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THE PROSPECTS FOR COMPOSITES BASED ON BORON FIBERS

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**Title and Subtitle**

THE PROSPECTS FOR COMPOSITES BASED ON BORON FIBERS

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**Translation**


**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.

**Key Words (Selected by Author(s))**

**Distribution Statement**

Unclassified-Unlimited

**Security Classif. (of this report)**

Unclassified

**Security Classif. (of this page)**

Unclassified

**No. of Pages**

24
Boron fibers - or filaments - are recent materials since 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 to 140 μ) 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 13 μ 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 FIBRILLARY REINFORCING SUBSTANCES AND THOSE OF CLASSICAL MATERIALS (ACCORDING TO REF. 7).**

<table>
<thead>
<tr>
<th>Nature</th>
<th>Densité</th>
<th>Résistance fraction (hb)</th>
<th>Modules d'élasticité (hb)</th>
<th>Module spécifique E/d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bore Ø 100 µ</td>
<td>2.62</td>
<td>280-350</td>
<td>40,000</td>
<td>110-130</td>
</tr>
<tr>
<td>Bore Ø 140 µ</td>
<td>2.55</td>
<td>350-420</td>
<td>40,000</td>
<td>130-160</td>
</tr>
<tr>
<td>Graphil HT</td>
<td>1.85</td>
<td>210-280</td>
<td>23,000-28,000</td>
<td>117-155</td>
</tr>
<tr>
<td>Graphil HM</td>
<td>1.95</td>
<td>180-240</td>
<td>35,000-41,000</td>
<td>100-123</td>
</tr>
<tr>
<td>PRD - 49 III</td>
<td>1.4</td>
<td>250</td>
<td>13,000</td>
<td>180</td>
</tr>
<tr>
<td>Verre E</td>
<td>2.55</td>
<td>175-275</td>
<td>7,400</td>
<td>98-140</td>
</tr>
<tr>
<td>Duralumin</td>
<td>2.8</td>
<td>45</td>
<td>7,500</td>
<td>6</td>
</tr>
<tr>
<td>Acier (III)</td>
<td>7.8</td>
<td>180-290</td>
<td>21,000</td>
<td>20-40</td>
</tr>
<tr>
<td>Boron</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glass</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steel (wire)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


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 B₄C 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).
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 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).


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.
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 BCl$_3$-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 BCl$_3$/B is small, thus requiring a complex treatment and recycling of the reagents,
- the starting materials are expensive (especially BCl$_3$ and tungsten).

![Fig. 2. - Morphology of the surface of a boron fiber (X 760)](image-url)
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 Cl₃-H₂ 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, in terms of the initial composition, when equilibrium is reached, resulting from the reduction of B Cl₃ in the presence of hydrogen and a tungsten substrate. Without entering into a detailed analysis, it seems that for some initial compositions B Cl₃ in/H₂ in < 0.28, 95% of the chlorine found in B Cl₃ 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 Cl₃ in/H₂ in > 0.28, the proportion of tungsten chlorides increases, which indicates significant effects on the substrate (2).
Figure 3. - Proportion of BCl₃ 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).

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 BCl₃ 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 < BCl₃ in / H₂ in < 5.10⁻¹), 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 TiB₂ 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-
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 (\(\text{B}_2\text{Cl}_3\cdot\text{H}_2\)) is being studied in our laboratory in terms of the initial composition.

Boron fiber can also be manufactured by thermal cracking of diborane \(\text{B}_2\text{H}_6\) 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.**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Production de fibres de bore (lbs)</td>
<td>30,000</td>
<td>35,000</td>
<td>40,000</td>
<td>50,000</td>
</tr>
<tr>
<td>2. Coût estimé du composite bore époxy (fibres B/W) ($/lb)</td>
<td>45</td>
<td>40</td>
<td>35</td>
<td>30</td>
</tr>
<tr>
<td>3. Coût estimé du composite bore époxy (fibres B/C) ($/lb)</td>
<td>100</td>
<td>90</td>
<td>80</td>
<td>75</td>
</tr>
</tbody>
</table>

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)
Fig. 4. - Proportion of consumed BCl₃ 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 \( R_b \), the modulus of elasticity \( E_m \), and the shearing strength \( \tau \), have, on an average, the following values: \( R_b = 200 \text{ hb} \quad E_m = 23,000 \text{ hb} \quad \tau = 8 \text{ hb} \).
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: 

\[
\begin{align*}
    R_b &= 350 \text{ hb} \\
    E_b &= 33,000 \text{ hb} \\
    \tau &= 10 \text{ hb}.
\end{align*}
\]

