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THE PROSPECTS FOR COMPOSITES BASED ON BORON FIBERS

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Translation of "Prospectives sur les composites à base de fibres de boron", L'Aeronautique et L'Astronautique, No. 65, 1977, pp. 25-36.

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15. Abstract

The fabrication of boron filaments and the production of composite materials consisting of boron filaments and organic or metallic matrices are discussed. Problems involving the use of tungsten substrates in the filament fabrication process, the protection of boron fibers with diffusion barrier claddings, and the application of alloy additives in the matrix to lessen the effects of diffusion are considered. Data on the kinetics of the boron fiber/matrix interaction at high temperatures, and the influence of the fiber/matrix interaction on the mechanical properties of the composite are presented.

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THE PROSPECTS FOR COMPOSITES BASED ON BORON FIBERS

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Boron fibers - or filaments - are recent materials since $\underline{/25}$* their discovery dates to the work of C.P.TALLEY et al. in 1959 (1). Their advantage as reinforcement materials in composite materials for use in aeronautics and aerospace lies in a number of remarkable physico-chemical and mechanical properties and in their very small volumetric mass (2.6 g. cm^3).

Boron fibers are filamentary materials (φ =100 co 140μ) obtained by chemical deposits in a gaseous state from a mixture (BCl_3-H_2) on a substrate which generally consists of a 12 to 13μ diameter tungsten wire (fig. 1). They are made of boron in its amorphous form (vitreous), having the characteristic appearance of a "corn cob" (fig. 2). These are fragile materials which may break during elastic deformation; this is caused by the presence of flaws introduced into the material during its manufacture. Table 1 indicates some of the properties of boron fibers.

The fragile nature of boron fibers and their very small diameter implies that these fibers are used within an organic or metallic matrix whose function is to transfer the applied load to the fibers, to keep them aligned and uniformly distributed, and lastly to protect them from harmful effects of the atmosphere.

The development of composite materials based on boron fibers is influenced by two kinds of factors:

1) the current cost of boron fibers which is very high compared with that of other fibers having good mechanical characteristics (glass, Kevlar 49, graphite), and which is related to

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* Numbers in the margin indicate pagination in the foreign text.

the method of manufacture and how tight the market for this kind of product is. This factor tends to limit the use of boron fibers in composites.

2) the mechanical properties of composites manufactured from boron, which are, in certain cases, superior to those obtained with other reinforcing elements (especially for boron-epoxy composites as far as compressive strength, rigidity, and resistance to fatigue are concerned). On the contrary, this factor is an incentive to develop the use of boron in association with other less effective fibers - but also less costly - within hybrid composites (Table 1).

TABLE I - MECHANICAL CHARACTERISTICS OF BORON FILAMENTS AS COMPARED WITH THOSE OF OTHER FILAMENTARY REINFORCING SUBSTANCES AND THOSE OF CLASSICAL MATERIALS (ACCORDING TO REF. 7).

1 Nature	2 Densité d	3 Résistance traction (hb) R	4 Modules d'élasticité (hb) E	5 Résistance spécifique R/d	6 Module spécifique E/d
7. Bore ⌀ 100 μ	2,62	280-350	40.000	110-130	15.000
Bore ⌀ 140 μ	2,55	350-420	40.000	130-160	15.700
Graphil HT	1,80	210-280	23.000-28.000	117-155	13.000à15.500
Graphil HM	1,95	180-240	35.000-41.000	100-123	18.000à21.000
PRD - 49 III	1,4	250	13.000	180	9.300
8 Verre E	2,55	175-275	7.400	98-140	2.900
Duralumin	2,8	45	7.500	6	2.700
9 Acier (fil)	7,8	180-290	21.000	20-40	2.700

Key: 1. Kind, 2. Density, 3. Tensile strength, 4. Modulus of elasticity, 5. Specific resistance, 6. Specific modulus, 7. Boron, 8. Glass, 9. Steel (wire)

The fact that the recent projects in American aeronautics have used simple or hybrid boron-epoxy composites (empennages, longerons, wing flaps and wing boxes, etc...) leads one to believe that these materials will become greatly developed in the near future.

When boron fibers are protected by a diffusion barrier of B_4C or SiC (an easy operation considering their method of manufacture, see fig.1) they have a good chemical compatibility with light metals (magnesium, aluminum, titanium, and their alloys)

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at a medium temperature (approximately 300 to 600°C). Moreover, they have a high degree of wetability by liquid metals having low melting points (especially aluminum).

Thus, it is reasonable to believe that a second generation /26 of composites, having metallic matrices, could eventually be developed industrially after the first generation of composites having organic matrices. Due to their nature, the metallic matrix composites would be reserved for high temperature applications (T 200°C) and each time that a property related to the metallic state could be beneficial (electrical conductivity, transverse mechanical properties, resistance to corrosion or aging, etc.)
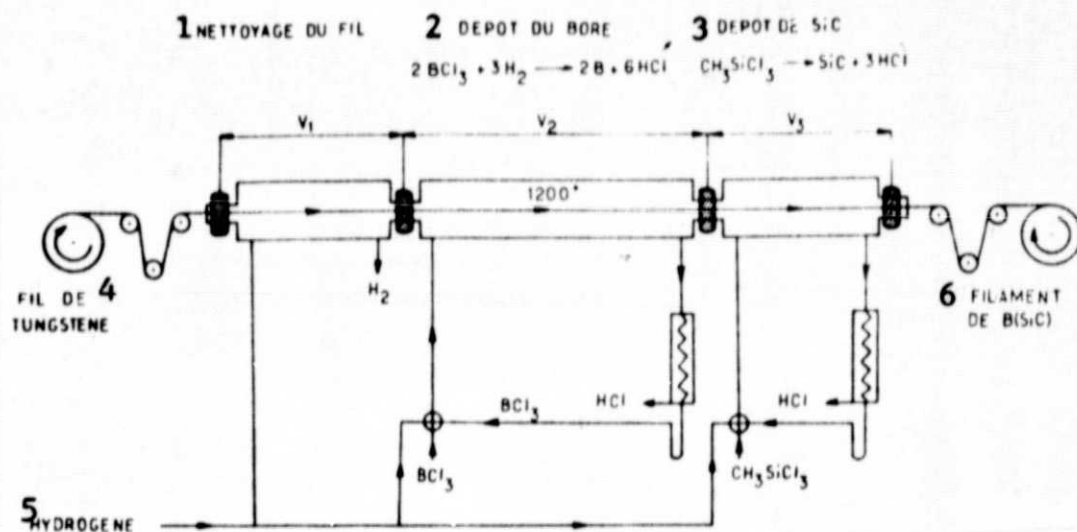

Fig. 1.- Principle of the manufacture of a boron fiber coated with a diffusion barrier (SiC).
Key: 1. Cleaning the wire, 2. Boron deposition, 3. SiC deposition, 4. Tungsten wire, 5. Hydrogen, 6. B(SiC)filament

In this report, the following points will be discussed:

-- the possible development of manufacturing conditions for boron fibers

-- composites with simple or hybrid organic matrices,

-- fiber/matrix chemical compatibility in metal matrix composites, and stability in temperature.

