

# PROCESSING OF CARBON FIBER REINFORCED TITANIUM MATRIX COMPOSITES

C. Arvieu<sup>1,2</sup>, C. Even<sup>1</sup>, B. Guillaume<sup>1</sup>, J.L. Bobet<sup>1</sup>, J.M. Quenisset<sup>1,2</sup> et P. Chadeyron<sup>3</sup>

<sup>1</sup> *Institut de Chimie de la Matière Condensée - CNRS*

<sup>2</sup> *Laboratoire de Génie Mécanique - IUT*

*Université Bordeaux 1, F-33405 Talence Cedex (France)*

<sup>3</sup> *Commissariat à l'Energie Atomique: CEA / CESTA*

*F-33114 Le Barp (France)*

**SUMMARY:** The development of a processing method based on Powder Metallurgy, for manufacturing titanium matrix composites selectively reinforced by carbon fibers has given rise to various types of study related to: (1) the preparation of very fine titanium powder (about 3  $\mu\text{m}$  in size) through the subdivision of titanium hydride without noticeable contamination thanks to the combination of hydriding / dehydriding cycles and grinding, (2) the protection of the carbon reinforcement against the titanium reactivity by coating fibers with either copper, pyrocarbon or boron nitride, (3) the choice of a totally fugitive polymeric vector for impregnating fibers yarns by the matrix powder and (4) the determination of a Pressure, Temperature, Time cycle allowing the matrix densification without excessive fiber / matrix interaction.

**KEYWORDS:** Metal matrix composites – Titanium matrix composites – Composite processing – Powder metallurgy – Fiber/Matrix interface.

## INTRODUCTION

During the last three decades, most studies related to titanium matrix composites (TMC's) have been dedicated to the reinforcement of titanium or aluminide alloys by large diameter filaments (100-140  $\mu\text{m}$ ) processed by chemical vapor deposition (CVD). However, the cost of this type of filamentary reinforcement, the related conditions of composite manufacturing and also the large size of the reinforcement, impede their development and their use in applications requiring a finer subdivision of the reinforcement and moderate manufacturing costs. For instance, that is particularly the case when thin wall titanium structures (less than 1 mm in thickness) have to be selectively reinforced in order to obtain better bending or buckling stiffness. In such cases, the incorporation within titanium base matrices of thin fibers (about 5-10  $\mu\text{m}$  in diameter) becomes a crucial problem which cannot be approached with the processing techniques devoted to filamentary reinforced TMC's [1-6].

Among the available fibrous reinforcement, carbon fibers are particularly interesting, since their stiffness can be so high that a rather small volume fraction of reinforcement (20 % of high modulus graphite fibers) is able to give an unidirectional composite the rigidity of steel without inducing an unavoidable embrittlement of the composite metallic component.

However, the reinforcement of titanium alloys by carbon fibers is only conceivable when it aims at short life applications at high temperatures or more durable applications at moderate or low temperatures. Thus, carbon fibers reinforced TMC's exhibit interesting perspectives provided to limit the fiber/matrix (F/M) interaction during composites processing. As a matter of fact, the high temperatures generally required for TMC manufacturing (800-900°C) and the particularly strong chemical reactivity of the Ti/C couple, inevitably give rise to the formation of a brittle carbide zone at the fiber/matrix interface resulting in undesirable notch effects and fibers degradation.

Various ways can be followed to overcome the difficulty of incorporating fine carbon fibers within titanium base alloys while limiting the F/M interaction:

- the use of a liquid infiltration route requires techniques which are not yet sufficiently rapid to avoid any excessive F/M interaction [7, 8],
- the vapor route based for instance on the physical vapor deposition, and followed by complementary operations of consolidation is rather expensive despite the flexibility of using impregnated fibers yarns or fabrics for manufacturing parts,
- the solid route can be used provided to subdivide finely the titanium base matrix in order to realize its coupling with fine fibers. Such a subdivision is possible in the case of filaments about a hundred microns in diameter thanks to the use of titanium foils or powders commercially available, but cannot be adapted to fibers about ten microns in diameter.

