be considered for high temperature structural applications.

Use of the experience from the fields of plastic and metallic composites can be made to forecast the mechanical properties of ceramic composites if elastic behaviour for both matrix and fibres is assumed.

At high temperatures reaction between fibre and matrix can be a limiting factor for many types of composites. Tests performed on ceramic composites of possible advanced application, however, seem to show that the temperature range can be appreciably increased with respect to the metals and alloys used for high temperature.

1 - Introduction

The application of ceramics as structural materials is of great interest for many scientific laboratories and industries that traditionally are concerned with advanced technologies and materials and extensive studies are being carried on in order to overcome some of the limitations presented by metals and their alloys employed at high and very high temperatures.

The basic properties of ceramics, however, including carbides, nitrides, oxides and other refractory compounds, have not yet been completely eliminated, because of the very nature of a ceramic material whose cristalline structure does not permit the existence or the movement of dislocations under any applied stress. This can be considered as the main source of the well known mechanical brittleness and poor thermal strength of ceramics.

The only promising mean to alter this situation seems to be the use of a method which has recently given demonstrations of its large possibilities, i.e. by reinforcing a ceramic matrix by ceramic fibrous elements of high mechanical properties.

The ceramic matrix-fibre composites show peculiar properties, that are now summarized.

It is to be noticed that high temperature resistant fibres of high mechanical properties are now fabricated on large scale, such as carbon or SiC fibres. These are characterized by a tensile strength and Young's modulus equal or even larger than the analogous quantities of the best quality steels at room temperature, and these values remain unaltered up to temperatures as high as 1500°C or more.

It has been definitely shown that the Young's modulus and the tensile strength of a fibrous composite can be calculated with a good approximation from the mixtures rule, in the fibre direction:

$$E_c = E_m (1 - V_f) + E_f V_f \qquad (1)$$

$$\sigma_c = \sigma_m (1 - V_f) + \sigma_f V_f \qquad (2)$$

where E is the Young's modulus, σ the tensile strength, V_f the reinforcement volume fraction, and the subscripts c, m and f refer to composite, matrix and fibre respectively. It is easily seen, from (1) and (2), that the composite properties depend upon the value of the volume fraction of the reinforcing filaments and that a substantial increase with respect to the matrix properties can be obtained up to a certain fraction of the fibres properties. These advantages are more evident at high temperature where the composite properties should be compared with those of other traditional materials.

The other principal effect due to the

presence of the fibres in a ceramic matrix is related to the toughness of the material. Although both matrix and fibres are usually brittle materials the composite can show different behaviours depending upon the type of bonding that the fabrication method has created at the fibre-matrix interface.

The type of bonding can be measured by the shear strength of the interface. If a partially weak bonding exists a beneficial effect upon the toughness arises without a decrease of the longitudinal properties. During static fracture the work necessary to propagate the crack all the way through the piece can be in fact increased noticeably for the presence of the fibres acting like obstacles to the transverse propagation and deviating the crack in the longitudinal direction or around the fibres, far from the more stressed region. In this way artificial ductility is created.

2 - Strength and elastic properties

The distribution of fibres within the matrix largely influences the physical properties of the composite depending upon the relation between type and direction of the applied stress and principal direction of the fibres. This phenomenon produces the known characteristic of anisotropy of a fibrous composite, whose mechanical and elastic properties assume the highest values in the direction of the fibre axis for an array of parallel fibres.

The large amount of theoretical and experimental research that has been made in the last few years on the elastic properties of fibrous composites hold also for ceramic composites. Due to the large interest shown by the case of parallel fibres this situation has been more deeply studied as far as elastic properties are concerned.

It is known that a composite with unidirectional fibres can be considered as an anisotropic macroscopically homogeneous material whose properties are entirely defined by 5 indipendent constants[1] which are related from the following relationships:

$$E_z = C_{33} - \frac{2C_{13}^2}{C_{11} + C_{12}}$$

$$G = G_{xz} = G_{yz} = C_{44}$$

$$\nu = \nu_{xz} = \nu_{yz} = \frac{1}{2}\left(\frac{C_{33} - E_z}{K_{xy}}\right)^{\frac{1}{2}} = \frac{C_{13}}{C_{11} + C_{12}}$$

