JOURNAL OF MATERIALS SCIENCE 31 (1996) 4533–4539

Mechanical properties of T300/Al composites. Embrittlement effects due to a B_4C coating

M. R'MILI, V. MASSARDIER, P. MERLE
Institut National des Sciences Appliquées de Lyon, GEMPPM, UMR CNRS 5510,
20 Avenue Albert Einstein, F 69621 Villeurbanne Cedex, France
H. VINCENT, C. VINCENT
Université de Lyon I, Laboratoire des Multimateriaux et Interfaces, UMR CNRS 5615,
43 Boulevard du 11 Novembre, F 69622 Villeurbanne Cedex, France

During the preheating treatment preceding the processing of C/Al composites, a decrease in the mechanical properties of the carbon fibres is generally observed, owing to the oxidation of the fibres. Thus, it implies the use of a surface coating likely to resist the oxidation of the fibres. In this work, we chose to protect the carbon fibres by a B_4C coating, using a RCVD process. This coating leads to an effective protection against oxidation, as was shown by the mechanical properties obtained by single fibre tests on the coated fibres before and after preheating. However, although this coating also protects the fibres against the reaction with liquid aluminium during processing, the tensile properties of the composite were very weak. An analysis of these results based both on the use of loose bundle tests and on a microstructural characterization of the reinforcement and of the composite by transmission electron microscopy (TEM) observations and by electron spectroscopy for chemical analysis (ESCA) led us to the conclusion that the local overthicknesses of the B_4C coating have an embrittling effect, leading to a premature failure of the composite.

1. Introduction

It is possible to produce a carbon fibre–aluminium matrix composites by a squeeze-casting technique. However, a surface coating is necessary to prevent the degradation of fibre strength due to the reaction between the two components of the composite. In order to reduce the reaction between the fibre and the aluminium matrix, different diffusion barriers for fibres have recently been proposed. Among these coatings, we have chosen boron carbide for several reasons:

1. Even if this carbide is not thermodynamically stable in aluminium environment [1–2], the reaction kinetics is low and a fibre attack should be limited.
2. A B_4C coating can be realized without notable loss of the tensile strength of the fibre [3].
3. The fibres have to be preheated before their infiltration by liquid metal. As this treatment must be performed in an inert atmosphere, this condition is not always compatible with an industrial process. This problem can be overcome by the use of a B_4C coating, since B_4C is an excellent protecting material against oxidation [4].
4. Finally, preliminary work has shown that a composite consisting in an A9 aluminium matrix reinforced with T300-B_4C coated fibres ($V_f = 55\%$) is characterized by a bending strength of 950 MPa [5], value higher than that measured when raw fibres are used. Consequently, it was expected that the use of B_4C coated fibres should lead to an increase in the strength of the Al/carbon composites processed by squeeze-casting.

However, these good mechanical properties were not confirmed by further experiments. Thus, this paper focuses on the problems which may arise from a non-uniform coating of the fibres and from the brittle behaviour of the reinforcement.

2. Materials and microstructural characterization of the B_4C coating

The carbon fibre Torayca T300, which is a polyacrylonitrile (PAN)-based fibre, was investigated. The bundle consisting of 6000 single filaments was coated with B_4C in a RCVD process from BCl_3–H_2 mixture. This process was chosen for its ability to form a uniform and thin coating on all filaments and to produce large amounts of coated fibres. A detailed description of the equipment and of the experimental conditions has been given previously [3]. The B_4C thickness was measured by the increase in weight of the fibres and by chemical analysis. Obviously, only the mean thickness of the coating may be obtained by these measurements. By varying the RCVD temperature and the treatment time (or the fibre speed in the reactor), it is possible to realize B_4C thin films with a mean thickness of a few to several tens of nanometres.

The fibre surface was analysed by electron spectroscopy for chemical analysis (ESCA), using the mono-