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Yet, it is evident that there is good reason to add a study of the development of the technology of these still very new materials. This will be undertaken in specialized reports.

Possible Development of Manufacturing Conditions of Boron Fibers

As we have seen, boron fibers are currently prepared by the chemical deposition, in a gaseous state, of boron on a very fine tungsten wire heated to 1150 to 1200°C (fig. 1). This preparation method is costly insofar as:

- it involves a delicate operation to be conducted at the industrial level,

- the operation of boron deposition, from a gaseous state of $B Cl_3$-H_2, is slow at the temperatures which are compatible with the formation of the amorphous variety (above 1200°C, boron is deposited in a crystallized form which is less mechanically desirable),

- the yield from each conversion phase of $B Cl_3/B$ is small, thus requiring a complex treatment and recycling of the reagents,

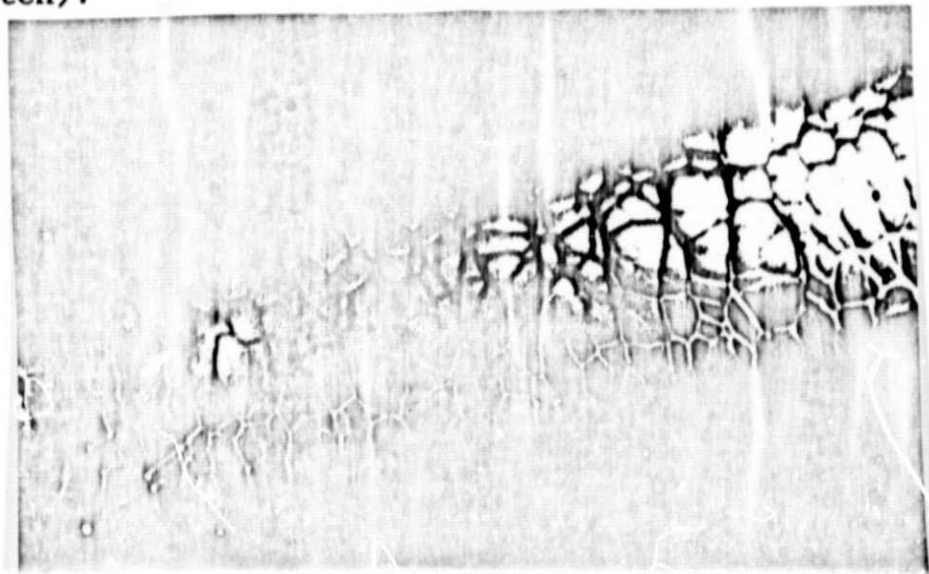- the starting materials are expensive (especially $B Cl_3$ /27 and tungsten).

Fig. 2. - Morphology of the surface of a boron fiber
(X 760)

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Also we are seeking to improve the situation by decreasing the cost price of the fiber. Besides technological modifications, whose importance cannot be minimized, the efforts of research and development concern - and will concern in the years to come - a fundamental plan and the optimal nature of the substrate to be used.

The conditions which the wire substrate must meet are known: the material must be refractory, retain good mechanical properties at 1200°C, and, at this temperature, be compatible with boron and the constituents of the gaseous phase. Moreover, it must be light and as inexpensive as possible.

A systematic study is underway in our laboratory on the problem of the chemical compatibility of various metals, which may be used as substrates, with boron and with the $B Cl_3$-H_2 mixtures. A thermodynamic approach on the computer, based on the minimization of the free energy system function, considering the material evaluations, is used (2). For a given initial state (composition of the gaseous state, temperature, total pressure and kind of substrate), it allows one to know the composition of the system when equilibrium is reached in the deposition reactor. This method can be used, for example, to qualitatively and quantitatively determine whether a given kind of substrate can be affected or not by the constituents of the gaseous phase.

By way of illustration, Figure 3 gives the kind and quantity of gases , interms of the initial composition, when equilibrium is reached, resulting from the reduction of $B Cl_3$ in the presence of hydrogen and a tungsten substrate. Without entering into a detailed analysis, it seems that for some initial compositions $B Cl_{3\ in}/H_{2\ in} < 0.28$, 95% of the chlorine found in $B Cl_3$ is converted into HCl (reduction by hydrogen). By comparison, the amount of tungsten chlorides formed (reduction by the substrate) is very small. Under these conditions, the tungsten substrate shows good chemical compatibility with the gaseous phase (initial stage of the boron deposition process). On the other hand, if $B Cl_{3\ in}/H_{2\ in} > 0.28$, the proportion of tungsten chlorides increases, which indicates significant effects on the substrate (2).
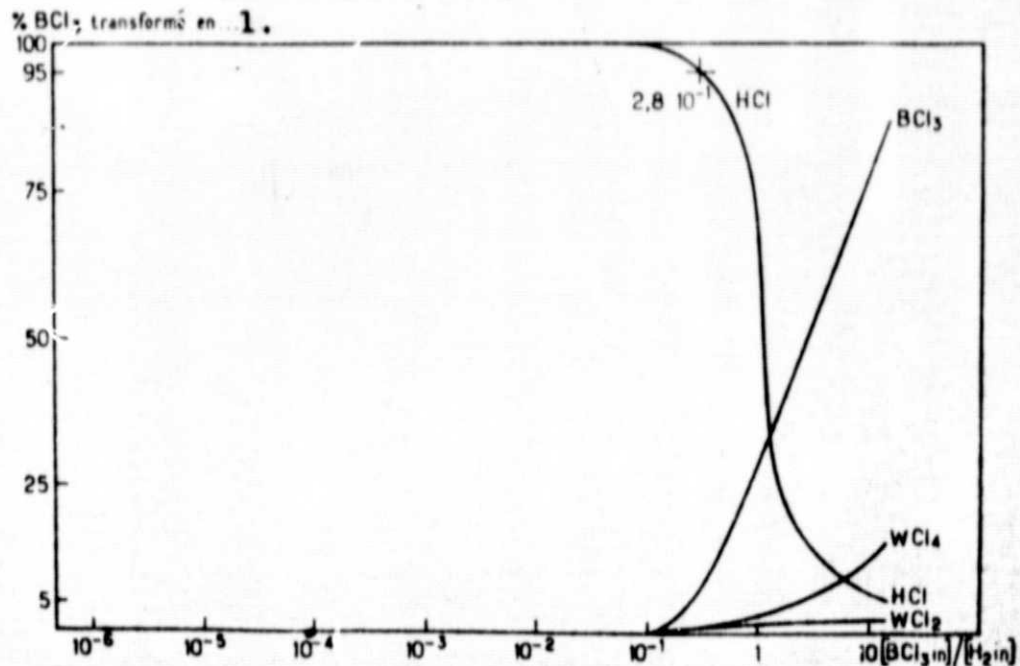
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% BCl₃ transformé en ...1.

Fig. 3. - Proportion of BCl_3 transformed at
equilibrium into HCl and into tungsten chlorides
in terms of the initial composition of the
gaseous phase (T=1300 K; p≃1 atm., excess of
tungsten).
Key: 1. transformed into...