$$K_{xy} = \frac{1}{2}(C_{11} + C_{12})$$

$$G_{xy} = \frac{E_x}{2(1 + \nu_{xy})} = \frac{1}{2}(C_{11} - C_{12})$$

$$E_x = E_y = \frac{4G_{xy} K_{xy}}{K_{xy} + \psi G_{xy}}$$

$$\nu_{xy} = \frac{K_{xy} - \psi G_{xy}}{K_{xy} + \psi G_{xy}}$$

$$\psi = 1 + \frac{4K_{xy} \nu^2}{E_z}$$

where z is the fibre direction, x and y two perpendicular directions in the cross-section, the coefficients C_{ij} are defined by the matrix equation:

$$\begin{bmatrix} \sigma_x \\ \sigma_y \\ \sigma_z \\ \tau_{yz} \\ \tau_{xz} \\ \tau_{xy} \end{bmatrix} = \begin{bmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{13} & 0 & 0 & 0 \\ C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{66} \end{bmatrix} \cdot \begin{bmatrix} \varepsilon_x \\ \varepsilon_y \\ \varepsilon_z \\ \gamma_{yz} \\ \gamma_{xz} \\ \gamma_{xy} \end{bmatrix}$$

E is the Young's modulus, G the shear modulus and K_{xy} is the plane strain bulk modulus for loading in the plane x-y without contraction along z.

Various treatments, most of them based on variational methods, have solved the equilibrium equations for the elastic moduli of a composite, and all of them yield an upper or a lower bound on each modulus and not the actual value, for it is impossible to find a treatable model which represents the more general case. This is due to the

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difficulty to specify exactly the volume of the composite representative of the macroscopic behaviour of the material and to apply on it a state of stress and strain which is compatible and equilibrated.

The model shown in Fig.1 is one that can be thought of as the representative volume and by working on this model some of the elastic moduli are easily calculated.
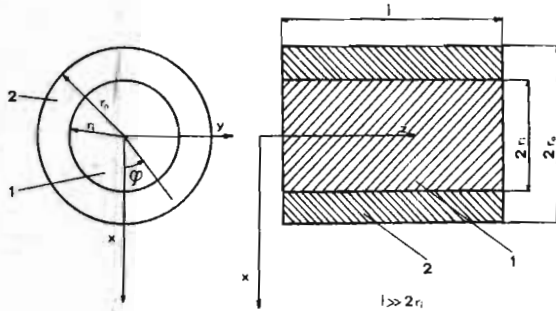

Fig.1-Composite cylinder as a representative volume element.

Expressions for E_z, ν_{xz} and K_{xy} are actually obtained in a straightforward manner considering the relative displacements of a point of the interface when supposed to belong to the fibre and to the matrix[2]. If fibre and matrix are not free to deform indipendently the value of E_z given by the mixtures rule, Eq.(1), is increased to:

$$E_z = E_f V_f + E_m(1-V_f) + 2 V_f \frac{p_i}{e}(\nu_m - \nu_f) \quad (3)$$

where ν is the Poisson's ratio, e is the longitudinal elongation of the composite and p_i the pressure that arises at the interface owing to the different lateral contraction of fibre and matrix. The ratio p_i/e can be easily found to be:

$$\frac{p_i}{e} = \frac{2(1 - V_f)(\nu_m - \nu_f)}{\dfrac{1-V_f}{K_{pf}} + \dfrac{V_f}{K_{pm}} + \dfrac{1}{G_m}} \quad (4)$$

Thus we have, from (3) and (4):

$$E_z = E_f V_f + E_m(1-V_f) + \frac{4 V_f(1-V_f)(\nu_m - \nu_f)^2}{\dfrac{1-V_f}{K_{pf}} + \dfrac{V_f}{K_{pm}} + \dfrac{1}{G_m}} \quad (5)$$

Similarly, the value of the longitudinal Poisson's ratio can be found and is given by:

$$\nu = \nu_{xz} = \nu_{yz} = \nu_m + \left(\frac{V_f}{K_{pm}} + \frac{V_f}{G_m}\right) \frac{\nu_f - \nu_m}{\dfrac{1-V_f}{K_{pf}} + \dfrac{V_f}{K_{pm}} + \dfrac{1}{G_m}} \quad (6)$$
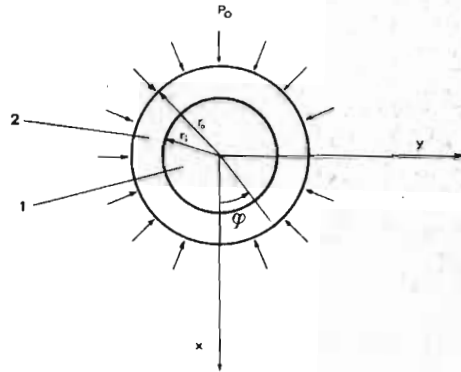

Fig.2-Composite cylinder under a uniform lateral pressure p_o.