0022–2461 © *1996 Chapman & Hall*

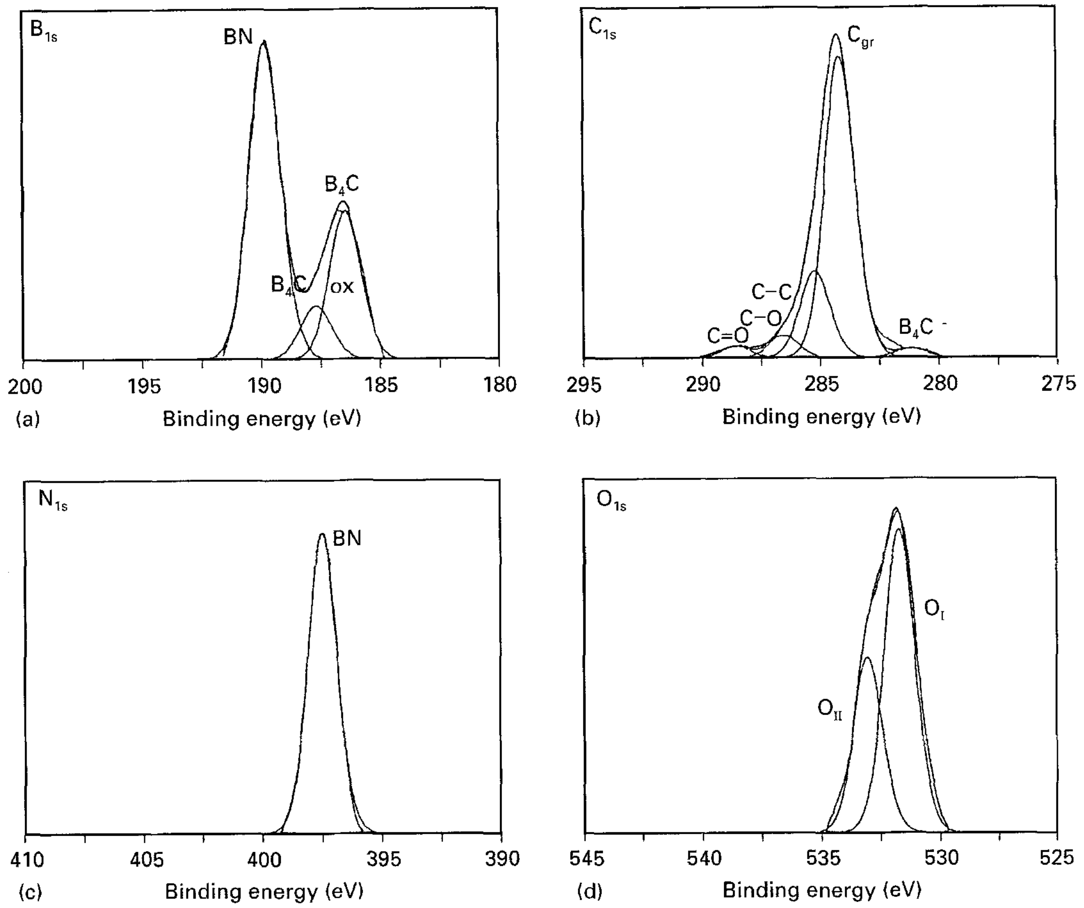

Figure 1 ESCA spectra of (a) B_{1s}, (b) C_{1s}, (c) N_{1s}, (d) O_{1s} from B_4C-coated T300 fibres.

chromatic AlK_α radiation ($h\nu = 1486.6$ eV). Fig. 1(a) and (b) show B_{1s} and C_{1s} spectra constructed by addition of theoretical Gaussian–Lorentzian components. The chemical shifts were referred to the C_{1s} line of graphite at 284.5 eV. For the B_{1s} photopeak, the presence of two components is evident: the peak at 187.1 eV corresponds to boron from the B_4C carbide and the one at 190.5 eV corresponds to boron from a nitride such as BN. A best fitting between experimental and calculated spectra is obtained with a third component which can be attributed to an oxidized form of B_4C. The nitride presence is confirmed by the N_{1s} peak at 398.0 eV (Fig. 1(c)), which has been already evidenced [6]. Its formation has been explained by a reaction between BCl_3 introduced in the reactor and nitrogen formed during the heating of the PAN-based fibre. The surface morphology of the coated fibres was observed by scanning electron microscopy (SEM). Fig. 2 shows two different aspects of the surface: most of the filaments present a smooth surface (Fig. 2(a)) and a few filaments have defects which have been identified as B_4C by electron microprobe analysis (EMPA) (Fig. 2(b)).

3. Experimental techniques

Composites were elaborated by the squeeze-casting technique. Unidirectional preforms of T300 fibres were preheated under a nitrogen atmosphere at a temperature of 700 °C during 30 min. Then they were moved into the squeeze-casting mould, the temperature of which was about 350 °C. The temperature of liquid aluminium was 700 °C. Preforms were infiltrated under a final pressure of 50 MPa. In these conditions, the contact time between liquid aluminium and the preform does not exceed 30 s. Unidirectional composite plates $2 \times 50 \times 90$ mm^3 were then obtained with a mean volume fraction of fibres of about 55%.

The microstructure of the composites was studied by transmission electron microscopy (TEM). Specimens were prepared by mechanical grinding to a thickness of 100 μm and dimpled to about 15 μm. They were then ion milled at 5 kV with argon ions at low temperature (100 K). Observations were made with a TEM-Jeol 200CX microscope.

