Interface Tailoring in Carbon Fibres Reinforced Metal Matrix Composites

J. Bouix, M. Berthet, F. Bosselet, R. Favre, M. Peronnet, J. Viala, C. Vincent, H. Vincent

► To cite this version:

J. Bouix, M. Berthet, F. Bosselet, R. Favre, M. Peronnet, et al.. Interface Tailoring in Carbon Fibres Reinforced Metal Matrix Composites. *Journal de Physique IV Proceedings*, 1997, 07 (C6), pp.C6-191-C6-205. 10.1051/jp4:1997616 . jpa-00255715

HAL Id: jpa-00255715

<https://hal.science/jpa-00255715>

Submitted on 1 Jan 1997

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Interface Tailoring in Carbon Fibres Reinforced Metal Matrix Composites

J. Bouix, M.P. Berthet, F. Bosselet, R. Favre, M. Peronnet, J.C. Viala, C. Vincent and H. Vincent

Laboratoire des Multimatériaux et Interfaces (LMI), UMR 5615 du CNRS, Université Claude Bernard Lyon I, 43 boulevard du 11 novembre 1918, 69622 Villeurbanne, France

Abstract : The fabrication of high performance metal matrix composites requires the optimization of the interfacial bonding, which supposes a strict control of the reactivity and of the wettability between the matrix and the reinforcement, specially for materials produced by casting techniques. In this scope, two methods are described consisting on the one hand, in the surface treatment of carbon fibres by a particular type of CVD and, on the other hand, in modifying the composition of the matrix. The two methods can be used either separately or in combination, successful tailoring of the interface being the result of thermodynamic or kinetic effects.

1. INTRODUCTION

The mechanical behaviour of inorganic composites (metallic and ceramic matrix) depends obviously on the characteristics of the reinforcement, consisting for instance of fibres and on these of the matrix, but also mainly on the nature of the interfacial bonding between the fibre and the matrix [1, 2].

This bonding must be strong enough to provide a good load transfer from the matrix to the fibres, but weak enough to trap the cracks by diverting them along the interface and to prevent their propagation through the fibre with a brittle rupture of the composite.

In the case of metallic matrix composites reinforced by ceramic fibres, the strength of the interfacial bonding is generally connected with the chemical interaction between the matrix and the fibre during the processing of the material. Relating to this problem, carbon fibres are very performant because of their lightness and high mechanical characteristics, which can be modified by changing the nature of the precursor and the conditions of their elaboration. For instance, those obtained by pyrolysis of a polyacrylonitrile yarn (T300 type) generally little graphitized, have a high tensile strength but are very reactive particularly with metals like aluminium, giving a carbide, or with oxygen, losing weight above 400°C in air. On the contrary, those obtained from a pitch are more graphitized, less reactive and have a higher modulus.

During the fabrication of an aluminium matrix composite reinforced by carbon fibres, it is difficult to prevent the formation of aluminium carbide, which weakens the fibre and causes the composite to become highly sensitive to corrosion by humid air.

a)

b)

Figure 1: P 55 carbon filament after treatment, during 15 min at 680°C in pure aluminium, showing a strong interaction giving aluminium carbide (a), during 5 hours at 730°C in pure magnesium without reaction or wetting (b).

As shown in figure 1a, this carbide has no protective effect on the fibre and it is then necessary to reduce as much as possible its formation. On the contrary, neither reactivity nor wettability occur between the same fibre and molten magnesium and the impregnation is very bad as shown in figure 1b. In the latter case, it is necessary to create a controlled reactivity for obtaining a satisfactory composite.

As far as we are concerned, we have developed two complementary approaches in view of optimizing this chemical interaction between the matrix and the reinforcement. The first, specially adapted to carbon fibres, consists in coating each filament (typically a few thousands) by a thin carbide layer protecting it against oxygen or metals. Such a result is obtained by using Reactive Chemical Vapor Deposition (RCVD), in which the coating growth is self-regulated by the diffusion of carbon through the as-formed layer. The second lies in incorporating into the matrix an addition element decreasing its chemical reactivity with the fibre coatings or, conversely, promoting a controlled reaction at the matrix/fibre interface.