If we suppose now that the solid is subjected to a uniform lateral pressure p_o as in Fig.2, the value of the plane strain bulk modulus can be found from the relationship:

$$K_{xy} = - \frac{p_o r_o}{2 U_o} \quad (7)$$

where r_o and U_o are radius and displacement of a point on the external surface of the cylinder. It is easily derived that K_{xy} is given by:

$$\frac{1}{K_{xy}} = \frac{V_f}{(1-V_f)} \left[\frac{1}{K_{pm} V_f} + \frac{1}{G_m} - \frac{\left(\dfrac{1}{K_{pm}} + \dfrac{1}{G_m}\right)^2}{\dfrac{1-V_f}{K_{pf}} + \dfrac{V_f}{K_{pm}} + \dfrac{1}{G_m}} \right] \quad (8)$$

The expressions shown of E_z, ν and K_{xy} coincide with the upper bound on these moduli found by other workers by more complex treatments[3].

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The value of the transverse properties is of high importance in the design of structural elements made of reinforced materials. Particularly in the case of ceramic composites when the longitudinal load has been accounted for, transverse stresses and strains can be dangerous because they are to be withstood mainly by the matrix that is by a brittle material and unespected failure of the structure may be initiated by small transverse strains.
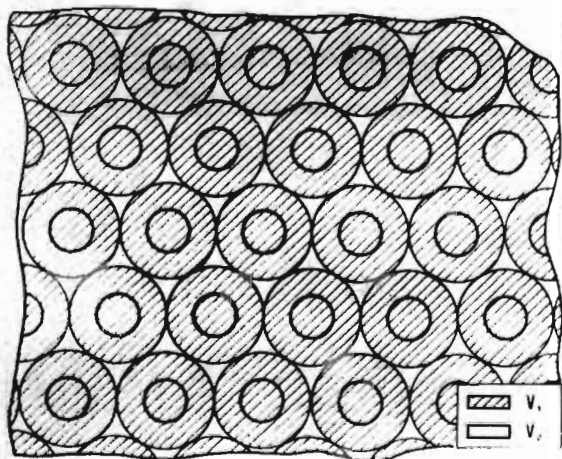
Fig.3—Subdivision of a composite cross-section in two parts V_1 and V_2.

At the contrary of what has been shown fro the longitudinal properties there is not a simple treatment for transverse elastic properties, like E_x. A recent model[4] has considered the entire composite cross-section made of a part V_1 and a part V_2 as shown in Fig.3 where V_1 consists of all the largest non-overlapping surfaces coaxial to the fibres. Applying along the boundaries between V_1 and V_2 an equilibrated state of stress σ_x it can be obtained by minimum energy principles:

$$E_x \geqslant \frac{1}{\dfrac{\xi_x^*}{\sigma_x} 0.906 + \dfrac{0.094}{E_m}} \qquad (9)$$

where E_m is the matrix Young's modulus and ξ_x^* the average strain in the x direction of the part V_1. The value of (9), that is a lower bound on E_x, has been plotted and Fig.4 shows a normalized diagram of $\overline{E_x}/E_m$ as a function of E_f/E_m where E_f is the