The mechanical properties of the T300 or T300-B_4C fibres were determined in the as-received state, immediately after the preheating stage and after the transfer of the reinforcement in the mould. After preheating or transfer, fibres were rapidly cooled by immersion in a cold gaseous nitrogen atmosphere produced by the evaporation of liquid nitrogen. The Weibull parameters of the strength distribution of B_4C coated or uncoated T300 carbon fibres were determined either by the single fibre tests (SFT) or by a method based on the loose bundle tests (LBT), assuming a spatial random distribution of the individual failures of fibres [7]. In this last case, the preparation of the specimen is more difficult than in the monofilament technique but sampling problems are avoided and the results represent an average

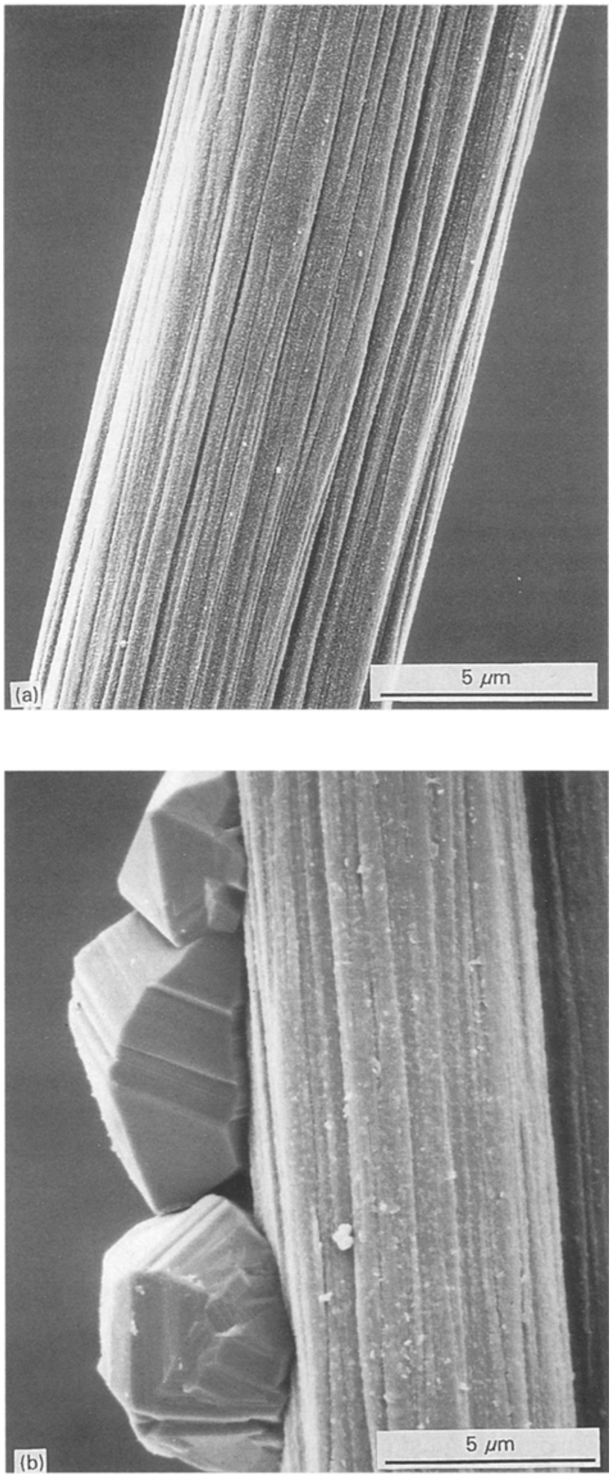

Figure 2 SEM micrographs of B_4C-coated T300 fibres (a) general aspect, (b) defects.

behaviour of a great number of fibres. In addition to the determination of the Weibull parameters, load-deformation curves give valuable informations on the lowest rupture strain of fibres. Results given in the two cases correspond to a 30 mm gauge length.

Fig. 3(a) shows the dogbone type specimens used for tension tests. In order to evaluate the interfacial strength between the fibres and the matrix, special notched specimens were designed: they were also machined from composite plates. The geometry of the notch is given in Fig. 3(b). This notch is 0.2 mm thick and was machined by electro-erosion. For all mechanical tests, the cross-head velocity of the testing machine was 0.1 mm s^{-1}. The tests were performed at room temperature.

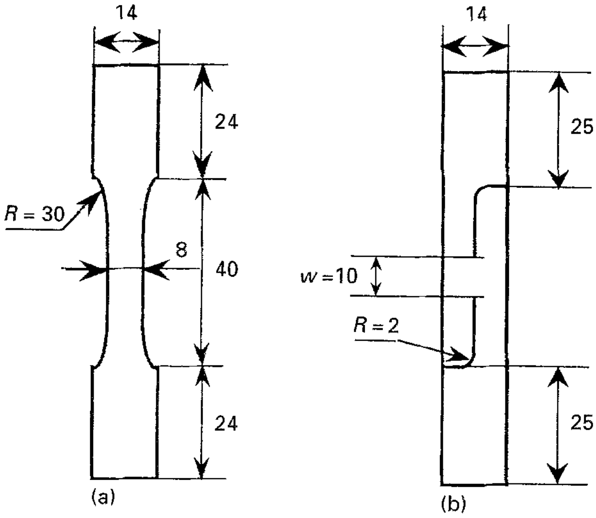

Figure 3 (a) Dogbone specimen used for tension tests; (b) notched specimen used for the evaluation of the interfacial strength.