Besides, techniques based on powder metallurgy have allowed the processing of refractory matrix composites, but the related ceramic or intermetallic matrices are sufficiently brittle to be easily ground into fine powders without excessive contamination. In the case of most titanium rich alloys, not only their significant ductility and reactivity makes much more difficult their subdivision without contamination, but also their densification by hot pressing in presence of carbon fibers requires particular conditions to control the highly reactive F/M interaction.

Thus, processing TMC through powder metallurgy techniques meets the following impeding difficulties, which are of concern in the present contribution :

- the preparation of fine titanium powders with grain size ranging between 1 and 10  $\mu\text{m}$ ,
- the protection of carbon fibers against the titanium chemical aggressiveness,
- the choice of a polymeric binder and the penetration of matrix powders within various fibrous architectures,
- the composite densification.

## PROCESSING OF A NON CONTAMINATED FINE TITANIUM POWDER

Generally, reinforcing metallic alloys with brittle ceramic fibers, gives rise to some embrittlement of the related composite compared to the matrix alone. Consequently, a selective reinforcement can be expected as sufficient to induce stiffening and strengthening requirements while preventing the concerned structure from catastrophic failure. For instance, the reinforcement of 50% of a thin wall structure thickness in the vicinity of its surfaces enables the increase in stiffness to be 90% of that obtained with a structure completely reinforced. Also, it means that thin wall structures of less than 1 mm in thickness necessitate small size reinforcement whose incorporation within the matrix requires its very fine subdivision.

Excluding the liquid and vapor routes due to the titanium reactivity and the rather high costs of PVD techniques, the incorporation of fine fibers about 5-10  $\mu\text{m}$  in diameter within titanium base matrices, can be achieved by powder metallurgy provided to have very fine titanium powders. In order to avoid any mechanical degradation of fibers during high pressure composite densification, a powder granulometry slightly lower than the fibers size (5  $\mu\text{m}$ ) has been considered suitable in a first approach but must be experimentally confirmed depending on the used densification pressure. As a matter of fact, it would be preferable to operate with powder size as large as possible since lower the powder specific surface, lower the significance of powder contamination by interstitial elements such as oxygen and nitrogen. It is one of the reasons why non-contaminated fine titanium powders are not commonly available in commerce. Thus, manufacturing TMC selectively reinforced by small diameter fibers demands first, the preparation of fine titanium powders.

The method generally used for producing fine titanium powder from titanium hydride has been improved to decrease grinding duration and impurities contamination. The method consists in combining hydriding/dehydriding cycles and grinding, which enables a faster subdivision of titanium. The procedure and efficiency of the method are detailed elsewhere [9]. It is noteworthy that a spontaneous subdivision of titanium hydrides by cycling hydrogen pressure at suitable temperature (400-500°C) is not possible contrary to many intermetallic hydrides [10, 11]. The titanium hydride decrepitation is impeded by the titanium ductility, which also impedes the direct subdivision of titanium powders.