fibre Young's modulus, for a couple of Poisson's ratios equal to 0.2 and 0.35, and for fibre volume fractions varying between 0.05 and 0.8.
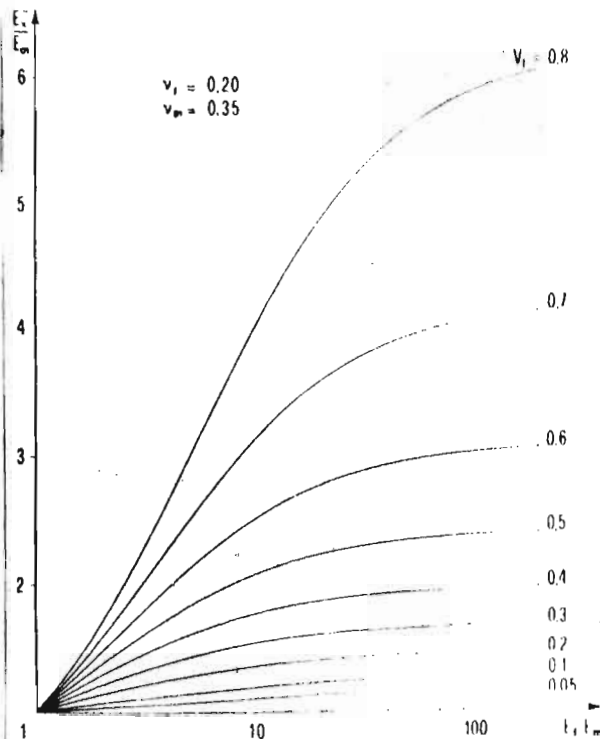
Fig.4—Normalized diagram of $\overline{E_x}/E_m$ vs. E_f/E_m.

The elastic properties of a composite material depend, as has been indicated, by the elastic properties of the components while interesting synergistic effects can be obtained for other properties like the type of fracture under a static or dynamic load, that is for the toughness of the material.

The type of fracture of a composite is strongly affected by the type of bonding at the interface. This is of extreme importance in the case of short discontinuous fibres as far as the trasmission of stress from the matrix to the fibres is concerned but much less important in the case of continuous fibres where the type of bonding can nevertheless strongly affect the value of the work of fracture, which is a measure of the toughness.

It is well known that the lack of any plasticity in ceramics is due to the difficult existence and movement of dislocations that are rarely present in covalent or ionic materials, and this is the source of the brittle fracture which always occurrs if the
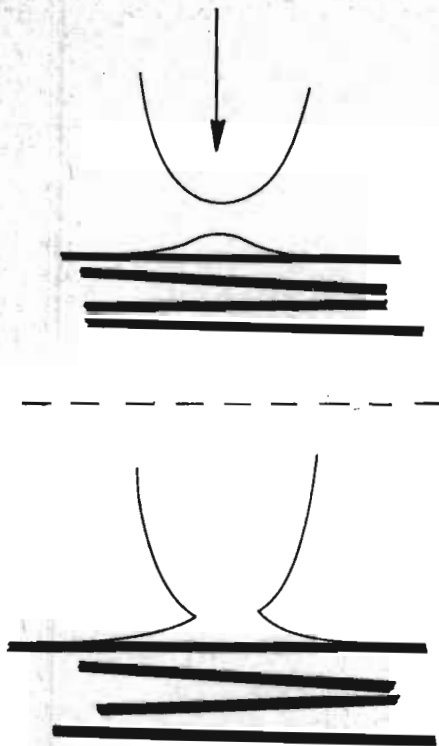
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Fig.5-Crack propagation deviated at the
fibre-matrix interface.

applied stress exceeds the elastic limit.

The presence of fibres transverse to
the microcrack propagation can artificially
eliminate the brittlness by deviating the
fracture toward regions far from the ini-
tial one. In Fig.5 is shown schematically
what can happen at the tip of a crack
advancing on a plane which contains the
fibres. It has been shown [5] that ahead
of a crack a complex state of stress is
present with tensile components at the
crack front which tends to detach the ma-
trix from the fibres. The crack propagation,
by this model, leads to the creation of
new surfaces, the previous interfaces, and
work must be spent in order to continue the
fracture.

The same model is of course valid for a
crack in a plane normal to the fibres. It
is clear that the possibility of the pre-
sence of the mechanism depends upon the
type of bonding at the interface because
for a given state of stress a lower
strength at the interface favours delami-
nation of the fibres. A bonding of chemical
nature, for instance, can make the interface
to resist very well to shear and tensile
actions from the matrix and the deviation
of the crack is made more difficult. The

type of fracture could in this case be brittle
as well without any effect due to the presen-
ce of the fibres. A type of bonding of a
simply physical nature, instead without al-
tering the longitudinal properties represents
a relatively weak bond which can be a proper
barrier to the advancement of the crack.

The described mechanism suggests that
further care must be taken during the life
of ceramic composites at high temperature,
because during an extended use a slow
reaction can occurr between fibres and
matrix that modifies the bonding from a
physical to a chemical nature, altering the
toughness characteristics of the material
during service.