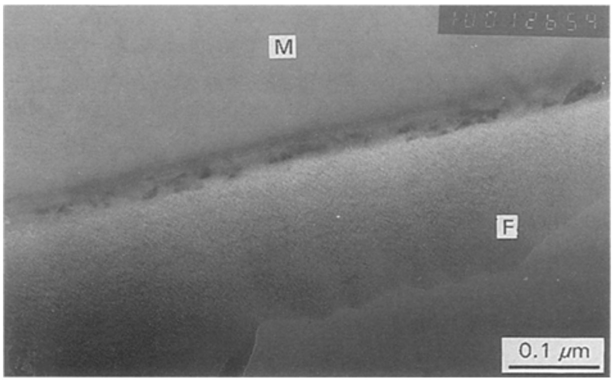

Figure 4 TEM micrograph showing the absence of reaction products at the interface between the matrix and the B_4C coating. Central part of the composite plate.

4. Experimental results

4.1. Chemical aspects

After infiltration by liquid aluminium, the composites were observed by TEM. These observations were performed on thin foils taken in different parts of the sample: central part or ends of the composite plate.

Micrographs in the central part of the plate reveal a clean interface between the fibre coating and the aluminium matrix (Fig. 4). In particular, no trace of Al_3BC and AlB_2 foreseen by thermodynamic results [1–2] was detected. This is probably due to the very short contact time between liquid aluminium and B_4C during processing.

Observations realized on the ends of the sample revealed an absence of coating on the carbon fibres and the existence of reaction products having the shape of thin plates (Fig. 5(a)). These reaction products were identified by electron diffraction as being Al_3BC (Fig. 5(b)). Occasionally, it was possible to detect the presence of Al_4C_3, which could form during the elaboration of the composite in the absence of

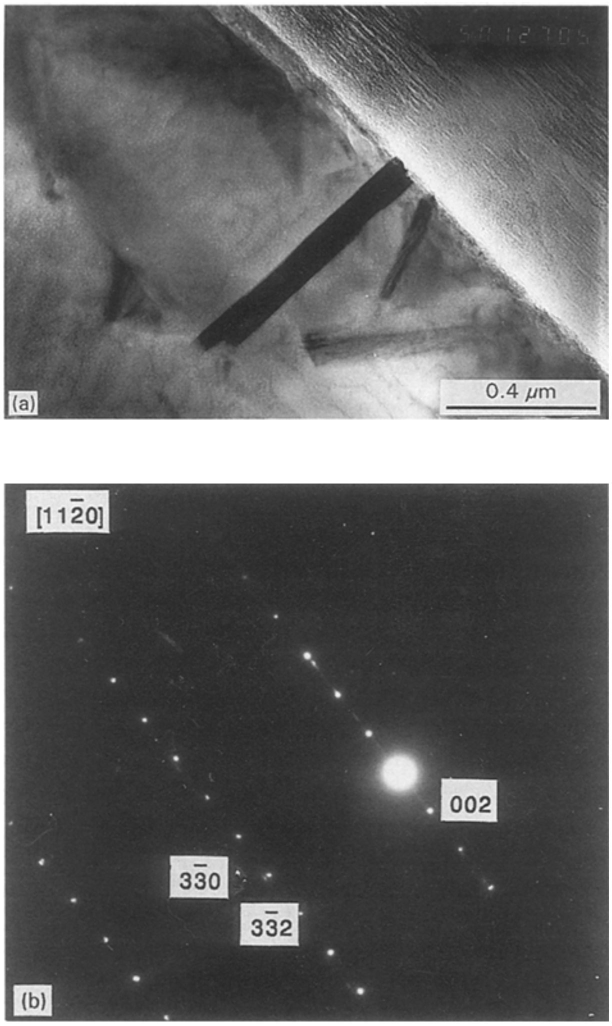

Figure 5 (a) TEM micrograph showing the existence of Al_3BC precipitates in the matrix of the composite. Ends of the composite plate. (b) Electron diffraction pattern of the precipitate shown in (a); zone axis: $[1 1 \bar{2} 0]$.