2. CERAMIC COATINGS ON CARBON FIBRES BY RCVD

Over recent years, a great deal of work has been done in the area of providing a thin coating of ceramics on carbon fibres to solve the problems of interfacial compatibilities in aluminium composites. An encountered problem arises from the difficulty in coating each filament of a tow, in particular, the deposit on the tow periphery must be avoided, and there are few methods which are satisfactory. Among these methods, reactive CVD or RCVD is interesting because the treatment takes place at normal pressure and the coating duration is lower than 1 min. In the RCVD process, the fibre is heated in a gaseous mixture which reacts with the carbon fibre, resulting in a conversion coating of carbide. This method is different from classical CVD because the gas phase brings only one of the two elements constituting the carbide, the carbon being brought by the fibre itself. The carbide coating is not grown on the fibre, but it results from the chemical transformation of a superficial layer of this substrate, which gives a very good bonding and adherence. The chemical reaction between the carbon of the fibre and a gas precursor provides a self regulation of the coating thickness, because the coating growth requires the diffusion of carbon through the formed carbide layer. In our laboratory, single layers of SiC, TiC or B₄C, mixed layers of TiC-SiC or SiC-B₄C and double layers of SiC/B₄C or B₄C/TiB₂ have been applied to different carbon fibres using RCVD method. Double layer coatings have been performed by a succession of two RCVD: formation of a carbide layer and conversion of a part of this carbide into a new ceramic (carbide, boride). The successful reinforcement of a composite with carbide coated fibres will require a coating of sufficient thickness to afford protection to the fibres but thin enough to limit the strength decrease of the fibre. Therefore, it is important to optimize the RCVD conditions and to deposit a C_{pyro} film on the raw fibers before the RCVD process. The effect of the various coatings on the tensile strength of the as-coated fibres and on the protection against aluminium and air were investigated.

2.1 Experimental techniques

A pilot plant in our laboratory permits the continuous coating of fibres with a total length of up to several hundred meters (Figure 2). The reactor consists of a horizontal silica tube (22 mm inner diameter) closed at either end by a stainless steel flange.

Figure 2: Schematic diagram of the coating apparatus

The flanges contain stainless steel spools; the spools permit the fibres to be transported through the reactor at a rate varying from 1 to 50 m.h⁻¹. The fibre is heated in an induction furnace; the temperature of the susceptor is measured by an optical pyrometer and it is taken as the deposition temperature. TiCl₄ is saturated in hydrogen and SiCl₄ vapour is carried in the reactor by hydrogen or by argon. The flow rates of H₂, BCl₃, C₃H₈ and Ar are monitored by gas mass flow meters. The RCVD experiments are performed under atmospheric pressure. A vacuum pump permits to evacuate the reactor before the coating process and to realized C_{pyro} films from C₃H₈ under low pressure in the same apparatus.

Three kinds of carbon fibres were used in this study : two high strength fibres (T300-99 and M40B from Torayca) and one high modulus fibre (FT500 from Tonen). T300-99 fibres are commercialized without surface treatment or sizing treatment. Prior to use, surfaces of M40B and FT500 fibres were cleaned of any organic substances by passing them through a furnace containing an argon atmosphere at 1000°C. After deposition, the samples were characterized using various techniques such as XRD, XPS, SEM, Raman, TEM and EPMA. Strength measurements performed on single filaments (20 mm) complete the characterization (crosshead speed : 0.1 mm.min⁻¹).

2.2 Thermodynamic approach

In order to improve the understanding of the RCVD process and the knowledge of its behaviour with respect to variations in temperature or concentrations of the various precursors, a chemical equilibrium thermodynamic analysis of the gas reactants-substrates system is required. In a RCVD system, the carbon substrate participates in the reaction, and its surface is covered by a layer of a new solid phase which isolates the carbon from the gaseous mixture. The carbide layer can grow as a result of carbon diffusion through the layer. The carbide formed on the substrate depends on the availability and the concentration of carbon at the reaction interface. Thermodynamic predictions remain possible on the basis of a heterogeneous system in which the parameters are the temperature, the initial composition of the gas phase and the amount of carbon. RCVD phase diagrams have been established in other publications [3-8]. The RCVD diagrams predict condensed phases in equilibrium under the given conditions of interest. Figure 3 is an example of a predominance diagram at 1300K. The initial system is defined by the number of moles of each species (n°_i). It evidences 4 domains : TiC_{0.95} + C, TiC_y (0.54 < y < 0.95), TiC_{0.54} + Ti and G (gaseous domain). This diagram shows that the chemical composition of a titanium carbide coating would not be constant during a RCVD experiment. Nevertheless, the use of a TiCl₄ partial pressure higher than 10⁻² atm permits to reduce the C gradient in the coating, and in the case of thin layer (< 0,1 μm) on carbon fibres, the C diffusion through the layer is quick, and it is supposed that the carbide composition is near TiC_{0.9}.

Figure 3: RCVD phase diagram in the TiCl₄-H₂-C(gr) system. The different lines indicate the composition y of the TiC_y phase at equilibrium under given conditions. It is noted that y increases with the initial pressure of TiCl₄ ($p^{\circ}\text{TiCl}_4$).

During a RCVD process, a gas mixture of constant composition sweeps the reactor continuously. The product gases are then forced out of the reactor. In other words, the time is an important parameter since the amount of gaseous reactants can vary from zero to infinity between the beginning and the end of the treatment and thus, transient solid phases may be formed. It is possible to use a predictive model on the basis that the RCVD process can be considered as a sequence of successive steps of same duration, at constant temperature.