3 - Ceramic composites -

Neglecting composites made by dispersed
particles there exists already a large
amount of work done on the field of fibrous
ceramic composites. A first subdvision
among them can be made with regard to the
type of fibres used and that can be either
metallic or ceramic.

Many initial composites made use of
metallic fibres and most of the work on this
field was made by Baskin and coworkers[6,7]
who studied a thoria matrix reinforced by
molybdenum wires, and by Tinklepaugh and
coworkers[8] who studied various ceramic
composites and in particular alumina rein-
forced by molybdenum and tungsten fibres.

When dealing with metal fibres in a ce-
ramic matrix one of the inconvenience to
overcome is connected with the thermal ex-
pansion behaviour of the two constituents
for the coefficient of metals are usually
smaller than those of ceramics.

This results in a different contraction
during cooling after consolidation of the
matrix if a hot stage is necessary during
fabrication.

All the initial composites presented
this drawback and cracking was evident in
the ceramic matrix reinforced by metal
fibres.

The properties of the composite were
lower than those of the matrix alone as far
as Young's modulus and tensile strength are
concerned although definite increases of
thermal shock resistance were observed,
particularly for multiple shock tests. The
higher shrinkage of the matrix produced
small interfibre crackings that were not
allowed to propagate in the whole specimen
being locked up by the fibres. These cracks,

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however, produced notch effects that lowered the mechanical strength of the material.

In the case of tungsten fibres reinforced alumina where matrix and fibres had the same expansion coefficient no cracking occurred during fabrication and the composites showed improved strength with respect to the matrix only for low reinforcement volume fraction. When the number of fibres was increased more than about 20% it was difficult to obtain, by hot pressing, uniform distribution of the reinforcing elements in the composite, and the strength fell for the presence of weak zones. The best conditions were achieved with approximately 20% volume of tungsten fibres that produced a strength of more than 21 Kp/mm^2 (30,000 psi), compared with 3.5 Kp/mm^2 (5,000 psi) of the matrix alone. Fig.6 shows the experimental results and the large band of scattering obtained for various percent of tungsten fibres in alumina matrix.
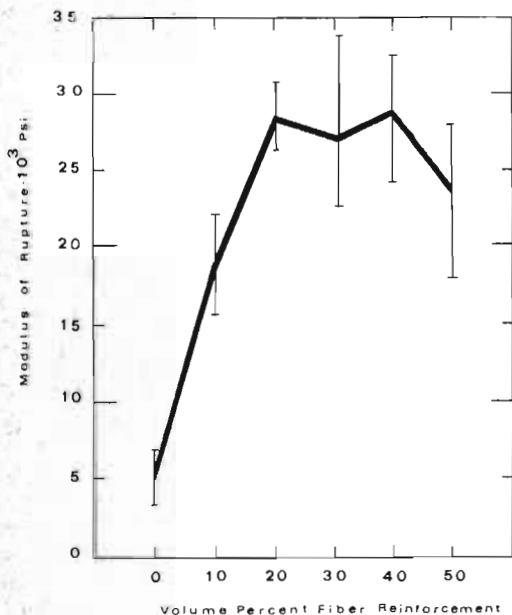

Fig.6-Experimental results for alumina reinforced with tungsten fibres (8).

Also in those cases where actual reinforcement is noticed duration problems at high temperature arise in a metal fibres composite because of the reactivity of the metal that leads to a fast degradation and fall of the fibre properties.

The main solution to this problem can be at present searched in the field of ceramic composites where both matrix and fibres are of ceramic nature. Table 1 shows the properties of some materials which can be actually used as reinforcement.

TABLE 1

fibre	E Kp/mm^2	σ Kp/mm^2	ν	γ g/cm^3
Be	31500	130	0.05	1.8
Steel	21000	250	0.30	7.9
W	36000	320	0.28	19.3
Mo	36000	230	0.34	10.3
B(W)	42000	280	0.20	2.3
SiO$_2$	7000	600	0.20	2.5
C	38500	280	0.20	1.9

Particularly interesting are the data for boron and carbon fibres. To these silicon carbide fibres must be added, which are since recently produced on a small scale with properties similar to those of C fibres.