coating. An important result of this study is that the Al_3BC ternary compound cannot result from a direct reaction between Al and B_4C. Indeed, the contact time between liquid aluminium and B_4C during the elaboration of the composite by squeeze-casting is very low. The absence of B_4C coating on some filaments and the presence of Al_3BC in the vicinity may be due to an oxidation of the boron carbide during the preheating stage, leading to the formation of a boron oxide which then dissolves during the processing of the composite in the injected aluminium. Indeed, this oxide is not stable at the processing temperature. This local oxidation of the coating can be explained by the fact that, due to their particular location in the mould, the ends of the sample preform are in permanent contact with the atmosphere of the preheating furnace; this atmosphere (nitrogen) contains residual traces of oxygen. As the metal is saturated in carbon, Al_3BC can precipitate from the liquid phase. This hypothesis is supported by the location of Al_3BC in the composite matrix and by the results of ESCA analysis which evidence the existence of a boron–oxygen phase in the coating after the preheating of the preform. These ESCA spectra are reported in Fig. 6. Disymmetries and linewidths of the B_{1s}, N_{1s} and O_{1s} peaks show that these signals do not correspond to the preceding peaks (Fig. 1). After resolution, it clearly appears that: (i) the characteristic components of a boron oxide (such as B_2O_3) are present (BE: 193.1 and 531.7 eV); and (ii) the intensity of the B_4C component peak has strongly decreased.

As a conclusion, the coating of B_4C (while it has not been transformed during preheating) acts as a diffusion barrier, and the fibres are not degraded by reaction with Al. However, in the squeeze-casting experiments, a partial oxidation of the boron carbide may occur and reaction products such as Al_3BC are possible. However, it should be noted that the Al_3BC precipitates are located on the ends of the samples and they should not interfere on the measured mechanical properties.

4.2. Mechanical aspects

Table I gives the mechanical properties of T300/Al and T300-B_4C/Al composites, and also of the reinforcement in the as-received state, after the preheating stage and just before infiltration. The given results concerning the reinforcement were obtained by the SFT technique. The gauge length used to determine Weibull parameters was 30 mm.

To follow the evolution of the properties of the reinforcement before the processing of the composite, bundles of fibres were heated in the preheating furnace.

The strength $\langle \sigma_r \rangle$ of uncoated fibres after a preheating of 30 min at 700 °C under a nitrogen atmosphere is about 50% of the strength of the as-received state, whereas it is roughly the same in the case of B_4C coated fibres. This severe loss of properties observed in the case of the uncoated fibres may be attributed to oxidation effects due to the residual oxygen existing in the nitrogen atmosphere of the preheating furnace. The mechanical properties of the fibres immediately before infiltration were evaluated after a transfer time of 20 s (which represents the maximum time between the end of preheating and the beginning of the infiltration of the preform). A further decrease in the strength is observed for uncoated fibres, which is, however, less important than the decrease observed during preheating. In the same situation, no degradation of the coated fibres could be observed. The protection of the fibres against degradation during the preheating of the preform is thus effectively well realized by the B_4C coating.

The tensile strength of unidirectional composites with a mean volume fraction of fibres of about 55%, was then measured. Observation of the results leads to two conclusions.

First the value σ_R of the ultimate tensile strength (UTS) of T300/Al composites is low. Evaluation of the interfacial strength by means of tension tests on notched specimens leads to a rather high value (46 MPa). Observations of the fracture surfaces of specimens evidence that this rupture is brittle and that practically no pull out of the fibres is observed. All these results show that the low value of tensile strength may be due to the simultaneous effect of two factors: a possible chemical degradation of the fibres