Figure 4 allows a comparison to be made of the chemical
compatibility of various types of metal substrates with the
gaseous phase. For each substrate, it gives the quantity of
consumed BCl_3 transformed into metallic chlorides by interaction
with the substrate, in terms of the initial composition of the
gas. It seems that under the usual conditions for manufacturing
boron fibers ($10^{-1} < BCl_{3\ in} / H_{2\ in} < 5 \cdot 10^{-1}$), only the tungsten
is not significantly affected by the substances present in the
gaseous phase and, due to this, is the best metal substrate.
We will point out that substrates of complex nature, such as
diboride TiB_2 for example, are even more inert than tungsten.
However, it would be very costly and technologically difficult
to obtain these substrates in the form of fine wire.

The result of our basic research - along with the experience
acquired by the manufacturers - suggests that, without a doubt,
it would be difficult to find a better metal substrate than
tungsten. Although tungsten has numerous advantages, it, never-

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theless has some serious disadvantages (high density, cost,
rapid boridization causing volumetric expansion of the metal
core during manufacture of the fiber). In order to lessen
these disadvantages, the use of substrates made up of carbon
monofilaments is being investigated and developed.

It would seem that a carbon substrate would allow a
40% increase in the speed of passage of the wire into the
cells of boron deposit. This would result in a significant
decrease in cost price of the fiber, as Table II suggests,
giving the change in the cost of the boron-epoxy composite in
terms of the demand for boron fibers estimated for the next
four years. The established production capacity for boron fiber
with a carbon core is currently 500 Kg/year for Avco, the main
boron fiber producer (3). The chemical compatibility of the carbon
substrate with the constituents of the gaseous phase ($B Cl_3-H_2$)
is being studied in our laboratory in terms of the initial
composition.

Boron fiber can also be manufactured by thermal cracking
of diborane B_2H_6 in contact with a substrate wire. This method
has the advantage that it can be implemented at a lower temperature.
However, it is not certain that this advantage can compensate
for the dangers which the handling of boranes on the industrial
level presents. Further research in this area would be desirable(4).

TABLE II.- ESTIMATION OF THE PRODUCTION OF BORON FIBERS AND THE
COST OF THE BORON EPOXY COMPOSITE (IN US $ 1975) ACCORDING TO
REF. 3.

	1978	1979	1980	1982
Production de fibres de bore (lbs)	30,000	35,000	40,000	50,000
Coût estimé du composite bore époxy (fibres B/W) ($/lb)	145	140	135	130
Coût estimé du composite bore époxy (fibres B/C) ($/lb)	100	90	80	75

Key: 1. Production of boron fibers (lbs), 2. Estimated cost of
boron-epoxy composite (B/W fibers)($/lb), 3. Estimated cost of
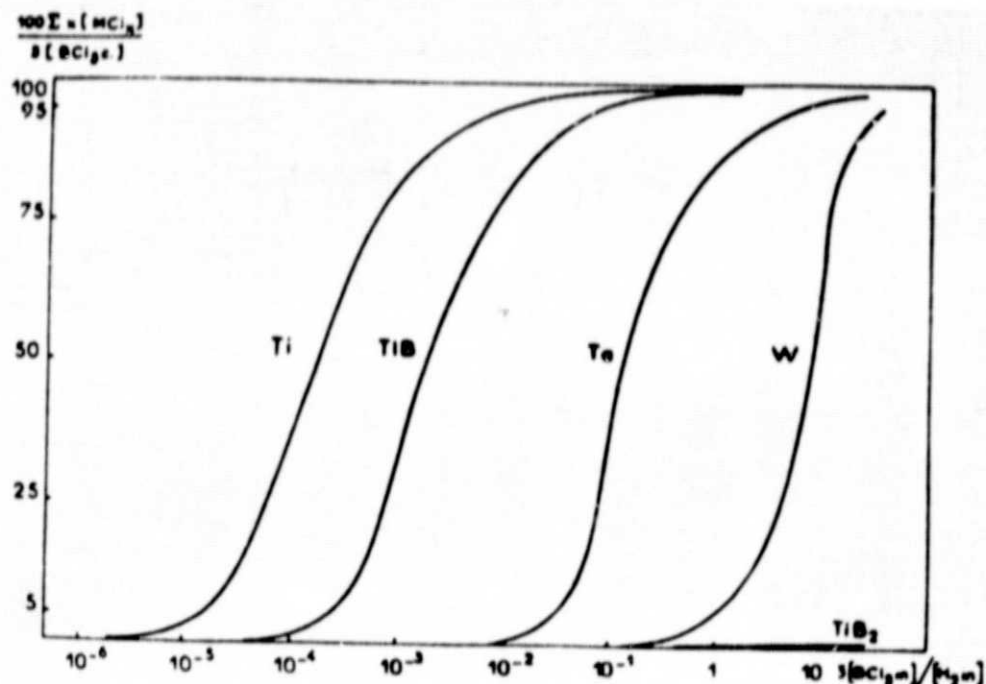boron-epoxy fibers (B/C fibers)($/lb)

$$\frac{100\,\Sigma\,[HCl_n]}{a\,[BCl_{gas}]}$$

Ti   TiB   Ta   W

TiB₂

10^{-6} 10^{-5} 10^{-4} 10^{-3} 10^{-2} 10^{-1} 1   10 $s[BCl_3=]/[H_2=]$

Fig. 4. - Proportion of consumed BCl_3 transformed into metallic chlorides, in terms of the initial composition of the gaseous phase and for various kinds of substrates (T = 1300 K; p = 1 atm.).

Boron Fiber Based Composites Having Organic Matrices

The main applications of boron fibers are currently in reinforcing plastics and especially epoxy resins. The boron-epoxy composite materials have a number of remarkable properties (rigidity and strength at least equal to that of steel, exceptional crushing and fatigue strength, for an approximate density of only 2, or less than that of aluminum, 2.7) which quite naturally seem to indicate their use in manufacturing structural components for aeronautics and aerospace.

Since we anticipate a specialized report on this type of material, we will only indicate, in Tables III and IV, a few characteristic properties of unidirectional and multidirectional boron-epoxy composites. For a composite whose volumetric portion of fibers is approximately 70%, the bending strength R_n, the modulus of elasticity E_n, and the shearing strength τ, have, on an average, the following values: $R_n = 200$ hb $E_n = 23,000$ hb $\tau = 8$ hb.

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However, F. E. Wagner points out that when using top
quality boron filaments and when particular care is taken
in choosing the composition of the resin and in the manufacturing
conditions of the composite, much higher values can be obtained
in the laboratory, as high as the following: (4)

$$R_{fl} = 350 \text{ hb} \quad E_{fl} = 33,000 \text{ hb} \quad \tau = 10 \text{ hb.}$$

These properties can be attributed both to the intrinsic
mechanical characteristics of the fibers and also to the good
physico-chemical compatibility of the boron fibers with the
epoxy resins, before and during polymerization. Thus, boron
fibers are well wetted by the epoxy resins, at the time of
coating, resulting in good fiber/matrix adhesion and satisfactory
shearing strength (peeling off), contrary to graphite fibers
for which surface treatment is generally necessary.