As far as B is concerned it seems that the use is limited to composites used at low or medium temperature, like of a plastic and aluminium matrices and a number of industrial applications are now at a stage of advanced design, for wing panels, propellers or helicopter blades. Higher temperatures present reaction problems and loss of strength.

Carbon fibres have their mechanical characteristics unchanged up to temperature as high as 1500°C as long as they are protected from oxidation which is highly active over about 700°C. This means that by embedding a large number of fibres in a ceramic matrix simply to protect them from the corrosive atmosphere it is possible to obtain a material whose mechanical properties can be very high at a very high temperature.

A number of attempts have been made by putting the fibres in various ceramic matrices. Glass-carbon composites[9] have shown interesting properties of toughness and thermal shock resistance, while some other attempts to incorporate carbon fibres in different matrices have proven to be practically inefficient[10].

We have recently been able to incorporate C fibres in a silica matrix[11] and the composite showed interesting values of tensile strength and toughness. As has been said, the latter property can be affected by controlling the bonding at the fibre-matrix interface and by the fabrication method used to produce silica-carbon composites the type of interface can be partially controlled, thus producing specimens of different
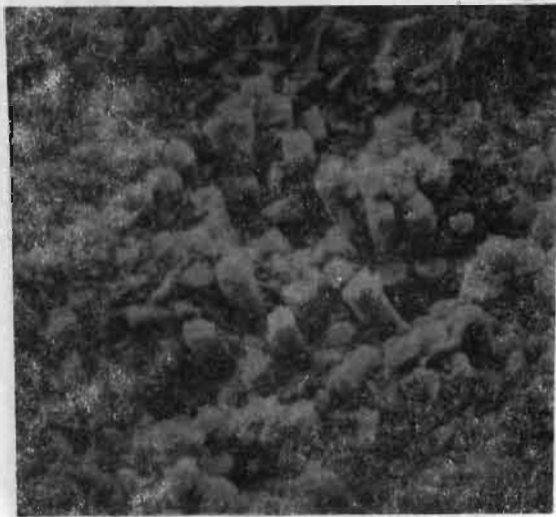
Fig.7-Electron scanning micrograph of the surface of fracture of a strongly bonded SiO_2 - C composite. X 500.

Fig.8-Electron scanning micrograph of the surface of fracture of a weakly bonded SiO_2 - C composite. X 1000.

toughness. Figg.7 and 8 show the appearence of the fractured surface of the two types of specimens of different fibre-matrix bonding.

Typical load deflection curve in bending of a tough specimen is shown in Fig.9. The values of the modulus of rupture and of the Young's modulus for that specimen were of 32.7 and 9,900 Kp/mm^2 (41,000 and 14×10^6psi) and the toughness number, measured as the work of fracture, was of 1.1×10^7 erg/cm^2.
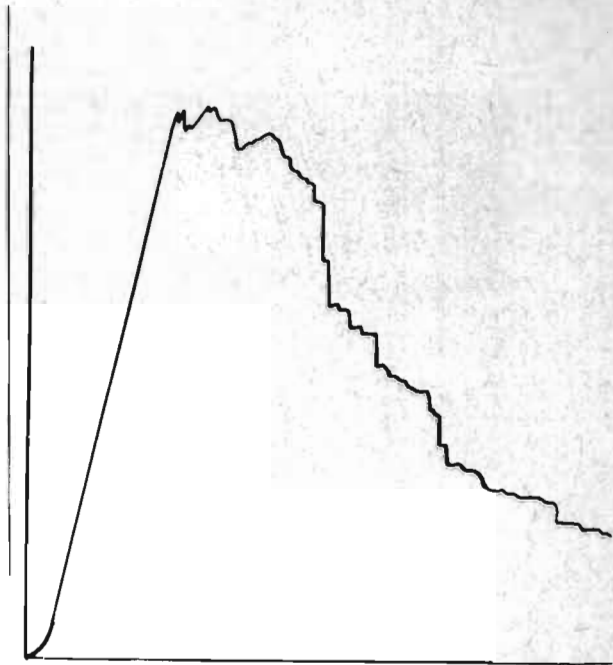
More recent results[12] show that

Fig.9-Load-deflection curve of a tough SiO_2 - C composite in bending (11).

silica-carbon composites can be obtained with a narrow band of scattering of properties and values of the modulus of rupture of about 35 ± 3 Kp/mm^2 (50,000 $\pm$ 5,000 psi).