Figure 4: Thermodynamic analysis for the various studied systems ($R = n^\circ_{\text{H}_2}/n^\circ_{\text{chloride}}$)

For the thermodynamic study of a coating, the method consists in calculating equilibrium compositions for different heterogeneous solid-gas systems: the first system is defined by an excess of the solid phase ($n^\circ_{\text{C}} = 1 \text{ mole}$, or $n^\circ_{\text{B}_4\text{C}} = 1 \text{ mole}$) and by a small quantity of gaseous reactants ($n^\circ_{\text{chloride}}$, $n^\circ_{\text{H}_2}$), each following system consists of the same values $n^\circ_{\text{chloride}}$ and $n^\circ_{\text{H}_2}$ and the amount of solid phases found in the precedent calculation. This model supposes that equilibrium is reached quickly; it enables the prediction of the chemical nature of the deposited phases as a function of reaction conditions, e.g. the total quantity of chloride ($n^\circ_{\text{t, chloride}}$) introduced in the reactor, and states more precisely the effects of treatment time on the chemical composition of the coating. It has been very useful for the choice of the input gas composition allowing the coating of a carbon fibre by a carbide, a mixture of carbides or a boride.

The curves a-d in figure 4 illustrate this approach for four cases, they give the variations of the mole numbers of solid species as a function of mole number of chloride ($n^{\circ}_{t, \text{chloride}}$) with all other parameters held constant at an arbitrary set of standard conditions (pressure = 1 atm, temperature, composition of the initial gaseous phase). For each case, two curves are given to evidence the influence of the R ratio between $n^{\circ}_{\text{H}_2}$ and $n^{\circ}_{\text{chloride}}$.

From this thermodynamic approach, the RCVD conditions can be deduced:

- In the $\text{SiCl}_4\text{-H}_2\text{-C}$ system, the two curves show that pure SiC or Si-SiC mixture can be deposited (figure 4a). A low dilution ratio R inhibits the silicon deposition.
- The formation of B_4C requires the H_2 presence in the input gas phase. The calculations predict always codeposition of B_4C and B (figure 4b). Nevertheless, B deposit amount will be limited by using an input BCl_3 -rich mixture.
- In the case of a C substrate heated in a $\text{SiCl}_4\text{-BCl}_3$ mixture, the thermodynamics foresees the formation of SiC, B_4C and SiB_6 (figure 4c). The boron silicide amount increases with H_2 partial pressure. The curve drawn for $R = 4$ shows that SiC- B_4C codeposition is possible without SiB_6 and that the ratio $n_{\text{SiC}}/n_{\text{B}_4\text{C}}$ evolves with the step number. Thus mixed deposits of different compositions can be obtained in a RCVD process.
- B_4C conversion into TiB_2 is thermodynamically possible (figure 4d). Conversion is improved when increasing H_2 partial pressure; however with a very rich- H_2 mixture, C coming from decomposition of B_4C can react with TiCl_4 to form TiC.

2.3 Experimental results and discussion

2.3.1 Coatings of a single layer of carbides

The coating of SiC, TiC and B_4C on the carbon fibres was carried out using the reaction between the carbon of the fibre and a gaseous mixture of H_2 and SiCl_4 , TiCl_4 or BCl_3 , at normal pressure and at a temperature higher than 1000°C . Table 1 gives a survey of the main temperatures and residence times for obtaining a coating thickness between 20 to 50 nm for each deposit. The layer thickness was determined from the weight of the bundle, the chemical analysis of the elements and the density of the carbide (3.21 g.cm^{-3} for SiC, 4.91 g.cm^{-3} for TiC and 2.52 g.cm^{-3} for B_4C) with the hypothesis that the thickness is the same on all the filaments of the bundle. Growth rate of a carbide layer is controlled by the diffusion of C atoms through this layer, thus the thickness increases linearly with square-root of the deposition time. However, as the treatment time was lower than 2 minutes, differences between the parabolic growth law and the experimental thickness was observed. This difference is certainly connected to microstructure and chemical reactivity of the fibres. Most of the graphite crystallites in the FT500 fibre have their basal planes aligned parallel to the fibre direction, thus few plane edges are exposed. Since the edges of the graphite planes are chemically much more reactive than the plane faces, higher-modulus fibres are less reactive than lower-modulus ones.

Table 1 : RCVD conditions for the formation of a single carbide coating on carbon fibres, R being the ratio between the flows of H_2 and halide

Coatings	RCVD conditions	thickness (nm)		
		T300	M40B	FT500
SiC	1200°C - 1 min - $R = 2.3$	40	35	20
TiC	1000°C - 0.8 min - $R = 59.6$	30	30	20
B_4C	1300°C - 1.5 min - $R = 1.5$	40	40	30
$\text{B}_4\text{C-SiC}$	1250°C - 1.5 min - $R = 10$	50		

SEM observation revealed that the surface morphology and the average diameter of the coated fibres are identical to those of raw fibres. The presence of the coating is evident after a complete gasification of the fibre carbon. The residue of a SiC coated fibre is shown in Figure 5. It consists in a thin and continuous shell that replicates the grooved morphology of the T300 fibre. This observation is the proof of a continuous initial carbide layer.

Figure 5: SiC-SiO₂ continuous shell evidenced after combustion of carbon.