Probably no other material has properties comparable to
those of boron epoxy composites as far as specific resistance
to compression and resistance to fatigue are concerned.

The cost of boron filaments will remain, in the years to
come, higher than that of graphite fibers, even in the case
where a carbon monofilament is substituted for the tungsten core.
For this reason, one may expect that boron fibers will mainly
be used in epoxy matrix hybrid composites, in association with
glass fibers and/or carbon fibers.

For example, by substituting only 8% of the glass fibers
by boron fibers, in a unidirectional composite with an epoxy
matrix (V_f#50%), its bending strength is increased 2.5 times
and its longitudinal modulus of elasticity is tripled (5) (Table V).
Thus, it can be seen that hybrid composites using boron fibers,
in places of great stress, can have better performance/cost ratios
than composites made only from less expensive but also less
effective fibers.

According to American sources, it seems that in certain
aircraft currently under study, 75% (in weight) of the structural
components could be made from hybrid composites, the boron
fiber content being approximately 10% (3.6).

TABLE III. - MECHANICAL PROPERTIES OF SOME UNIDIRECTIONAL EPOXY MATRIX COMPOSITES

1 Nature de la résine époxy	(Vf (%)	2 Densité	3 Rupture en flexion (hb)	4 Module d'élasticité en en flexion (hb)	5 Résistance au cisaill. (hb)	6 Résistance en compress. (hb)	References
DEN 433 (Dow)	70	-	140-210	21,000-28,000	8	190-250	(4)
ERLA 0400 (Union Carbide)	70	-	-	-	7	175-270	"
DEN 438 SN 389	73,4	-	320	32,000	10	-	"
SN 390	74,0	-	345	33,000	10	-	"
SN 391	74,0	-	350	33,000	-	-	"
SNPE - non précisée 7	58	2,08	235	22,700	9,2	-	(5)
EHR 101	-	-	200	20,000	9	150-120	(7)
Graphite HT - epoxy	-	1,5	150	14,000	8	-	"
HM - epoxy	-	1,6	100	20,000	6	50	"
PRD Type III - epoxy	-	1,3	65	7,200	4	20	"
8 Verre E - epoxy	-	2,0	130	4,400	6	70	"

Key: 1. Kind of epoxy resin, 2. Density, 3. Flexure break, 4. Flexure elasticity modulus, 5. Shearing strength, 6. Compressive strength, 7. Not specified, 8. Glass

TABLE IV. - MECHANICAL PROPERTIES OF COMPOSITES HAVING EPOXY MATRICES AND CROSSED FIBER LAYERS (0°, ±45°, 90°, 50% OF WHOSE FIBERS ARE IN 0°). THE PRICES ARE ESTIMATED FOR 1981-83 ON THE BASIS OF THE 1975 US DOLLAR. THE PROPERTIES ARE MEASURED IN THE 0° DIRECTION (ACCORDING TO REF. 3).

Matériau 1.	2 Rupture traction (hb)	3 Rupture compress. (hb)	4 Module (hb)	5 Densité	6 Prix (US $/lb)
Bore (B/C) époxy 7.	70	175	13,000	2,0	75
Hybride époxy : 0° : bore / ± 45°: graphite	63	150	12,000	1,80	50
Graphite époxy	68	65	7,000	1,60	25

Key: 1. Material, 2. Tensile break, 3. Compression failure, 4. Modulus, 5. Density, 6. Price, 7. Boron (B/C epoxy), 8. Boron

TABLE V. - EFFECT ON MECHANICAL PROPERTIES OF THE INTRODUCTION OF A SMALL PERCENTAGE OF BORON FIBERS IN A GLASS EPOXY COMPOSITE (ACCORDING TO REF. 5)

1 Fibres de verre Vf (%)	2 Fibres de bore Vf (%)	3 Rupture en flexion (hb)	4 Module d'élasticité (hb)
55	0	53	2,200
44	8	128	6,500

Key: 1. Glass fibers, 2. Boron fibers, 3. Flexure break, 4. Modulus of elasticity

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The resistance to temperature of boron-epoxy composites /30
is necessarily limited due to the nature of the matrix. Table VI
shows that at 175°C, a notable decrease in all mechanical
characteristics is already observed. The temperature limit
in using boron-epoxy laminates is probably approximately
100 - 125°C (5). The use of thermostable resins (for example
polyamides) in principle allows the use of organic matrix
composites to be extended to temperatures of 250-300°C. However,
these resins are expensive and require delicate implementation.
It is not certain, under these conditions, that the use of an orga-
nic matrix is still an advantage at these temperatures, compared
with the use of a metal matrix (aluminum, for example). In any
case, in-depth research should be pursued on this subject.

TABLE VI. - CHANGE OF MECHANICAL CHARACTERISTICS OF A BORON-EPOXY
COMPOSITE WITH TEMPERATURE (WITTAKER-NARMCO RESIN)(ACCORDING TO REF. 5).

Temperature (°C)	1 Rupture en flexion (hb)	2 Cisaillement (hb)	3 Module d'élasticité (hb)
20	161	10,6	20,800
175	137	5,1	19,000

Key: 1. Flexure break, 2. Shearing, 3. Modulus of elasticity

Composites With Metallic Matrices Reinforced by Boron Fibers

The current development of composites with metallic matrices
is modest compared with that of composites with organic matrices.
The coating with a metallic matrix of boron fibers is mainly
done within aluminum for use in aeronautics and aerospace.
However, other metals can also be considered; for example,
titanium and its alloys. Let us mention, in another area,
the reinforcement of lead by boron filaments which spectacularly
improves its mechanical characteristics (with $V_f \approx 5\%$, the resistance
to breaking increases from 1.7 hb, for pure lead, to 14 hb).

One of the main advantages of a metallic matrix is the
possibility of using the composite at elevated temperatures.
Moreover, composites with metallic matrices have good electrical

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and thermal conductivity, age well, are hardly sensitive to ultraviolet radiation and atmosphere corrosion, and lastly, have good transverse mechanical characteristics.

Their industrial implementation meets with two kinds of problems: (a) the need to manufacture them at high temperatures (by infiltration or hot pressing) and (b) deterioration of mechanical properties under stress of heat due to phenomena of chemical fiber/matrix interaction.

The problems presented in manufacturing will be dealt with within the framework of the report devoted to boron-aluminum composites[1] whose industrial applications are being developed (compressor blades, tubes, extrusions, panels). Here we will only study the chemical fiber/matrix compatibility and its effects on the mechanical properties of the composite, dealing especially with the case of the materials with titanium matrices which have been studied in our laboratory for several years.

General Problems Presented by Chemical Fiber/Matrix Compatibility

Boron, like carbon, has a marked affinity for most of the metals used in aeronautic construction. It reacts under heat with aluminum, magnesium, and the transition metals to rapidly produce one or several borides. Figure 5 , by way of illustration, gives the equilibrium diagram of the boron-titanium system which involves two borides TiB and TiB_2 (8).