With this value of the strength is then highly impressive the value of the toughness obtained which should be compared with the work of fracture of other usual materials, reported in Table 2 [13].

TABLE 2

Material	Work of fracture erg/cm^2
Dural	$1-4 \times 10^8$
Copper	5×10^7
Key steel	5×10^7
Brass	3×10^7
Teak wood	6×10^6
Cast iron	4×10^6
Deal wood	2×10^6
Cellulose	2×10^6
Polystyrene	10^6
Reactor graphite	10^5
Firebrick	$2-7 \times 10^4$
Alumina	4×10^4
Beryllia	2×10^4
Whiteware	2×10^4
Magnesia	10^4

Fig.10 shows the surface of a bent specimen where the fracture line has been deviated along the C fibres with an

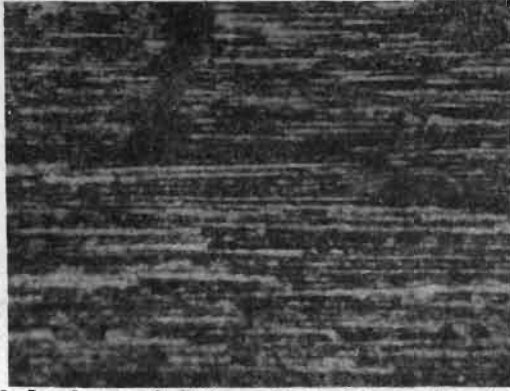Fig.10—Surface of SiO_2 – C specimen showing deviation of the crack path. X 100.

Fig.11—Regular distribution of C fibres in a commercial refractory paste. X 100.

increment of the work of fracture.

Unfortunately, the use of carbon fibres is made difficult by the unconfortable dimensions of the fibres that are supplied in the form of tows of about 10,000 fibres each 7μ in diameter.

The manipulation of such array is rather unconfortable and is difficult to design practical methods to uniformly incorporate the fibres in a proper ceramic matrix. Methods similar to a slip-casting technique are now being under test, and some initial result is shown in Fig.11 that shows an area of fairly regular dispersion of C fibres in a commercial refractory paste and in Fig.12 that shows a region rich of matrix within two zones rich of fibres. As can be seen from the figures the main difficulties are to achieve a large value of V_f and to avoid weak zones depleted of fibres.

The presence of weak zones of this type lowers considerably the strength of the composite, although thermal shock resistance is increased anyhow, due to the presence of the fibres that transfer heat along the specimen levelling off its temperature and avoiding thermal cracking.

4 – Fibre-matrix reactions

The use of fibres as C or SiC allows the design of new materials that can withstand high temperatures. But at these temperatures the same phenomenon occurring to metal fibres at lower temperatures can initiate and chemical reactions can occurr at the fibre-matrix interface. Besides a protection from the oxidizing atmosphere it is also necessary to prevent possible reactions
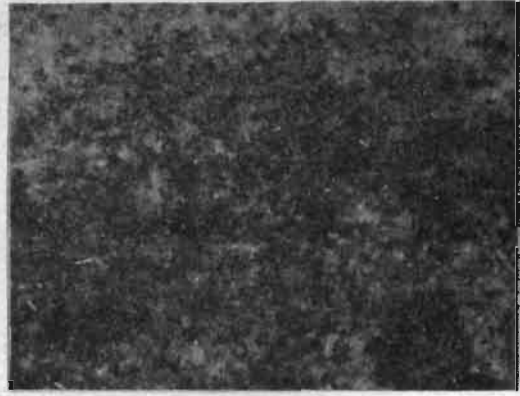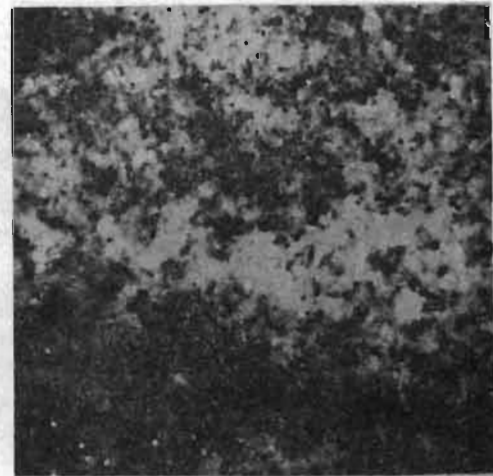

Fig.12—Common distribution of fibre depleted regions in a composite of C fibres in a commercial refractory paste.X100

between fibres and matrix. This in fact can be a limiting factor also for the use of ceramic fibres, although it should be more critical for metal fibres.