The effect of the different carbides on the tensile strength was investigated as a function of the thickness of the carbide layer. The results of the tensile tests for T300/SiC, T300/TiC and T300/B₄C fibres are shown in table 2. All strength data are related to the total cross section, carbon filament plus coating.

Table 2 : Tensile strength of carbide coated fibres (MPa)

thickness (nm)	10	20	50	70	100
T300/SiC	3000	2900	2000	1700	1500
T300/TiC	2950	2500	1500	1200	1000
T300/B ₄ C	3050	3000	2500	1700	870
Weibull parameter	5 - 5.5	4 - 4.5	3.6 - 4	2.3 - 3.5	1.5 - 1.9

It was suspected that the reduction of the strength is caused by the presence of a brittle coating on the surface of carbon fibres and by the consumption of the carbon to give carbide and hydrocarbon gas during the treatment. Moreover, temperature leads to an improvement in the degree of graphitization of the fibres. A second series of strength measurements were performed after the carbide coating had been removed with a mixture of HNO₃ and HF. No practical difference in strength was observed between the carbide-removed fibres and the raw ones. This suggests that the observed change in the strength of the layered fibre is not caused by the attack of the carbon of the fibre during the RCVD process but it is caused by the existence of a brittle coating causing notches due to premature fracture. The fibres and the coating have different thermomechanical parameters as it is shown in table 3.

Table 3: Thermomechanical parameters

Materials	α (10 ⁻⁶ .°C ⁻¹)	ϵ_R x 100	σ_R (MPa)	K _{1C}	E (GPa)	ν (Poisson)	Ref.
SiC	4.8	0.09	400	4.4	450	0.14	[9]
B ₄ C	4.5	0.09	345	2.9-3.7	360-460	0.14 - 0.18	
TiC	7.7	0.18	690-855	5	410	0.19	[9, 10]
T300	$\alpha_L = -0.5$ $\alpha_T = 6.8$	1.5	3180		$E_L = 210$ $E_T = 23$	$\nu_L = 0.26$ $\nu_T = 0.39$	[11, 12]

Accordingly, when a tensile stress is applied to such a fibre, the coating layer first fractures and cracks are formed. When the thickness of the layer is above a certain value, the crack extends into the carbon fibre if the interfacial bonding between the coating and the carbon fibres is strong. In such a case, the strength of the coated fibre is proportional to the inverse of the square-root of the layer thickness [13-14]. The results of the tensile tests for T300-SiC, T300-TiC and T300-B₄C fibres are plotted against the inverse of the square-root of the layer thickness in Figure 6 and they confirm that all the coated fibres are fractured by such a mechanism. For the three systems T300/TiC, T300/B₄C and T300/SiC, the strength of the fibres begins to decrease when the thickness of the carbide layer is higher than 16 nm.

Figure 6: Variation of σ_R as a function of $(\text{thickness} - \text{nm})^{-1/2}$

2.3.2 Double coatings

2.3.2.1 Double coating : Pyrolytic carbon - carbide. The raw fibres were coated with a pyrolytic carbon film before the RCVD process. Propane was used as a source of carbon, and argon was used as a carrier gas. As the deposition rate of pyrolytic carbon must be controlled by the reaction of cracking and not by the diffusion rate of the gases to the fibre surface, the deposition was performed under 10 kPa. The concentration of propane was 20% while maintaining a total flow rate of 120 sccm. For providing the formation of bridges, the maximum C coating thickness is limited up to 0.1 μm .

The results of the tensile tests for C/C_{pyro} fibres are shown in table 4. Substantial improvement in strength over that of the raw fibres was observed. Pyrocarbon has not only higher values of fracture elongation due to their laminar structure parallel to the surface, but also diminish the notches on the fibre surface itself.

Table 4: Tensile strength values of fibres coated by a carbon film

	σ_R (MPa)	
	without coating	with C _{pyro} coating
T300-99	3150	4250
M40B	2740	3400
FT500	3650	4300

The σ_R values of fibres coated a double layer of carbon and of a carbide are higher than ones measured on the fibres coated with the same carbide but without carbon underlayer (table 5). Most of them are higher than the one of the raw fibres. These results give proof that the carbon film acts effectively as an arrester of cracks formed in the upper layer of carbide.

Table 5: Tensile strength of fibres coated doubly by a carbon layer and a carbide layer

	without coating	σ_R (MPa)		
		C _{pyro} + SiC	C _{pyro} + TiC	C _{pyro} + B ₄ C
T300-99	3150	3200	2700	3800
M40B	2740	3200	3750	-
FT500	3560	3900	-	3480

In this case, the interfacial bonding is weak, debonding occurs owing to shear stress at the interface during the deformation of the fibre under tension, and the crack edge is blunted in diminishing stress concentration. As a result, no loss in fibre strength takes place. Figure 7 confirms this hypothesis in the case of a TiC/C_{pyro}/FT500 fibre: after a weak traction applied to a coated fibre, only the carbide layer is cracked.