A composite material made up of boron fibers coated with $\underline{/31}$ a metallic matrix, for example titanium, when heated to a high temperature, is thus in thermodynamic disequilibrium. Consequently, the phenomena of chemical diffusion occur at the fiber/matrix interfaces, resulting in the progressive formation of a layer of borides around each fiber whose thickness increases as a function

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[1] Communication presented at the Conference on New Materials in Bordeaux, April 20 and 22, 1977.
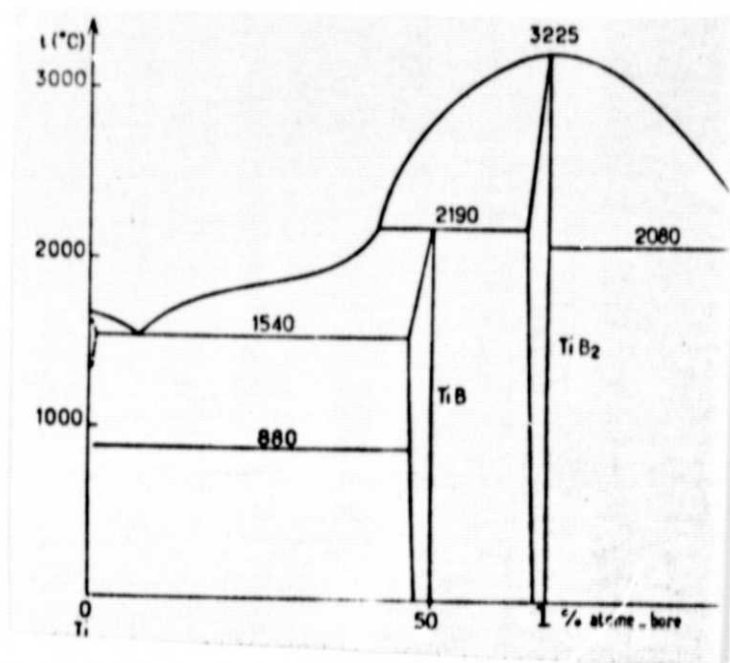
of temperature and time.

The phenomena of diffusion at the interfaces can have two kinds of opposite effects: if they are low intensity, they effectively contribute to reinforcing the fiber/matrix adhesion; if they are very intense, on the other hand, they can - by introducing a fragile zone between fiber and matrix -greatly decrease the cohesion and resistance of the composite as Figure 6 illustrates.

Fig. 5.- Schematic representation of the equilibrium diagram of the boron-titanium system (according to ref. 8).
Key: 1. % atom_boron

During its life, a boron-metal composite is subjected to high temperatures at least once, at the time of its manufacture and then possibly during its use. It is thus indispensable to know the maximum fiber-matrix interaction which each kind of composite will tolerate (before its mechanical characteristics deteriorate) and the formation kinetics of the interaction zone. This infor- /32 mation, which can only be obtained following in-depth laboratory studies, is essential to the manufacture and use at high temperatures of metallic matrix composites, although set-backs involving mechanical properties could be avoided if more importance was given to the physico-chemical phenomena which occur at the interfaces in composites.

At high temperatures, the chemical compatibility of boron fibers - like that of carbon fibers - with aluminum and titanium is poor. However, it is possible to make it sufficient by protecting

the fibers by means of a diffusion barrier (SiC, B_4C, BN, for example) and/or by replacing the pure metal by an alloy of carefully chosen composition. The search for effective barriers and the development of new alloys are undoubtedly areas of research to be pursued. As an illustration, we will give the first results of the work carried out in Bordeaux on titanium alloys concerning this topic.
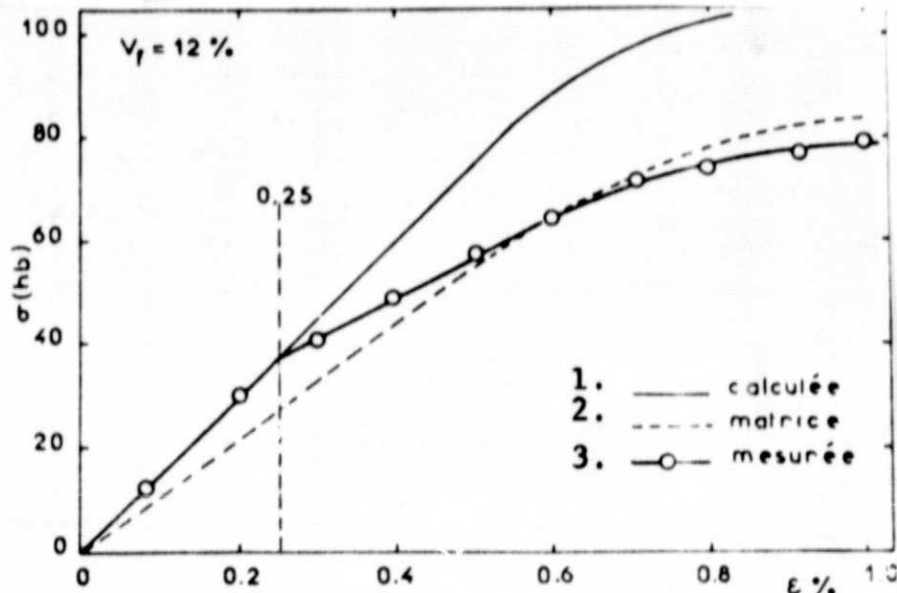
/33
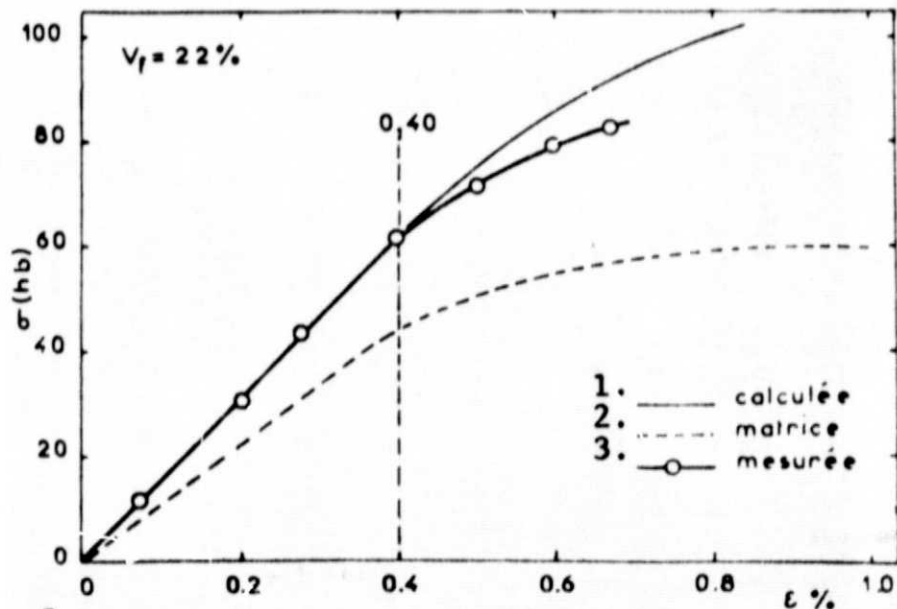
Figure 6. - Stress-deformation curves of boron-titanium composites according to ref. 13.
Key: 1. calculated, 2. matrix, 3. mesured, 4. high fiber-matrix interaction, 5. low fiber-matrix interaction