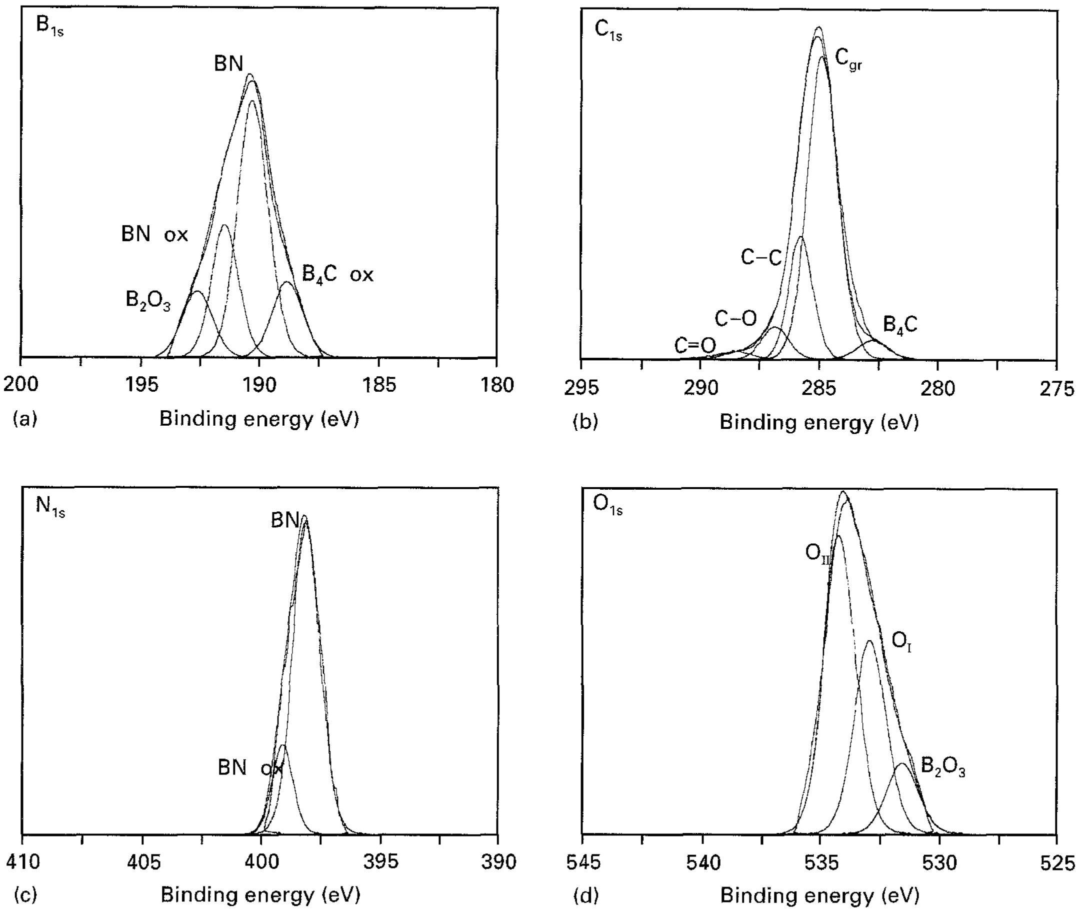

Figure 6 ESCA spectra of (a) B_{1s}, (b) C_{1s}, (c) N_{1s}, (d) O_{1s} from B_4C-coated T300 fibres after oxidation.

TABLE I Tensile strengths of the reinforcement (SFT technique) and of Al/C composites

	Fibres						Composite ($V_f = 55\%$)	
	As-received		Preheated (30 min at 700 °C)		Before infiltration			
	$\langle\sigma_r\rangle$ (MPa)	m	$\langle\sigma_r\rangle$ (MPa)	m	$\langle\sigma_r\rangle$ (MPa)	m	σ_R (MPa)	τ_u (MPa)
T300	2950	5.5	1600	5	1400	3.7	350	46
T300-B_4C	2930	5.4	2800	4.7	2760	5.2	300	40

before infiltration and the rather high strength of the fibre/matrix interface.

Second, in spite of an effective protection of the fibres during infiltration, the ultimate tensile strength of T300-B_4C/Al composites is lower than that obtained with uncoated fibres and failure occurs in a brittle manner. The study of the evolution of the mechanical properties of the reinforcement during preheating shows that the mechanical strength of uncoated fibres should be less or equivalent to that of coated fibres, depending on the importance of the oxidation phenomena. Evaluation of the interfacial strength shows that the value obtained is of the same order than in the previous case.

5. Discussion

The eventual damages due to chemical degradation of fibres are not likely to explain the relative level of the strength of composites elaborated with coated or uncoated fibres. We tried to explain this result by analysing more accurately the behaviour of as-received fibres (Table II). The SFT technique leads to rather close values of the strength of as-received coated and uncoated fibres. Experiments by means of the LBT technique lead to mean values of the rupture strength which are slightly lower than those given by the SFT technique. The same result is observed for the values of the Weibull parameter m. It can also be observed that the rupture strength and the Weibull parameter of coated fibres are slightly lower than those of the uncoated fibres.

However, the consideration of these mean values is not sufficient to explain the large differences in UTS of the composites. In order to explain these results, it is necessary to compare the load–strain curves (P–ε curve) of the as-received T300 and T300–B_4C bundles. These curves are shown in Fig. 7. They have been

TABLE II Weibull parameters obtained by SFT and LBT techniques

T300 fibres	Monofilament		Bundle		
	$\langle\sigma_r\rangle$ (MPa)	m	$\langle\sigma_r\rangle$ (MPa)	m	ε_0 (%)
As-received	2950	5.5	2860	4.4	0.51
B_4C-coated	2930	5.4	2600	3.1	0.37

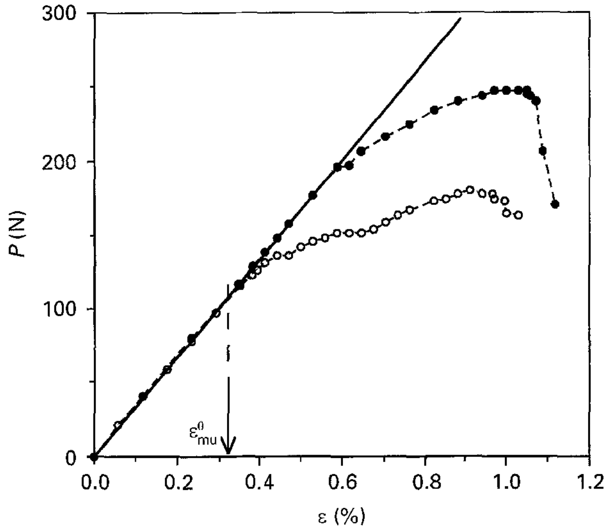

Figure 7 P–ε curves of the as-received T300 (●) and B_4C-coated T300 (○) bundles obtained by the LBT technique.