Figure 7: SEM image of FT500 fibre covered by a double layer $C_{\text{pyro}}\text{-TiC}$

2.3.2.2 Double coating: carbide - carbide or carbide - boride. The raw fibres were coated with a first film of carbide, then a second RCVD process was performed to transform a part of the carbide into a new layer. Double coatings $\text{SiC}/\text{B}_4\text{C}$ and $\text{B}_4\text{C}/\text{TiB}_2$ were obtained by this way. After optimization of the coating conditions, the mechanical properties of the as-coated fibres are near the ones of the fibres with a single coating (table 6).

Table 6: Effect of a carbide coating on the failure strength of T300 fibres

Coated fibres	σ_R (MPa)	$\Delta\sigma_R/\sigma_R$ (%)	Thickness (nm)
T300 (SiC)	2630	- 15	SiC : 20
T300 (B_4C)	2870	- 19	B_4C : 30
T300 ($\text{B}_4\text{C}/\text{SiC}$)	2750	- 19	B_4C : 20 SiC : 10
T300 ($\text{B}_4\text{C}/\text{TiB}_2$)	2200	- 30	B_4C : 24 TiB_2 : <10

2.3.3 Protecting effect of the coatings

The efficiency of SiC, B_4C and SiC- B_4C mixed layer was demonstrated in the case of Al/C composites manufactured by squeeze-casting technique (table 7).

Table 7: Tensile strengths of coated T300 fibres and Al-C composites

	σ_R (MPa)	
	fibres	Al-C composites
T300	3150	370
T300/TiC	2500	425
T300/SiC	2700	1050
T300/ B_4C	2870	990
T300/ B_4C -SiC	2970	-
T300/ B_4C -SiC extracted from Al matrix	3100	-

The SiC, B_4C and B_4C -SiC coatings prevent reaction between the fibre carbon and aluminium. Pull-out was observed on rupture facies of composites (Figure 8a) and no reaction product was evidenced at the interface by TEM as it is shown in Figure 8b [15].

Figure 8a: SEM observation of the rupture facies of a Al-T300/SiC composite.

Figure 8b: TEM observation of the interface in a Al-T300/B₄C composite.

This absence of reactivity was confirmed by tensile tests on monofilaments performed after metal dissolution (see table 7).

The following results confirm that the single or duplex layers of carbide coatings are able to slow down the gasification of carbone fibres in oxygen. For this study, oxidation experiments in dry flowing oxygen were carried out at 600°C via thermogravimetric analysis. The coated T300 fibre behaviour is summarized in Figure 9.

Figure 9: Thermogravimetric curves of coated T300 (600°C, $p_{O_2} = 1$ atm)

The thermogravimetric curves confirm that all the B₄C-based coatings have a better protecting behaviour than the SiC based ones, whatever the oxidation time. Borosilicate and boron oxide glasses are formed during the exposure and provide a similar inhibition behaviour during the first two hours of exposure to oxygen. For a longer duration, the mixed layer seems to be the best protective coating because borosilicate coating is more stable than boron oxide [16].

Concurrently, we have measured the mechanical properties of the fibres as a function of the oxidation time (Table 8). The σ_R values of the raw T300 fibre drop strongly. Above ten minutes, the filaments are very brittle and they can not be tested. B₄C-based coated fibres lead to better results than SiC-coated fibres. The double layer and the mixed layer coated fibres are found to retain the σ_R values during an oxidation run time of 30 minutes : the decrease is only 0 - 7% compared to the initial σ_R value, whereas the single B₄C or SiC coated fibres present respectively 15% and 30% strength losses. Table 8 evidences that the tensile strength lowering and the measured weight losses have not a direct relation.

Table 8: Evolution of fibre tensile strength and weight loss as a function of oxidizing time, at 600°C.

Fibres	Time (min)	Weight loss (%)	$\Delta\sigma/\sigma_R$ (%)
T300	0	0	0
	10	- 10	- 40
	15	- 20	-
T300 (SiC)	0	0	0
	10	- 0.6	-15
	20	- 1.2	- 30
	60	- 5.1	- 40
T300 (B ₄ C)	0	0	0
	30	1	- 15
	60	1	- 30
T300 (SiC/B ₄ C double layer)	0	0	0
	30	- 0.2	0
	60	- 2.1	0
T300 (SiC-B ₄ C mixed layer)	0	0	0
	30	-1	-7
	60	-2	- 25

3. OPTIMIZATION OF THE METAL MATRIX COMPOSITION

In addition to surface treatments, a better control of the reactivity and bonding in carbon fibre reinforced metal matrix composites may be achieved by optimizing the composition of the matrix. For reactive systems such as Al-C composites, the composition of the matrix will be modified in order to reduce its chemical reactivity with the outer fibre coatings. For non-reactive systems such as Mg-C composites, the objective will be to induce a controlled interfacial reaction promoting wetting and bonding. Such approaches will be illustrated by the three forthcoming examples.