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(a)
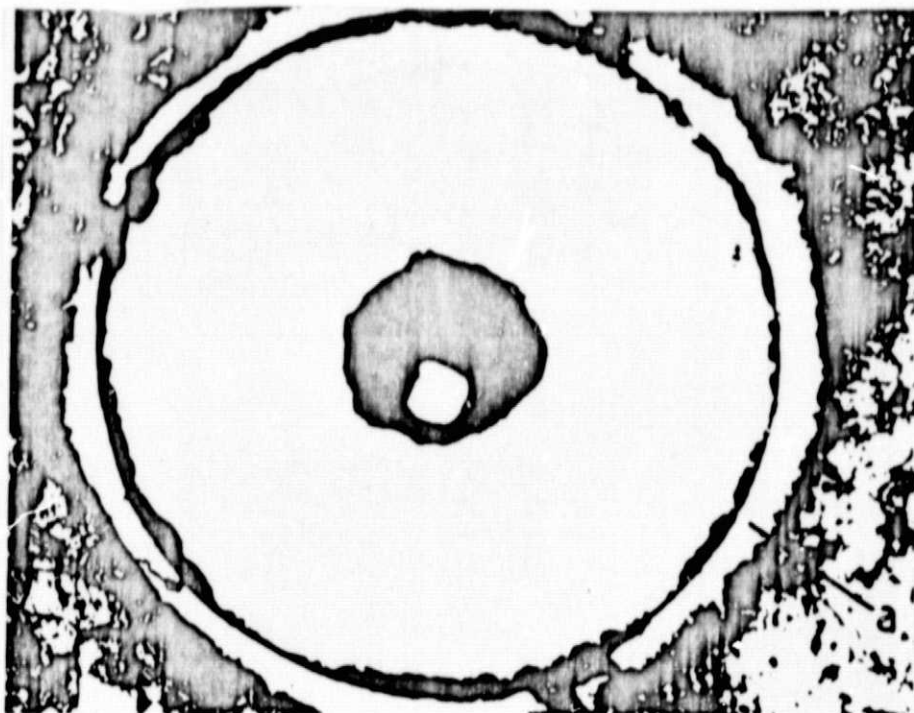
(b)

Fig. 7. - Chemical interaction zone between a
titanium matrix (50 hours, 845°C) and (a)an uncoated
boron fiber, (b) a boron fiber coated with a
diffusion barrier of B_4C.

Protection of Boron Fibers by Diffusion Barriers

Figure 7a shows an uncoated boron fiber with a non-alloyed titanium matrix after severe diffusion treatment (50 hours at 850°C). It appears to be surrounded by a white ring, mainly made up of TiB_2 which results from the fiber-matrix interaction. At a given temperature, the thickness x of this ring increases linearly with the square root of the time. The coefficient of proportionality k - called the coefficient of penetration - defines the kinetics of the phenomenon (fig. 8).
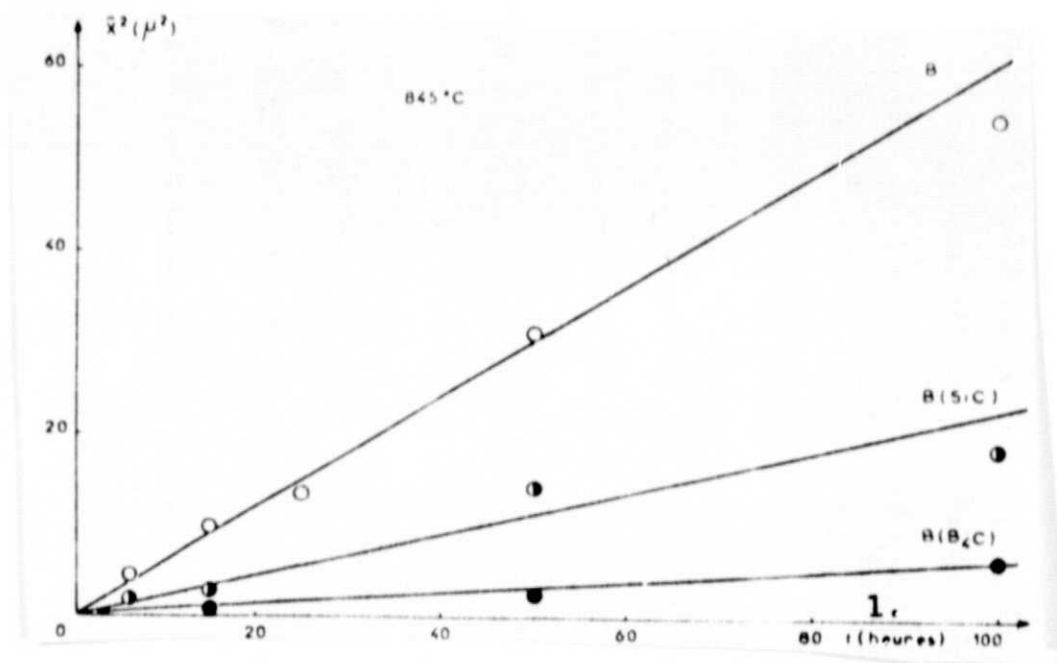

Fig. 8. - Variation of the square of the thickness of the fiber/matrix interaction zone (TiB_2) as a function of time for titanium matrix composites rein- forced by uncoated boron fibers or boron fibers coated with B_4C or SiC.
Key: 1. hours

In order to decrease the speed of fiber/matrix interaction, certain boron fiber manufacturers deposit a fine layer (a few microns) of a material intended to act as a diffusion barrier at the end of the manufacturing process (for instance SiC, B_4C or BN) (fig. 1) (9). Figure 7b shows a boron fiber (B_4C) having undergone the same treatment (diffusion) as the uncoated fiber in figure
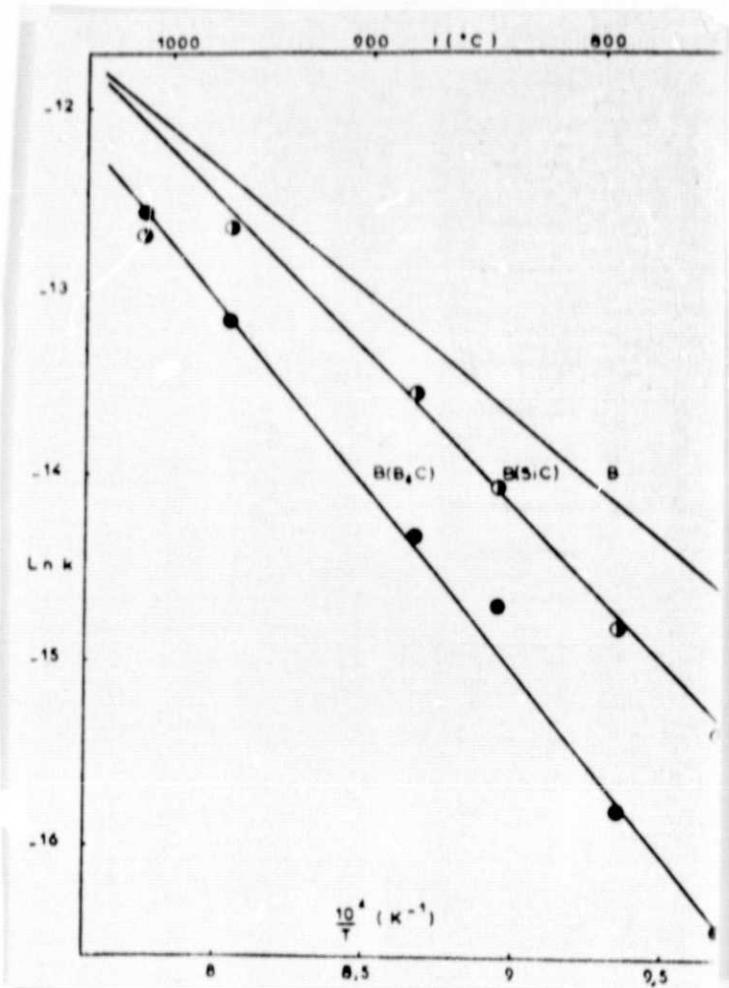
Fig. 9. - Variation with temperature of the coefficient of penetration l, for composites with titanium matrices reinforced with bare boron fibers or boron fibers coated with a diffusion barrier of B_4C or SiC.