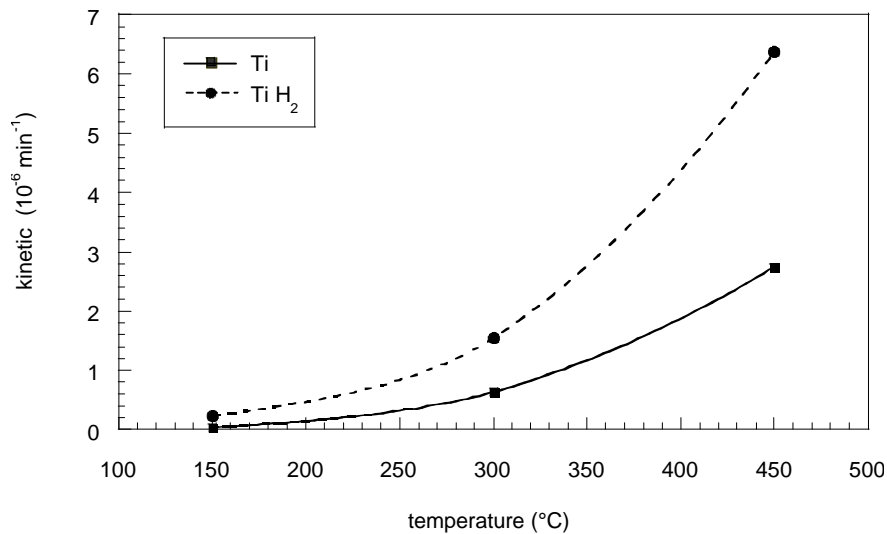


Fig. 1: Oxidation kinetics of hydride and unhydrided titanium powders

After 20-30 hydriding/dehydriding cycles at 500°C under maximum and minimum hydrogen pressures of  $10^5$  Pa and  $10^{-1}$  Pa followed by only 7 min of grinding, the resulting titanium hydride powder exhibits a granulometry of about 5  $\mu\text{m}$  and a low contamination (300 ppm of iron).

Besides, oxidation tests performed on titanium hydride and unhydrided titanium has shown as illustrated in Fig.1, that titanium hydride powders are more sensitive to oxidation than titanium powder, which would incites to use titanium powder as starting material for composite manufacturing rather than titanium hydride. However, when on the one hand, fine titanium base powders are inclined to agglomerate during their dehydriding, on the other hand, titanium hydride powder densification has been shown to be easier than that of titanium powder [12]. Thus, considering the kinetic of titanium hydride oxidation remains small at low temperature and that particular care can be taken to confine powders, titanium hydride has been chosen as starting material.

## **PROTECTION OF CARBON FIBERS**

When notch effects induced by moderate interactions (for instance 1  $\mu\text{m}$  in thickness) between titanium matrices and carbon coatings of filaments can be undergone by large diameter filaments (100-140  $\mu\text{m}$  in diameter), such effects are unbearable by small fibers (5-10  $\mu\text{m}$  in diameter). Thus, not only carbon fibers reinforced TMC cannot be used at temperatures exceeding 400 °C or at higher temperatures for short life duration, but also the conditions of processing must be carefully chosen to prevent the fiber degradation and the formation of brittle interphases thicker than 200 nm. Knowing that the conditions generally used for consolidating TMC by hot pressing (half an hour at 900 °C) give rise to the formation of more than 1  $\mu\text{m}$  of titanium carbide and the elimination in part of the filament carbon coating, it seems impossible to avoid any fibers degradation even if processing times and temperatures are minimized.

Various types of carbon fibers protection were tested: (1) the interposition of an ephemeral metallic barrier at the F/M interface, (2) the coating of carbon fibers by a less reactive pyrolytic carbon layer, (3) the deposition on fibers of a quasi chemically inert boron nitride layer.

In the first case, the great stability of the C/Cu/W system, also the slow and favorable W/Ti interaction (W helps ductile  $\text{Ti}\beta$  formation) led to consider Cu/W coatings as interesting candidates for fibers protection. The study of this system has been detailed elsewhere and shows its rather low efficiency although the presence of a W layer impedes copper spreading within matrix and TiC formation [13]. Besides, a 1.5-2  $\mu\text{m}$  electroless copper coating of carbon fibers gives rise to only 300 nm of TiC after half an hour at 800 °C. Considering the related notch effect, such a F/M interaction is nearly acceptable but already reveals a noticeable fiber degradation and an extensive diffusion of Cu in Ti.

The second case, corresponding to the deposition on fibers of 70 nm of pyrolytic carbon, aims at decreasing the reactivity at the F/M interface thanks to a more favorable orientation of graphitic planes on fibers surface. That allows the formation of carbide interphase without partly consuming fibers. As shown by AES analyses presented elsewhere, this type of pyrocarbon protection leads to the formation of 250 and 150 nm of TiC after isothermal exposures at respectively 750 and 700°C during half an hour [14]. The results related to this

second case study has also demonstrated how efficient can be a decrease of some tens degrees on the limitation of the brittle interphase thickness.