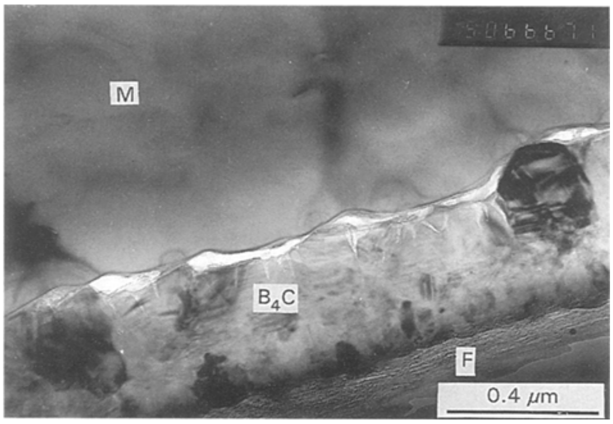

Figure 8 TEM micrograph showing the presence of large thickness coatings.

chosen so that the number of initially loaded fibres was equivalent for the two bundles, which leads to equivalent initial slopes. They exhibit a well defined maximum showing that the failure of the bundle is of a controlled type. Some fundamental differences appear between the two curves: (i) the strain ε_0 corresponding to the beginning of the fibre failures and the ultimate load are much lower for the coated than for the uncoated fibres; and (ii) a wider maximum is observed for T300–B_4C samples.

Electron microscopy observations of the interface between the matrix and the coating showed us that there is no reaction between them, as far as the coating has not been transformed by oxidation phenomena. However, these observations also evidenced a great variation in the thickness of the coating. While the mean value of this thickness is about 50 nm, as was shown on Fig. 4, some observations revealed the presence of coatings of larger thickness (around 400 nm) (Fig. 8). Electron diffraction patterns allowed us to clearly identify that these coatings consist of B_4C, which has not been transformed. Theoretical works [8–10] have shown that the presence of a brittle layer on a fibre may drastically reduce its ultimate tensile strength. This is due to the fact that a circumferential notch is formed on the fibre surface owing to the premature fracture of the coating. This has no effect on the strength of the fibre if the thickness of this layer is low, but reduces this strength beyond a critical thickness δ_c which is given approximately by the relation:

$$\delta_c = \frac{K_{IC}^2}{\pi(1.12\sigma_0)^2}$$

where σ_0 and K_{IC} are the strength and the fracture toughness in mode I of the fibre. A more precise relation is:

$$\delta_c = \frac{K_{IC}^2}{\pi(Y\sigma_0)^2}$$

with

$$Y = 0.5(a/b)^{1/2}[1 + 0.5(a/b) + 0.375(a/b)^2 - 0.363(a/b)^3 + 0.731(a/b)^4]$$

where Y is the K-calibration function depending on the shape of the specimens, a is the radius of the fibre and $b = a + \delta_c$.

Estimations of δ_c by Himbeault *et al.* [11] or Honjo and Shindo [12] for high modulus or high strength carbon fibres give values less than 100 nm which is much lower than the maximum thickness we observed by electron microscopy experiments.

Fig. 9 shows the evolution of the mean value of the strength of T300-B_4C fibres, obtained by the SFT technique, with the mean thickness of the B_4C coating. A strong decrease is effectively observed for values between 50 and 100 nm.

This result and the P–ε curve (Fig. 7) allows us to assume that the rupture of the T300-B_4C composite is due to the brittle coating.

The mean strength of coated fibres is nearly the same as that of uncoated fibres; this signifies that the mean thickness of the coating is such that it has no influence on this strength. However, the low value of ε_0 obtained for coated fibres indicates the presence of low strength fibres. This may be due to local overthicknesses like the one observed by electron microscopy (Fig. 8). Fig. 10 shows that the rupture of the composite occurs in a brittle manner and is thus due to the rupture of a few neighbouring fibres. The probability for this phenomenon to occur at low stress is increased by the presence of defects identified as being overthicknesses. The rupture strength of the material should thus be governed by the mechanical resistance

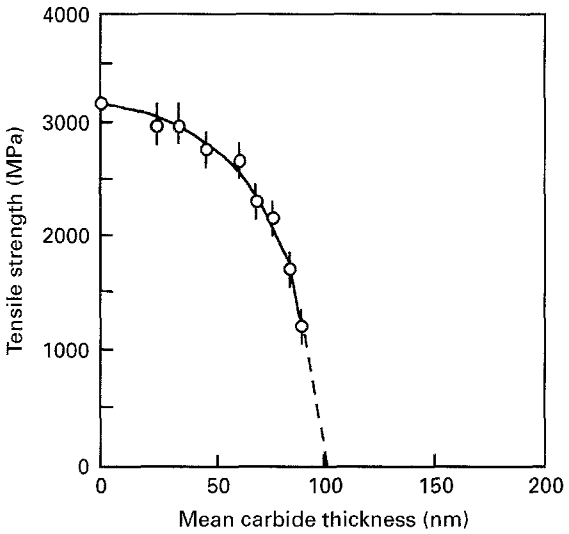

Figure 9 Evolution of the mean value of the strength of B_4C-coated T300 fibres obtained by the SFT technique with the mean thickness of the coating.