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

<table>
<thead>
<tr>
<th>Nature de l résine epoxy</th>
<th>Densité (Vr (%)</th>
<th>Rupture en flexion (hb)</th>
<th>Module d'elasticité en flexion (hb)</th>
<th>Résistance au cisaillement (hb)</th>
<th>Résistance en compress. (hb)</th>
<th>Références</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEN 433 (Dow)</td>
<td>70</td>
<td>140-210</td>
<td>21,000-28,000</td>
<td>8</td>
<td>190-250</td>
<td>(4)</td>
</tr>
<tr>
<td>ERLA 0400 (Union Carbide)</td>
<td>70</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>DEN 438 SN 389</td>
<td>73,4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SN 390</td>
<td>74,0</td>
<td>-</td>
<td>32,000</td>
<td>10</td>
<td>175-270</td>
<td>-</td>
</tr>
<tr>
<td>SN 391</td>
<td>74,0</td>
<td>-</td>
<td>33,000</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SNPE - non préciséée</td>
<td>58</td>
<td>2,08</td>
<td>20,000</td>
<td>9</td>
<td>150-120</td>
<td>(5)</td>
</tr>
<tr>
<td>EHR 101</td>
<td>-</td>
<td>200</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Graphite HT - epoxy</td>
<td>-</td>
<td>150</td>
<td>14,000</td>
<td>6</td>
<td>40</td>
<td>-</td>
</tr>
<tr>
<td>Graphite HM - epoxy</td>
<td>-</td>
<td>100</td>
<td>20,000</td>
<td>8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PRD Type III - epoxy</td>
<td>-</td>
<td>70</td>
<td>7,200</td>
<td>4</td>
<td>20</td>
<td>-</td>
</tr>
<tr>
<td>Verre E - epoxy</td>
<td>-</td>
<td>130</td>
<td>4,400</td>
<td>4</td>
<td>40</td>
<td>-</td>
</tr>
</tbody>
</table>


### 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).

<table>
<thead>
<tr>
<th>Matériel 1.</th>
<th>2 Rupture traction (hb)</th>
<th>3 Rupture compress. (hb)</th>
<th>4 Module (hb)</th>
<th>5 Densité (hb)</th>
<th>6 Prix (US $/lb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bore (B/C) epoxy 7.</td>
<td>70</td>
<td>175</td>
<td>13,000</td>
<td>20</td>
<td>75</td>
</tr>
<tr>
<td>Hybride epoxy : 0°: bore / ±45°: graphite</td>
<td>63</td>
<td>150</td>
<td>12,000</td>
<td>1,80</td>
<td>50</td>
</tr>
<tr>
<td>Graphite epoxy</td>
<td>68</td>
<td>65</td>
<td>7,000</td>
<td>1,60</td>
<td>25</td>
</tr>
</tbody>
</table>


### 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)

<table>
<thead>
<tr>
<th>Fibres de verre VI (%)</th>
<th>2 Fibres de bore VI (%)</th>
<th>3 Rupture en flexion (hb)</th>
<th>4 Module d'elasticité (hb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>55</td>
<td>44</td>
<td>53</td>
<td>2,200</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>128</td>
<td>6,500</td>
</tr>
</tbody>
</table>

**Key:** 1. Glass fibers, 2. Boron fibers, 3. Flexure break, 4. Modulus of elasticity
The resistance to temperature of boron-epoxy composites 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 organic 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).

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>1 Rupture en flexion (hb)</th>
<th>2 Cisaillement (hb)</th>
<th>3 Module d'élasticité (hb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>161</td>
<td>10,6</td>
<td>20,800</td>
</tr>
<tr>
<td>175</td>
<td>137</td>
<td>5,1</td>
<td>19,000</td>
</tr>
</tbody>
</table>

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 \( V_f = 5\% \), 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...
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 TiB₂ (8).

A composite material made up of boron fibers coated with 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

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 information, 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, B₄C, 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.

Figure 6. - Stress-deformation curves of boron-titanium composites according to ref. 13.
Key: 1. calculated, 2. matrix, 3. measured, 4. high fiber-matrix interaction, 5. low fiber-matrix interaction
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 seven diffusion treatment (50 hours at 850°C). It appears to be surrounded by a white ring, mainly made up of TiB₂ 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).

![Graph](image)

**Fig. 8.** Variation of the square of the thickness of the fiber/matrix interaction zone (TiB₂) as a function of time for titanium matrix composites reinforced by uncoated boron fibers or boron fibers coated with B₄C 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, B₄C or BN) (fig. 1) (9). Figure 7b shows a boron fiber (B₄C) having undergone the same treatment (diffusion) as the uncoated fiber in figure
Variation with temperature of the coefficient of penetration \( k \), for composites with titanium matrices reinforced with bare boron fibers or boron fibers coated with a diffusion barrier of \( B_4C \) or SiC.

Fig. 9. - Variation with temperature of the coefficient of penetration \( k \), for composites with titanium matrices reinforced with bare boron fibers or boron fibers coated with a diffusion barrier of \( B_4C \) or SiC.

According to A. G. Metcalfe, a boron-titanium composite 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 0.4\( \mu \) 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 \( t_{0.4} \), which leads to the formation of a 0.4\( \mu \)
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$_4$C)/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$_4$C 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)
Improvement of Fiber-Matrix Compatibility by Addition of Alloving 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 extent of the existence of borides and the stoichiometric deviations. It is possible to modify the stoichiometric deviation especially of the MB₂ 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).

Fig. 11. - Variation of the time necessary to obtain a zone of fiber/matrix interaction of critical thickness of 0.4 μ as a function of temperature in the B/Ti and B(B₄C)/Ti composites.

Figures 12 and 13 effectively show that the kinetics of interaction of the uncoated or the B₄C 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
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 B(B4C)/Ti and B(B4C)/TA6V composites. Key: 1. B(B4C) fibers-titanium matrix, 2. B(B4C) 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 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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9. The BORSOC fiber is a Hamilton Standard product, the B(BN) fiber an AVCO product and the B(B4C) a SNPE product.