7a within a matrix of non-alloyed titanium. It is clear that the diffusion ring, whose main constituent is still TiB_2, is much narrower than for the uncoated fiber, which indicates, consequently, less interaction and proves that, by slowing down the speed of boron atom migration in titanium, B_4C is an effective diffusion barrier. Figure 8 allows a comparison of the kinetics of interaction between the non-alloyed titanium matrix and the uncoated boron fibers or those coated with B_4C or SiC.

By studying the kinetics of interaction at various temperatures, it is shown that the phenomenon is thermally active. Figure 9 gives the variation of the penetration coefficients k with temperature for three kinds of fiber in non alloyed titanium.

According to A. G. Metcalfe, a boron-titanium composite /34 would retain mechanical characteristics close to the theoretical values as long as the ring of TiB_2 surrounding the fibers has a thickness less than a critical value (approximately 0.4μ for non-alloyed titanium)(10). Beyond that, the longitudinal breaking strength falls and tends towards that of the matrix (fig. 6 and 10). From this observation and the results of the kinetics study, it is possible to calculate , in terms of the temperature, the time $\zeta_{0.4}$ which leads to the formation of a 0.4μ

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ring of TiB_2 around the fibers. Figure 11 shows that a B/Ti composite would have a chemical life of seven hours at $700°C$, whereas at the same temperature, that of a B (B_4C)/Ti composite would be 1000 hours.

This kind of study, when joined more closely with measurements of mechanical characteristics, should thus allow optimal conditions of manufacture and use of these materials to be established. The use of coated boron fibers (with B_4C or SiC) which seemed promising for titanium, has already lead to a satisfactory solution to the less delicate case of coating boron fibers with aluminum matrices.
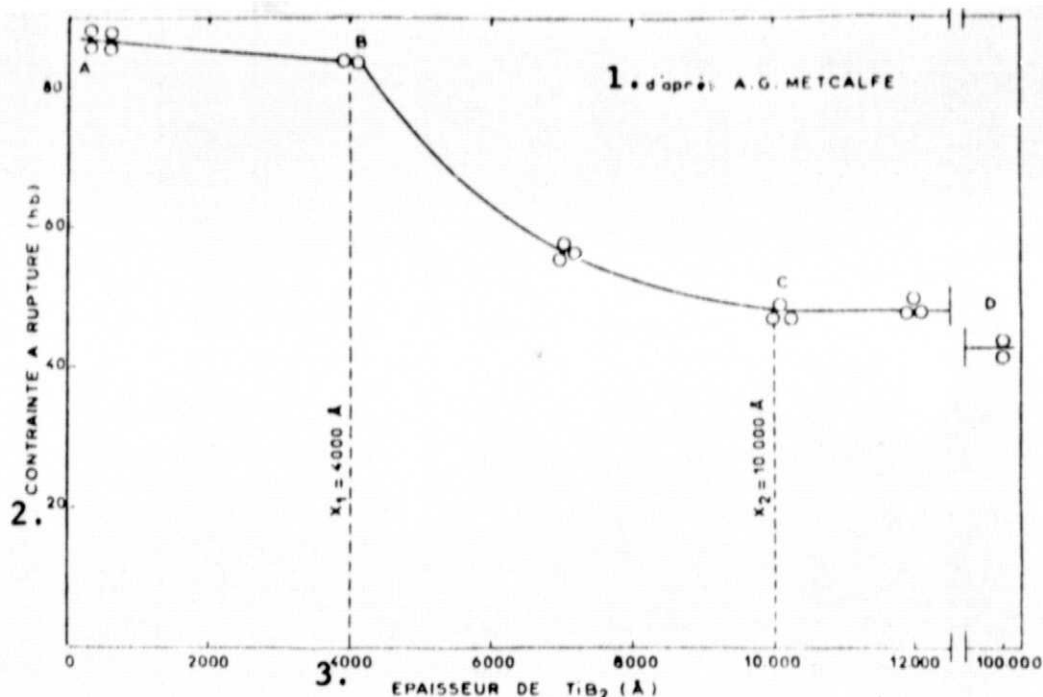

Fig. 10. Variation of the breaking strength of a composite with titanium matrix reinforced by boron fibers, as a function of the thickness of the zone of fiber/matrix interaction (according to ref. 10).
Key: 1. According to A. G. Metcalfe, 2. Resistance to breaking, 3. Thickness of TiB_2 (a)

Fig. 11. - Variation of the time $\tau 0.4$ necessary to obtain a zone of fiber/matrix interaction of critical thickness of 0.4μ as a function of temperature in the B/Ti and $B(B_4C)/Ti$ composites.

Improvement of Fiber-Matrix Compatibility by Addition of Alloying Elements to the Matrix