3.1 Reactivity control at the Al/SiC interface

In the continuation of previous works by Bermudez [17] and by Iseki et al. [18], a model based on stable and metastable phase equilibria has been developed for describing the chemical interaction under atmospheric pressure between Al and SiC at low and medium temperatures [19]. According to this model, an invariant transformation (quasi-peritectic reaction) occurs in the Al-C-Si system at $650 \pm 3^\circ\text{C}$. This transformation which can be written :

corresponds to a non-reactive/reactive transition for the Al-SiC couple (L_0 designates a binary Al-Si liquid containing 1.5 ± 0.4 at.% Si). In other words, SiC is in thermodynamic equilibrium with solid aluminium at temperature lower than 650°C and reacts with solid ($650 < T < 660^\circ\text{C}$) or liquid ($T > 660^\circ\text{C}$) aluminium at any temperature higher than 650°C , producing Al_4C_3 and silicon. The phase field arrangements typical for these two different temperature ranges are represented in Figure 10.

According to this model, no reaction will occur at the Al/SiC interface as long as the temperature will remain lower than 650°C (in this low temperature range, the mutual solubilities between Al and SiC are negligible). This is illustrated by the micrograph presented in Figure 11 that has been taken on a α -SiC quasi-single crystalline particle annealed for a very long time (1200 hours) at 570°C in the presence of pure Al. On the other hand, decomposition of SiC into Al_4C_3 and Si will generally be observed at temperatures higher than 650°C , the reaction rate increasing with the temperature. Figure 12 illustrates the rapid formation, via a dissolution-precipitation mechanism, of Al_4C_3 crystals at the surface of α -SiC particles after 1 hour heating at 1000°C [20]. It can however be remarked that a three-phased monovariant equilibrium between SiC, Al_4C_3 and an Al-Si liquid phase exists in the ternary Al-C-Si phase diagram at temperatures higher than 650°C . The silicon content of the Al-Si liquid phase involved in this monovariant equilibrium has been determined at different temperatures: it increases regularly from 1.5 at.% at 650°C to 12.7 at.% Si at 1000°C [19]. Consequently, if silicon is added in sufficient amounts to the aluminium matrix, decomposition of SiC can be avoided. This is illustrated by the micrograph presented in Figure 13

where it can be seen that no reaction has occurred at the surface of α -SiC particles heat-treated for 1 hour at 1000°C (same conditions as in Figure 12) in an Al-Si alloy containing 13 at.% Si. Practically, to avoid the formation of Al_4C_3 at the Al-SiC interface at 730°C (the highest temperature at which liquid phase infiltration of fibre reforms is generally performed) the silicon content in the aluminium matrix should be higher than or equal to 5 at.% [19].

Figure 10: Typical isothermal sections of the Al-C-Si phase diagram below and above the invariant transformation at 650°C

Figure 11: The Al/ α -SiC interface after annealing for 1200 hours at 570°C: no interface reaction.

Figure 12: Strong reaction at the Al/ α -SiC interface after heating for 1 hour at 1000°C.

Figure 13: Al/ α -SiC interface after 1 hour heating at 1000°C.

In this first example, the control of the chemical interaction at the matrix/reinforcement interface is based on thermodynamics: the operating parameters are adjusted (temperature lower than 650°C or addition of a sufficient amount of silicon to aluminium) in such a way that equilibrium conditions are realized. We will now describe another example, the Al/TiC couple, where the control of the interfacial reaction may be based either on thermodynamics or on kinetics.

3.2 The case of the Al/TiC interface

From a thermodynamic point of view, the chemical behaviour of the Al/TiC interface is opposite to that of the Al/SiC interface in the sense that this interface is reactive at low temperature and non-reactive at medium

or high temperature. The reactive/non-reactive transition corresponds to the invariant transformation (quasi-peritectic reaction) :

where L designates an Al base liquid phase containing about 0.3 at.%Ti and TiC_x a carbon-rich titanium carbide phase with $x > 0.9$. This transformation has been found to occur at $812 \pm 15^\circ\text{C}$ [21]. Consequently, as shown by Figure 14, aluminium and titanium carbide react at temperatures lower than 812°C to give the two solid phases Al_4C_3 and Al_3Ti and are in equilibrium at temperatures higher than 812°C . Exploitation of these thermodynamic principles provides a first mean to avoid the chemical interaction at the Al/TiC interface. It suffices to increase the processing temperature up to a level higher than 812°C and to cool rapidly the material at the end of the process. It can be remarked that in the absence of precise thermodynamic data, such a solution would not have appeared as obvious.

Figure 14: Isothermal sections of the Al-C-Ti phase diagram below and under the invariant transformation at 812°C .

Figure 15: TiC_x single crystal after annealing for 150 hours at 730°C in a large excess of pure aluminium.

Figure 16: TiC_x single crystal after annealing for 150 hours at 730°C in a 1 at.%Ti Al-Ti alloy.