Concerning the third case, the interposition of 0.8-1.1  $\mu\text{m}$  of BN between carbon and titanium appears to be efficient to protect carbon fibers. As a matter of fact, processing TMC reinforced by BN coated carbon fibers, at 700 °C during half an hour leads to F/M interfacial zones quasi free of TiC. As illustrated in Fig. 2, AES analyses performed in line have shown as expected a rather large F/M interfacial zone, about 1-1.2  $\mu\text{m}$  in thickness corresponding to the protective coating. However, in this interfacial zone, the shape of the peak related to the Auger transition of carbon cannot be related to that involved in TiC chemical bonding. It means that if TiC formed at the F/M interface during TMC processing, its presence is limited to very small parts of the interfacial zone, lower in thickness than the lateral resolution of the Auger microprobe (about 100 nm). Nevertheless, the simultaneous presence of carbon, nitrogen and boron at the carbon fiber surface requires further investigations, for instance by TEM, to identify clearly the nature of interphases whose brittleness would be unfavorable.

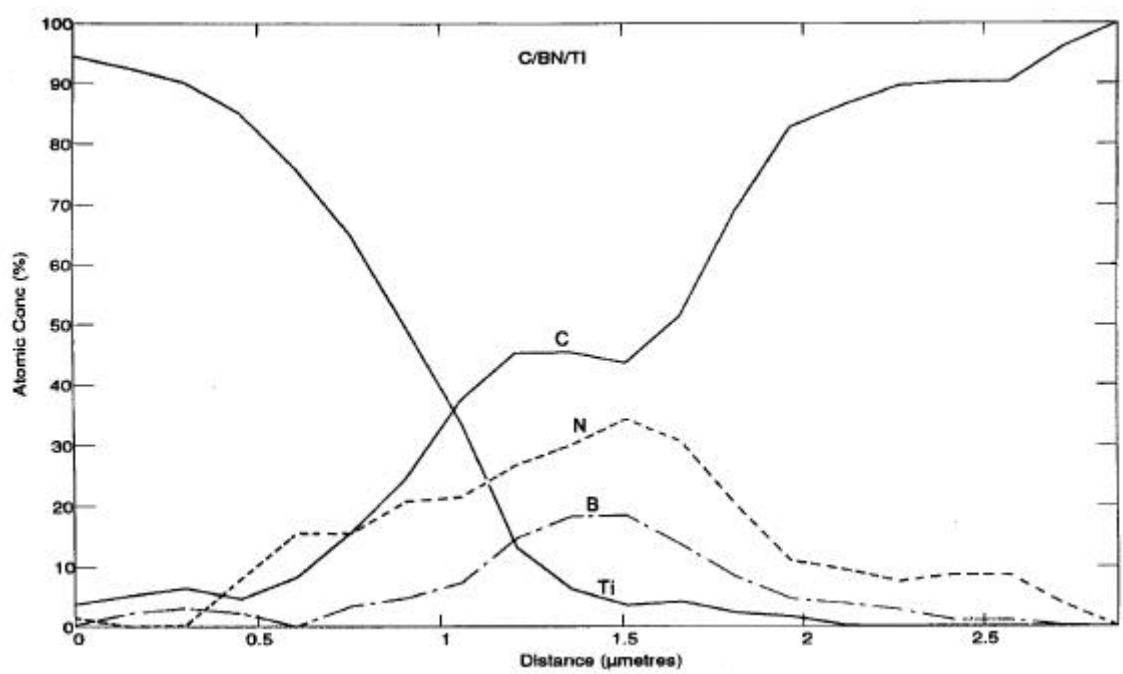


Fig. 2: AES concentration profiles related to TMC reinforced by BN coated carbon fibers

Anyway, the various tests of carbon fiber protection whose main illustrative results are gathered in Table 1, show that processing carbon fibers reinforced TMC's at temperatures of about 700°C, is not inevitably accompanied by the formation of brittle interphases in such thicknesses that carbon fibers could not undergo the related notch effects.