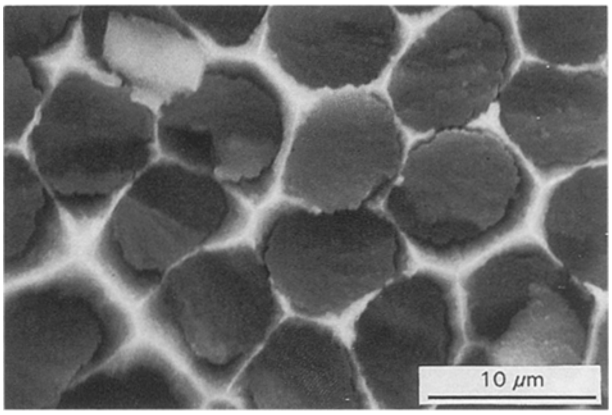

Figure 10 SEM micrograph of the fracture surface of composite samples tested at room temperature.

of the weakest fibres rather than by their mean rupture strength. This is supported by the fact that the theoretical stress suffered by the composite at the strain ε_0, given by $E_c\varepsilon_0$, is equal to 440 MPa. This value is close to the rupture stress of the composite (300 MPa).

6. Conclusions

Microstructural and micromechanical comparative studies on coated and uncoated T300 carbon fibres allowed us to evidence the interest of this coating and its conditions of use.

1. It has been confirmed that the B_4C coating is an effective protection against chemical degradation of the fibre caused by the environmental atmosphere during the preheating stage and by the liquid metal during the infiltration stage.
2. The analysis of the mechanical properties of as-received fibres by the SFT technique leads to rather identical values of the mean rupture stress for coated or uncoated fibres. A more precise analysis of the strength distribution of fibres by the LBT technique shows however a slight increase of the population of the low-strength fibres in the case where they are coated.
3. Microstructural studies show that this low-strength population results from the existence of defects identified as local overthicknesses of the coating.
4. It is shown that these defects have a detrimental consequence on the mechanical properties of unidirectional Al/T300 composites. Thus, a rigorous control of the thickness of the coating is necessary to ensure its efficiency for the mechanical properties of the composite.

Acknowledgement

The authors gratefully acknowledge the Direction de la Recherche et des Études Techniques (DRET) of the Ministère de la Défense for financial support of this study.

References

1. J. C. VIALA, G. GONZALES and J. BOUIX, *J. Mater. Sci. Lett.* **11** (1992) 711.
2. G. GONZALES, C. ESNOUF and J. C. VIALA, *Mater. Sci. Forum* **126–128** (1993) 125.
3. H. VINCENT, C. VINCENT, H. MOURICHOUX, J. P. SCHARFF and J. BOUIX, *Carbon* **30** (1992) 495.
4. T. PIQUERO, H. VINCENT, C. VINCENT and J. BOUIX, *Carbon* **33** (1995) 455.
5. J. BOUIX, R. FAVRE, C. VINCENT, H. VINCENT, S. CARDINAL, P. FLEISCHMAN, P. F. GOBIN and P. MERLE, in Proceedings of the "Colloque Franco-Japonais", Tokyo (Japan) October 1990.
6. C. VINCENT, H. VINCENT, H. MOURICHOUX and J. BOUIX, *J. Mater. Sci.* **27** (1992) 1892.
7. M. R'MILI, T. BOUCHAOUR, P. MERLE, in Proceedings of the $9^{\text{èmes}}$ Journées Nationales sur les Composites JNC9, (France) November 1994, edited by J.-P. Favre and A. Vautrin (1994) p. 1009.
8. M. Kh. SHORSHOROV, L. M. USTINOV, A. M. ZIRLIN, V. I. OLEFIRENKO and L. V. VINOGRADOV, *J. Mater. Sci.* **14** (1979) 1850.
9. S. OCHIAI and Y. MURAKAMI, *ibid.* **14** (1979) 831.
10. S. OCHIAI, K. OSAMURA and K. HONJO, *Mater. Sci. Engng.* **A154** (1992) 149.
11. D. D. HIMBEAULT, R. A. VARIN, K. PIEKARSKI, *J. Mater. Sci.* **24** (1989) 2746.
12. K. HONJO and A. SHINDO, *ibid.* **21** (1986) 2043.

Received 10 August
and accepted 21 December 1995