Another means to control the interfacial reaction between aluminium and titanium carbide has arisen from further investigations of the kinetic aspect of the chemical interaction at the Al/TiC interface. In these investigations, we have found that decomposition of titanium carbide by reaction with liquid aluminium below 812°C proceeded in two successive stages:

- in a first stage, Al_4C_3 crystals nucleate and grow whereas titanium simply dissolves in liquid aluminium. This first stage reaction which progresses at a rather fast rate is depicted by the SEM

micrograph reported in Figure 15. Al_4C_3 crystals grown by dissolution-precipitation can be observed near the surface of a carbon-rich titanium carbide single crystal that has been immersed for 150 hours at 730°C in a large excess of pure aluminium. It can be noted that the single crystal surface has become rough while the aluminium matrix still exhibits a single-phased appearance;

- when the titanium content in the aluminium base liquid has attained its saturation value (about 0.2 at. % Ti at 730°C), one enters in a second stage reaction where Al_4C_3 continues to grow as previously but where Al_3Ti crystals also nucleate and develop in the liquid phase. This second stage reaction proceeds, however, at a much slower rate than the first one. As illustrated by the SEM micrograph reported in Figure 16, no trace of Al_4C_3 is visible at the interface between a TiC_x single crystal and a Ti-saturated aluminium matrix after 150 hours immersion at 730°C . In that case, the surface of the TiC_x single crystal is smooth. Al_3Ti globular crystals are present in the matrix but they do not result from the decomposition of TiC_x ; they were formed at the beginning of the heat-treatment by precipitation from the Ti-saturated aluminium base alloy (initial Ti content 1 at. %).

Decomposition of TiC_x by liquid Al below 812°C can thus be controlled, to a certain extent, by exploiting these chemical kinetics data. Accordingly, if the aluminium matrix is just saturated in titanium prior to liquid phase processing below 812°C , only the second stage reaction will be possible at the metal/carbide interface and this second stage reaction will progress only at a very slow rate.

3.3 Reactivity control at the Mg/C interface

In the two preceeding examples, the considered systems were reactive and the objective was to avoid the degradation of the fibre coatings, SiC or TiC, by chemical reaction with the matrix and the subsequent formation of a too strong interfacial bonding. In this third example concerning the Mg/C couple, the system is essentially non-reactive [22] and liquid magnesium does not wet carbon, as illustrated by Figure 1b. In that case, the objective will then consist in promoting a controlled reaction in order to improve wetting and bonding at the metal/fibre interface.

It has been found that this could be achieved by adding little amounts of zirconium to the magnesium matrix [23]. Effectively, when a carbon fibre tow (3000-6000 filaments) is immersed at $650\text{-}750^\circ\text{C}$ under an atmospheric pressure of argon in a liquid magnesium base alloy saturated in zirconium, i.e. containing 0.15-0.2 at. % Zr, the liquid metal penetrates within the filaments of the tow and the latter can be completely infiltrated by the matrix, as shown by Figure 17a. One of the main factors that determines this very interesting wetting behaviour is the fact that a layer of zirconium carbide ZrC_x is rapidly formed at the surface of the carbon filaments by chemical reaction with the liquid alloy. Figure 17b illustrates three characteristic features of this layer: microcrystalline character, continuity and uniform thickness. It also shows that after 1 hour immersion at 680°C , the ZrC_x layer surrounding M40B type carbon fibres (ex-PAN, 6 μm in diameter) has a mean thickness of 0.5 μm . For a shorter immersion time, 15 minutes, the ZrC_x layer is thinner, about 0.25 μm , but already continuous (Figure 18).

Figure 17: M40B carbon filaments embedded in a Zr-saturated Mg-Zr matrix (0.15-0.2 at. % Zr) after immersion for 1 hour at 680°C ; (a): general view; (b) detailed view showing the ZrC_x interfacial layer about 0.5 μm thick.

In fact, a study of the mechanism of the chemical reaction between carbon fibres and liquid Mg-Zr alloys has revealed that the growth of the ZrC_x layer proceeds via a unidirectional solid state diffusion of carbon from the fibre surface to the Mg-Zr matrix. As a consequence of this unidirectional diffusion of carbon, Kirkendall voids form at the outer part of the carbon fibres, just below the ZrC_x/C interface. A weakened zone is then created between the fibre and the ZrC_x layer and it is in this weakened zone that cracks will propagate when a stress is applied to the material. Such a situation is depicted in Figure 19. It can then be easily understood that, by varying the infiltration time and temperature, one can adjust to a certain extent the strength of the bonding between the carbon fibres and the Mg-Zr matrix.

Such an interface tailoring is rendered possible by the particular mechanism of growth of the ZrC_x reaction layer at the metal/fibre interface. Effectively, if the growth of the reaction layer does not proceed by solid state diffusion of carbon but by liquid phase dissolution-recrystallisation, which is the case if aluminium replaces zirconium in the magnesium matrix, a carbide reaction layer, Al_2MgC_2 [24] also forms but this layer is very irregular and the fibre is severely attacked. In that case, the interface exhibits exactly the same morphology as that presented in figure 1a.

Figure 18: Detailed view of the interface between M40B carbon filaments and a Mg-Zr alloy (0.15-0.2 at.% Zr) after immersion for 15 minutes at 680°C: the ZrC_x layer thickness is about 0.25 μm.