M40 C fiber coating	None	1.7 μm of Cu		0.7 μm of pyr.C		0.9 μm of BN
Processing time (min)	30	30	20	30		30
Pressure P (MPa)	200	15	20	40	50	200
Processing T (°C)	700	830	750	750	700	700
Interfacial zone (μm)	0.5	4	1.5	0.25	0.15	1.2
TiC thickness (μm)	0.5	1.4	0.4	0.25	0.15	< 0.1

Table 1: F/M interaction zone depending on the nature of carbon fiber protection

## **PENETRATING THE MATRIX POWDER WITHIN FIBROUS REINFORCEMENT**

The matrix / reinforcement association that is the impregnation of the fibrous architecture (yarns or fabrics) by titanium base powders is a major difficulty of the studied processing method. To penetrate any fibrous preform, a fluid sufficiently viscous to prevent excessive filter effect must drag titanium powder. Using a thermoplastic binder allows impregnated preforms to be formed at moderate temperatures. In addition, complete binder elimination must be possible at rather low temperatures (300°C) in order to avoid any contamination of the titanium matrix.

After testing various polymers, two thermoplastics were selected for thermogravimetric investigations concerning the conditions of their elimination at moderate temperatures.

Analyses up to 400°C have shown the SBS decomposition (Styrene-Butadiene-Styrene) begins at 243°C with a kinetic increasing up to 360°C. This temperature can be considered as the limit above which carbon waste is able to be a source of contamination for titanium matrix. A 3 hours isothermal exposure at 340°C allows the binder to be completely eliminated under vacuum, despite the fine powder subdivision.

In the case of the PMMA (Polymethylmetacrylate), a lower temperature (250°C) enables the decomposition and the complete elimination of the polymer after 5 hours in air without leaving any residual binder. Furthermore, the use of a PMMA solvent allows its viscosity to be easily adjusted for facilitating fibrous preform impregnation.

It is worthy of note the binder elimination time is obviously strongly dependent on structure shapes. Higher the structure surfaces for a given volume, shorter the binder elimination time. That is particularly the case of thin wall structures.

## **COMPOSITES COMPACTION**

In order to study the conditions of composite densification and to evaluate the efficiency of the carbon fiber protections previously presented, short carbon fibers were used for manufacturing composites with reinforcement volume fraction of about 20-30 %.

Lowering the densification temperatures and therefore limiting the F/M interaction, can be expected by increasing the compaction pressures of the matrix powder / carbon fibers mixture. Thus, a hot unidirectional pressing apparatus schematically illustrated in Fig. 3 was designed and set up to perform various specimen shapes. The maximum pressure which can be reached on a 12 mm diameter cylindrical specimen is 1000 MPa.

After eliminating binder and residual hydrogen of the titanium hydride at temperatures ranging between 250 °C and 450°C, under a  $10^{-4}$  Pa vacuum, composite specimens are heated at the temperature of densification for which the pressure is progressively applied according to given pressure-temperature-time (PTT) cycles.

These PTT cycles aim at generating the following sequences of composite densification:

- titanium base particles surrounding carbon fibers are plastically deformed as the compaction pressure increases. Although the plastic flow stress of the matrix remains significant at the densification temperatures, this mechanism of plastic deformation is

important because of the small contact surfaces between particles. Also, this step is capable of causing mechanical fiber degradations,

- then, particles creep is able to carry on the densification thanks to diffusion mechanisms within particles. This step is not expected to provoke fiber mechanical degradations, although, during short times (half an hour), the driving force of the related mechanism is as much pressure as temperature,
- the sintering mechanism involving inter particles diffusion is able to close residual pores and to induce particles bonding, but also it must be related to F/M interaction. Thus, more efficient the fiber protection, more complete can be the matrix densification and consolidation.

It remains from the previous considerations, the necessity of optimizing PTT cycles to prevent any fiber breakage while reaching the full matrix density.