The rate of diffusion of boron atoms through the ring of borides which forms at the fiber-matrix interface depends on the gradients of concentration which prevail and, consequently, on the extend of the existence of borides and the stoichiometric deviations. It is possible to modify the stoichiometric deviation especially of the MB_2 diborides - by adding alloying substances to the matrix. According to G. K. Schmitz, et al., this is the case when vanadium (and to a lesser degree aluminum, zirconium, molybdenum, or tungsten) is added to titanium (11).
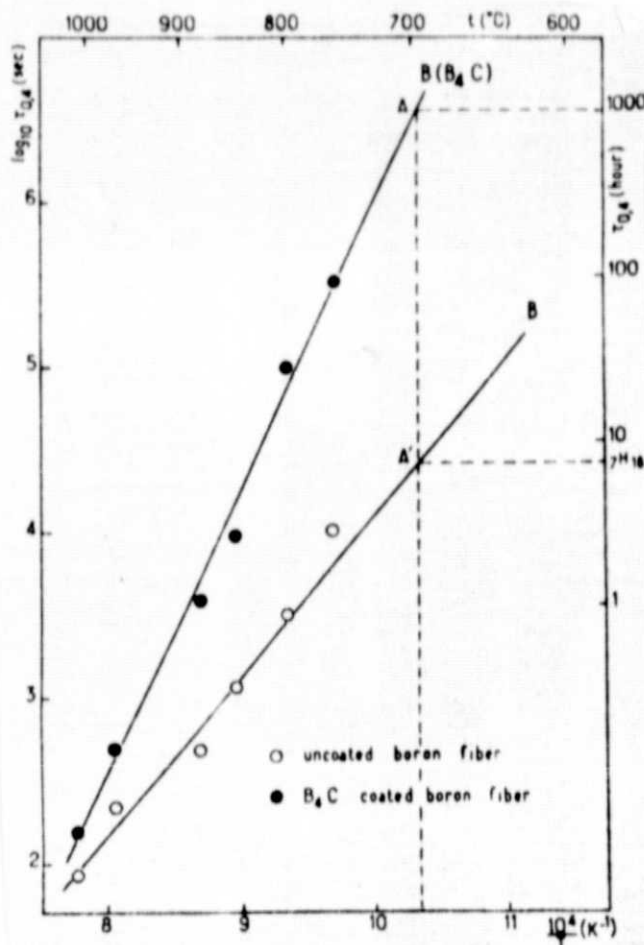
Figures 12 and 13 effectively show that the kinetics of interaction of the uncoated or the B_4C coated boron fibers for example are less rapid in the commercial alloy TA 6 V (which however contains only 6% Al and 4% V) than in the non-alloyed titanium (12).

A systematic study of the influence of adding increasing amounts of vanadium to titanium is being made. It should result in a definition of those titanium alloys which present a compatibility at increased heat in respect to boron fibers. Let us point out that G. K. Schmitz et al. have already proposed the alloying of Ti-13V-10Mo-5Zr-2.5Al which, along with uncoated boron fibers, would allow composites to be made whose life would be

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multiplied, at 750°C, by a factor greater than 500 as compared with those manufactured with non-alloyed titanium.
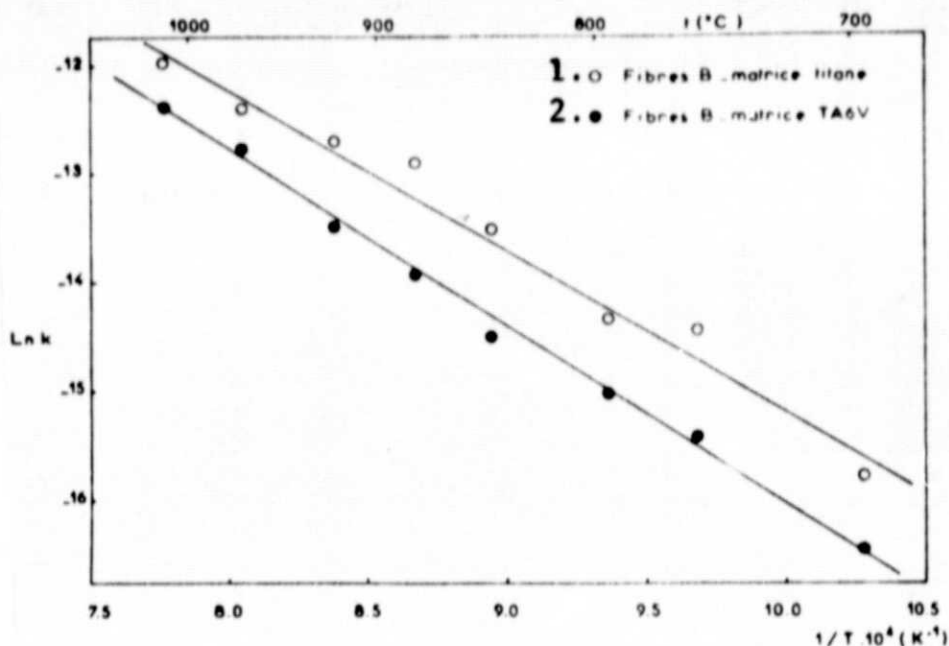

Fig. 12.- Comparison of the kinetics of fiber/
matrix interaction in B/Ti and B/TA6V composites.
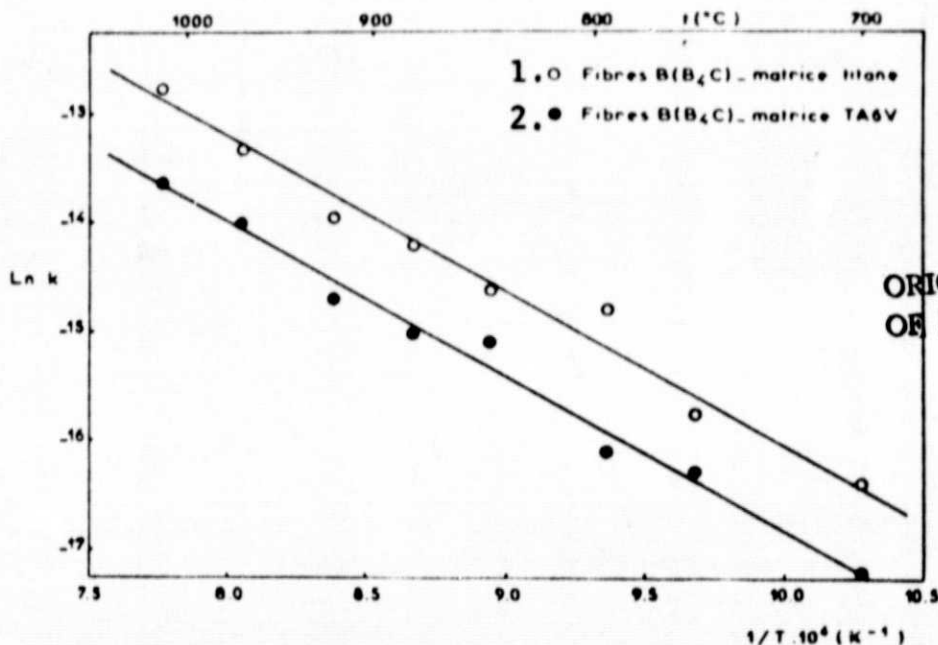Key: 1. B fibers-titanium matrix, 2. B fibers-
TA6V matrix

Fig. 13. - Comparison of the kinetics of
fiber/matrix interaction in B9B$_4$C)/Ti and
B(B$_4$C)/TA6V composites
Key: 1. B(B$_4$C) fibers-titanium matrix,
2. B(B$_4$C) fibers- TA6V matrix

One can thus believe, that by joining the use of coated fibers with that of alloys of carefully chosen composition, it will be possible, in the near future, to satisfactorily solve the problem of chemical compatibility of boron fibers $\underline{/36}$ with most of the metallic matrices used in the field of aeronautics. Temperature limits of approximately 400°C for composites with aluminum matrices and approximately 600°C for composites with titanium matrices can be hoped for in the near future.

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