A detailed analysis of the reaction occurring in the SiO_2 – C composite has been made[14], studying the production of SiC at the interface. It is interesting to note that one of the results can perhaps be used to prevent oxidation up to a certain temperature. The diagram of Fig.13 shows some of the reaction curves indicating the percentage of SiO_2 transformed to SiC as a function of time at temperatures between 1350°C and 1650°C. It can be seen that at the higher temperatures the reaction proceeds quite rapidly while at 1350°C the
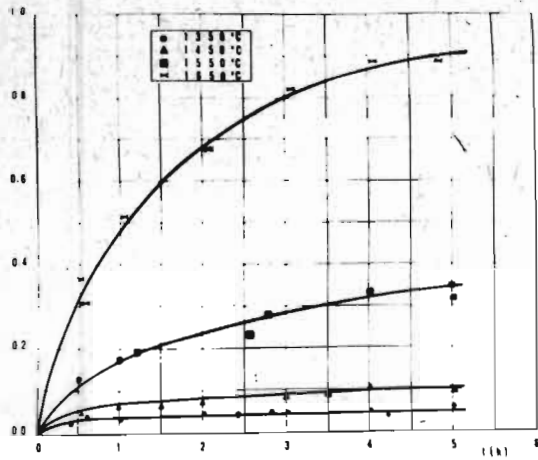
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Fig.13-Percentage of SiO_2 transformed in SiC during high temperature reaction vs. time of reaction (14).
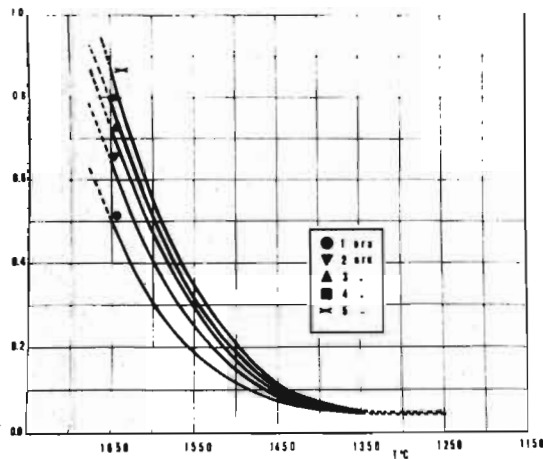

Fig.14-Percentage of SiO_2 transformed in SiC during high temperature reaction vs. temperature of reaction (14).

reaction curve presents a low slope after an initially fast stage.

This behaviour is verified from the curves of Fig.14 which shows the percentage of SiO_2 transformed to SiC as a function of temperature.

It can be seen that even after prolonged times the amount of reaction occurred at temperatures lower than about 1250°C seems to be stabilized. This phenomenon can be explained by envisaging two different reaction mechanisms active at low or high temperature respectively such that at a temperature of about 1200°C a thin layer of SiC is formed around the fibres preventing temporarily further advance of the reaction.

The initial stage of corrosion could be

exploited by permitting the formation of the layer at a temperature of about 1300°C in an inert atmosphere such that the fibres are then protected during the use in a oxidizing atmosphere, at a lower temperature that still is much higher than the temperature at which fibre oxidation becomes normally important.

5 - Conclusions

The actual application of ceramic fibrous composites for structural elements is now closer because of the interesting results shown by many exapmles of this type of materials.

The principal advantages can be summarized as essentially due to the possibilities of presenting higher mechanical properties at high temperatures with a lower density with respect to the traditional materials so far used for high temperature applications and much larger mechanical and thermal strength with respect to ceramics.

The structural anisotropy of these materials can be advantageously exploited in those cases when mainly unidirectional or plane stresses are present, as long as care is taken of any other stress or strain in a direction other than that of the fibres.

The use of ceramic fibres of recent production has permitted to obtain already very interesting composites. Their use at high temperature, however, can be still limited by reactions between fibres and matrix. Preliminary treatments can in some case be designed to protect the fibres from corrosion. This type of operation can be of difficult application when dealing with very small fibres likewise the technological problem of the incorporation and uniform distribution of a large amount of small fibres in a full dense ceramic matrix.

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