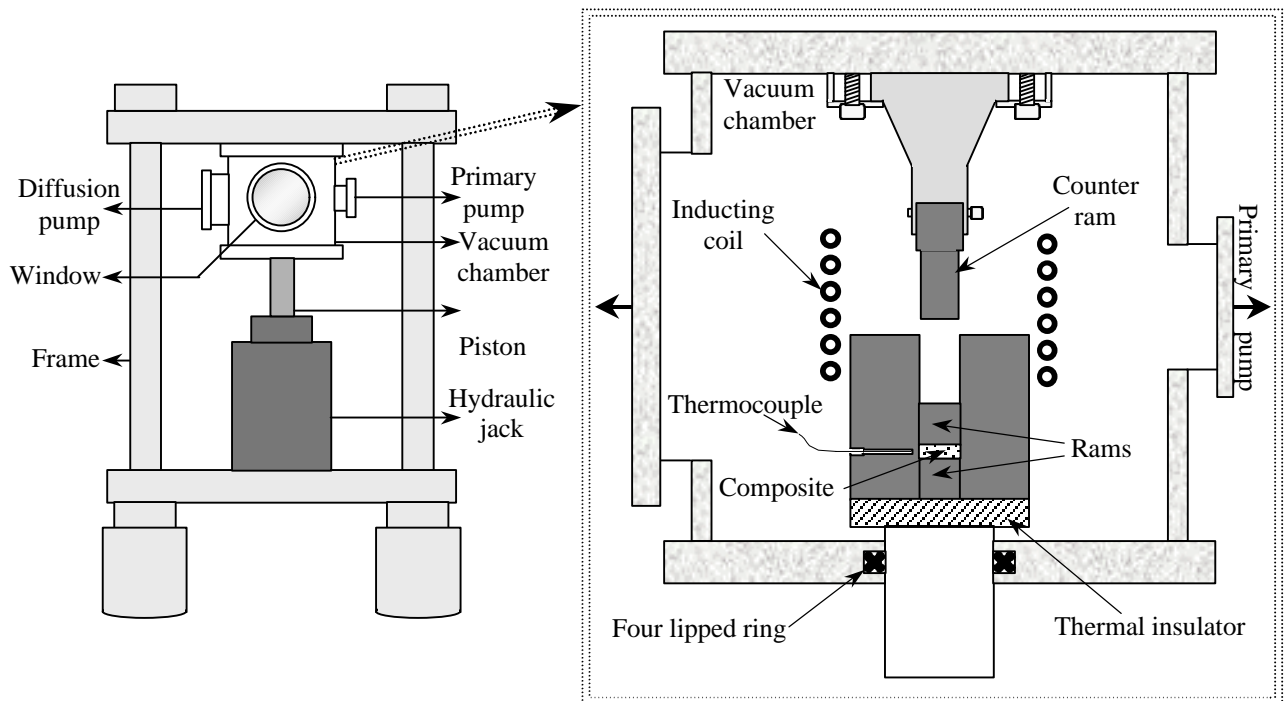


Fig. 3: Schematic representation of the hot pressing apparatus used for TMC processing

The apparatus enables first the elimination of binder and then the titanium dehydriding under vacuum of  $5.10^{-3}$ - $10^{-4}$  Pa, which allows the use of moderate temperatures and consequently only induces very small oxygen contamination. At higher temperatures, related to the matrix densification, the confinement of the titanium powder in the die also limits this matrix contamination by interstitial elements. Depending on the vacuum quality, particularly just before applying high pressure, the oxygen content within the matrix is ranging from 800 to 15000 ppm. Thus, the temperature to be optimized is that of dehydriding, which must enables a complete elimination of hydrogen without inducing any matrix contamination whatever the duration of this processing step.

Besides, in any case, with the conditions of processing reported in Table 1, the matrix microstructure was observed to be very fine and free of pores as illustrated in Fig. 4. Below

temperatures of 800°C, the microstructure size is close to the fiber diameter, which is like expected since coarsening effects have not enough time to develop at the densification temperature.