Figure 19: Crack propagation along the C/ ZrC_x interface (weakened by Kirkendall voids) in a M40B/Mg-Zr micro-composite.

4. CONCLUSION

As already emphasized, avoiding the degradation of the reinforcement by chemical interaction with the matrix and controlling the nature and strength of the interfacial bonding are two keys to the development of high performance metal matrix composite materials. As shown by the different results reported in the present paper, this can be achieved in C-Al or C-Mg composites both by surface treatment of the reinforcing fibres and by optimization of the metal matrix composition. In this regard, an Al-Si matrix should be more appropriate than a pure Al matrix for infiltrating SiC-coated carbon fibres near 700°C. In the same connection, using a Ti-saturated Al matrix should be better than using pure Al for infiltrating carbon fibres with a TiC coating.

Whatever the solution developed, it is clear that successful tailoring of the interface properties of composite systems will always require a thorough understanding of the chemistry of these systems, in terms of thermodynamics, kinetics and reaction mechanisms. It is with this care in mind that we are conducting further studies on metal matrix composites. In the case of carbon fiber reinforcements, this task is complicated by the existence of a wide variety of fibers that may exhibit very different chemical reactivities towards metal matrices.

References

- [1] Chawla K.K. in "Materials Science and Technology", Cahn R.W., Haasen P. and Kramer E.J. Eds., Vol. 13 (VCH, Weinheim, 1993) p. 121-182.
- [2] Maruyama B., Barera E.V. and Rabenberg L., in "Metal Matrix Composites Processing and Interfaces", (Everett R.K. and Arsenault R.J. Eds., Academic Press, 1991) p.181-216.

- [3] Bouix J., Cromer M., Dazord J., Mourichoux M., Ponthenier J.L., Scharff J.P., Vincent C., Vincent H., Bernard C., *Rev. Int. Hautes Temp. Réfract. Fr.* **24** (1987) 5-26
- [4] Vincent C., Dazord J., Vincent H., Bouix J., *Thermochim. Acta* **138** (1989) 81-96
- [5] Vincent H., Mourichoux H., Scharff J.P., Vincent C., Bouix J., *Thermochim. Acta* **182** (1991) 253-272
- [6] Piquero T., Bouix J., Scharff J.P., Vincent C., Vincent H., *J. Alloys and Compounds* **185** (1992) 121-144
- [7] Vincent C., Piquero T., Berthet M.P., Vincent H., Bouix J., *Mater. High Temp.* **13**(1) (1995) 17-28
- [8] Piquero T., Vincent H., Vincent C., Bouix J., *J. Mater. Synt. Process.* **3**(4) (1995) 231-245
- [9] Shaffer P.T.B., *Engineered Materials : Handbook of Ceramics and Glasses*, ASM International, vol.4, pp. 804-811
- [10] Toth L.E., "Transition metal carbides and nitrides", Academic Press, 1971
- [11] Villeneuve J.F., Naslain R., Severy J., Fourmeaux R., ECCM5, Bordeaux 7-10 April 1992, A.R. Bunsell, Jamet, A., Massiah ed., pp.753-758
- [12] Menessier E., Dumont J.P., Guette A., Pailler R., Rabardel L., Naslain R., *Ceram. Engineering Science Proceedings* **10** (1989) 1426-1334
- [13] Ochiai S., Murakami Y., *J. Mater. Sci.* **14** (1979) 831-840
- [14] Ochiai S., Murakami Y., *Metall. Trans.* **12A** (1981) 1155-1161
- [15] Vincent H., Vincent C., Berthet M.P., Bouix J., Gonzales G., *Carbon* **34**(9) (1996) 1041-1055
- [16] Piquero T., Vincent H., Vincent C., Bouix J., *Carbon* **33**(4) (1995) 455-467
- [17] Bermudez V.M., *Appl. Phys. Lett.* **42** (1983) 70-73.
- [18] Iseki T., Kameda T. and T. Maruyama, *J. Mater. Sci.* **19** (1984) 1692-1698.
- [19] Viala J.C., Fortier P. and Bouix J., *J. Mater. Sci.* **25** (1990) 1842-1850.
- [20] Viala J.C., Bosselet F., Laurent V., Lepetitcorps Y., *J. Mater. Sci.* **28** (1993) 5301-5312.
- [21] Viala J.C., Vincent C., Vincent H. and Bouix J., *Mat. Res. Bull.* **25** (1990) 457-464.
- [22] Viala J.C., Fortier P., Claveyrolas G., Vincent H., Bouix J., *J. Mater. Sci.* **26** (1991) 4977-4984.
- [23] Abiven H., Bouix J., Claveyrolas G., Picouet L., Viala J.C., Composite material combining a magnesium alloy containing zirconium with a carbon reinforcement and its production process, US Patent Demand US 08/417 444 accorded 2 Feb. 1996.
- [24] Viala J.C., Bosselet F., Claveyrolas G., Mentzen B.F. and Bouix J., *Eur. J. Solid State Inorg. Chem.* **28** (1991) 1063-1070.