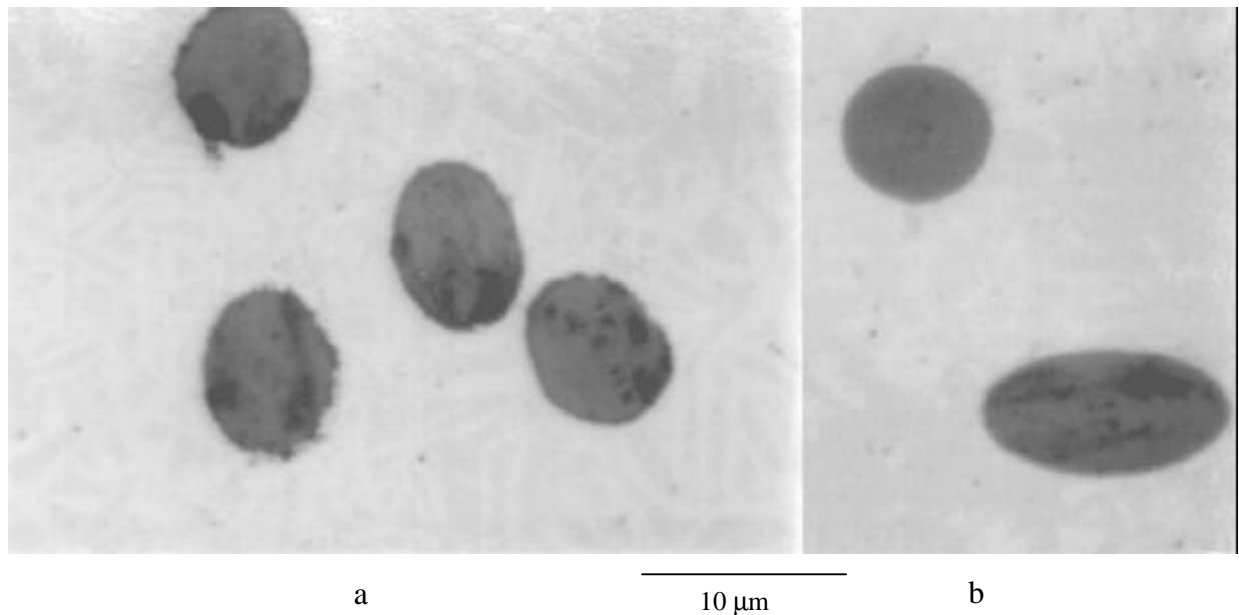


Fig. 4 : Optical micrographies of carbon fibers reinforced CMT's

(a)  $P = 200 \text{ MPa}$ ;  $T = 700 \text{ }^{\circ}\text{C}$ ;  $t = 30 \text{ min}$

(b)  $P = 650 \text{ MPa}$ ;  $T = 600 \text{ }^{\circ}\text{C}$ ;  $t = 30 \text{ min}$

Also Fig. 4 shows how profitable is a decrease in the processing temperature for the F/M interface. In the case of C coated carbon fibers, a reduction of 100 °C of the processing temperature enables a quasi elimination of the F/M interaction zone (Fig. 4 b), but the corresponding processing pressure (650 MPa) is uneasy to use on large parts in an industrial context. Furthermore, very high pressures require an optimization of the PTT cycle in order to prevent excessive fibers breakage.

## CONCLUSION

The selective reinforcement of titanium structures by small diameter carbon fibers has required the use of a processing method based on powder metallurgy. The identification of the main difficulties to be overcome has given rise to various studies related to (1) the preparation of fine titanium powders thanks to a hydriding/dehydriding cycles technique, (2) the protection of carbon fibers by pyrocarbon or boron nitride coatings, (3) the use of a polymer binder for coupling titanium powder and carbon fibers and (4) the composite densification at moderate temperatures under high pressures. The evolution of the process tends to decrease the processing temperatures in order to simplify the carbon fiber protection, which leads to increase the consolidation pressure up to a limit related to fibers mechanical degradation. A possible densification of the titanium matrix at 600 °C during half an hour under 650 MPa and the limitation at less than 0.2 μm of the TiC layer thickness formed at 700 °C during half an hour at the F/M interface, allows the processing conditions to be optimized through further investigations.



## ACKNOWLEDGEMENTS

The authors are grateful to M. LAHAYE for AES microprobe analyses and would like to thank H. VINCENT from LMI (University of Lyon 1) for supplying both C and BN CVD coated carbon fibers.

## REFERENCES

1. Metcalfe A.G., « Fiber Reinforced Titanium Alloy » in « Metal Matrix Composites », Kreider K.C., *Composite Materials* edited by Broutman and Krock R.H., Academic Press, N.Y., Vol. 4, Chap. 6, 1974, pp.269-318.
2. Pailler R., Martineau P., Lahaye M. et Naslain R., *Revue de Chimie Minérale*, 18, 1981, pp 520-543.
3. Naslain R., Pailler R., Quenisset J.M. « Matériaux Composites Synthétiques à Matrice Métallique », *Introduction aux matériaux composites*, Tome 2, 1985, pp. 315-383.
4. Leucht R. & Dudek H.J., « Properties of SiC fibre reinforced titanium alloys processed by fibre coating and isostatic pressing », *Materials Science Engineering A188*, 1994, pp. 201-210.
5. Vassel A., Indrigo C., Pautonnier F., « Processing of Fibre Reinforced Titanium Matrix Composites by Physical Vapour Deposition », *Proceeding of the Eighth World Conference on Titanium*, edited by Blenkinsop P.A., Evans W.J., Flower H.M., Birmingham, UK , 22-26 oct. 1995, pp 2739-2746.
6. Della Martina F., Coutand B., Le Petitcorps Y., Quenisset J.M., « Effect of isothermal exposure on the failure behavior of 1D-SCS6/Super- $\alpha_2$  matrix composites », *Composites Science and Technology*, 53, 1995, pp. 65-75.
7. Toloui B., *Proceeding of ICCM-5*, edited by Harrigan W.C., Strife J. and Dhingra A.K., Warrendale , Pa, TMS, YAIME, N.Y., 1985, pp. 773-777.
8. Warrier S.G. and Lin R.Y., *Proceeding of the 9<sup>th</sup> International Conference on Composite Materials*, edited by Mirvavete A., published by the University of Zarotoga, Spain, 1993, pp. 720-727.
9. Deletang K., Even C., Bobet J.L., Arvieu C. and Quenisset J.M., « A new method for producing ultrafine powder of titanium dihydride », *Proceedings of Powder Metallurgy World Congress*, Granada, Spain, October 18-22, 1998.
10. X.G.Li, A.Chiba, K. Ohsaki, Y.Morita, M.Uda, « Preparation of fine Nb<sub>3</sub>Al powder by hydriding and dehydriding in an arc-melting chamber », *Journal of Alloys and Compounds*, 238, 1996, pp. 202-209.
11. Li X.G., Chiba A., Takahashi S., « Disintegration and fine powder preparation of Nb<sub>75</sub>Si<sub>25</sub> via hydrogenation », *Journal of Alloys and Compounds*, 260, 1997, pp. 153-156.

12. Greenspan J., Rizzitano F.J. and Scala E., «Titanium powder metallurgy by decomposition sintering of the hydride » *Titanium Science and Technology*, Vol.1, 1973, pp 365-379.
13. Even C., Arvieu C., Chadeyron P. and Quenisset J.M., « Processing of carbon fibres reinforced titanium matrix composites by powder metallurgy », *Proceedings of Powder Metallurgy World Congress*, Granada, Spain, October 18-22, 1998.
14. Deletang K., Even C., Arvieu C., Bobet J.L., Quenisset J.M., « Mise en œuvre de matériaux composites à matrice de titane renforcée par des fibres microniques » *Proceedings of JNC 11*, Arcachon, France, 1998