

# NUMERICAL SIMULATION OF HEAT AND MASS TRANSFER DURING HIGH SPEED LIQUID ROUTE PROCESSING OF TITANIUM MATRIX COMPOSITES

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## Abstract

*A numerical simulation, based on a thermo-metallurgical model has been developed to describe a liquid route process for coating SiC filaments by Ti alloys. This model describes the physical phenomena which occur during the process: the carbon transfer from the carbon coated SiC filament toward the liquid titanium, the different types of heat exchanges, the TiC interphase formation at the filament surface and finally the solidification of the titanium coating. After validation of the model, numerical simulations allow the influences of the processing conditions to be depicted.*

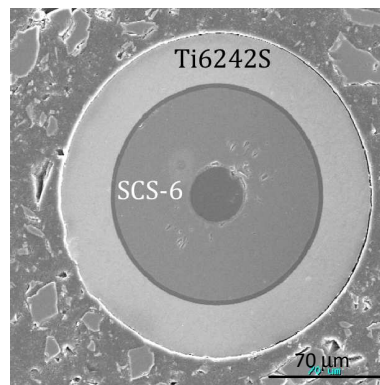
## 1 Introduction

Aiming at the elaboration of titanium matrix composites (TMC), a costless process for coating carbon coated SiC filaments with high reactive titanium based alloys has been developed. It consists in running the ceramic filaments through the liquid metal bath in electromagnetic levitation at very high speed [1]. High temperature interaction between C coated SiC filaments and Ti alloys, gives rise to carbon transfer and formation of titanium carbide  $TiC_{1-x}$  which could be a source of mechanical performance degradation. The influence of processing conditions, particularly filament speed and cooling rate, on carbon transfer from the filament surface to the matrix, was studied through modelling and the numerical simulation of the process in order to improve filamentary composite performance. Firstly, the physical phenomena of heat and mass transfer which occur during the high speed coating process are explained. Then, the modelling of these phenomena and their numerical simulation are described and validated. Attention is focused on the coupling mechanisms between levels of temperature and carbon concentration.

## 2 Physical and chemical interactions between filament and matrix

During the process, RF induction is used for heating the liquid bath and for maintaining it in levitation. A SiC filament (SCS-6) coated with a thin carbon layer, runs through a titanium alloy liquid bath (Ti6242) at very high speed (several meters per second). Then, the liquid metal coated filament is cooled through a cooling device which allows cold inert gas flows to

be concentrated on the filament. After the solidification of the coating, the resulting filamentary composite (figure 1) is wound around a pulley.



**Figure 1.** SEM observation of coated SCS-6 filament

### 2.1 Mass and heat transfer

During the running of filament through the bath the filament/matrix chemical interaction consists in the dissolution of carbon in the liquid metal near the filament/liquid metal interface. A significant amount of carbon is transferred from the filament surface to the liquid metal coating. When the carbon concentration is sufficiently high, that is to say the liquidus temperature is higher than the actual liquid temperature, carbide is able to form. In the present case, more or less stoichiometric  $TiC_{1-x}$  precipitates [2].

The carbon transfer is controlled by carbon dissociation and dissolution in liquid Ti before any  $TiC_{1-x}$  formation occurs. But the carbon transfer is controlled by carbon diffusion through the  $TiC_{1-x}$  interphase as soon as  $TiC_{1-x}$  forms.

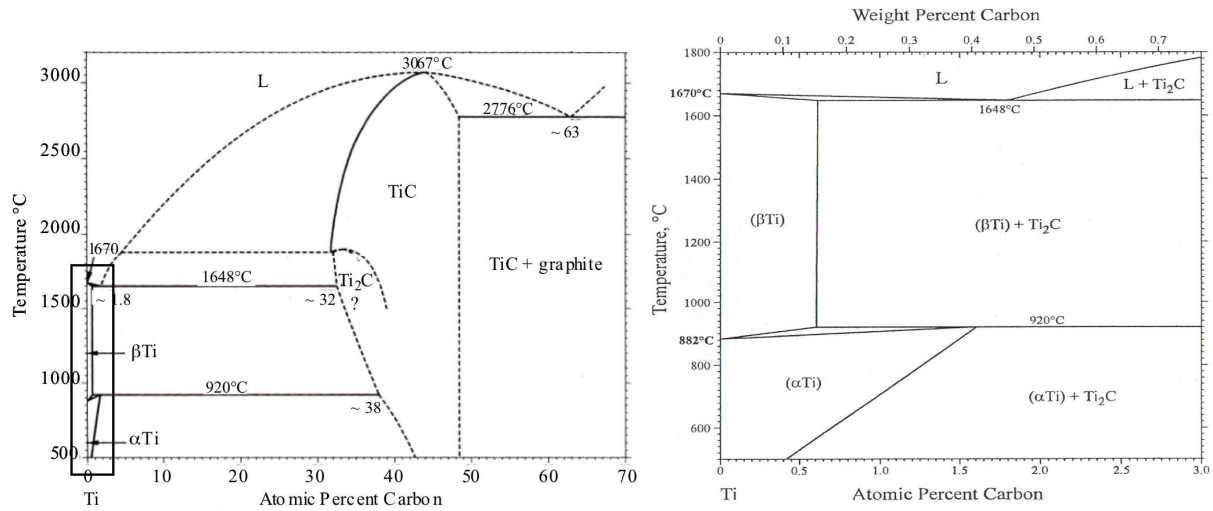
The very great temperature difference between the filament (about 20°C) and the titanium bath (1720°C) induces a first solidification phenomenon as soon as the filament enters the bath. However, this is quickly reversed by a re-melting phenomenon once the filament temperature is close to that of the bath.

Otherwise, when the filament coming out of the bath is cooled, mainly by radiation, before it reaches the cooling device, its decreasing temperature is able first to reach, either the titanium solidification temperature or the  $TiC_{1-x}$  precipitation temperature, which strongly depends on the carbon concentration within the carbon solution in liquid Ti at the filament/liquid interface (figure 2). Thus, depending on carbon transfer kinetics, filament coating solidification may begin either, at the coating surface, firstly due to heat extraction by radiation and subsequently by convection in the cooling device, or at the filament/matrix interface due to carbon dissolution leading to carbide precipitation.

### 2.2 Titanium carbide formation

Before any  $TiC_{1-x}$  formation, the liquid titanium is not able to wet the filament surface and thus cannot be carried along the filaments coming out of the bath. Thus, formation by chemical interaction of a  $TiC_{1-x}$  layer on the filament surface is a major requirement for high speed coating. It has been observed that without any filament wetting by liquid titanium, the Ti coating cannot be concentric to the SiC filament [3]. To ensure  $TiC_{1-x}$  formation on the filament surface, carbon concentration in the liquid titanium near the filament surface must reach the carbon solubility limit in the liquid Ti at the bath temperature.  $TiC_{1-x}$  composition is dependent on the liquid metal from which it forms (figure 2). In fact,  $Ti_2C$  is assumed to be the carbide in contact with the liquid Ti, whereas TiC is assumed to be the carbide in contact

with the filament C coating. It is considered that the related carbon concentration gradient in the carbide interphase controls the carbon transfer from the filament to the liquid Ti bath.



**Figure 2.** Titanium/Carbon phase diagram [4]: phase diagram and zoom of the Ti rich part of the phase diagram

Finally, the kinetic of mass transfer governs the significance of the amount of carbon at the filament/liquid interface, while the kinetics of heat transfer control temperatures. Consequently, both transfers control the kinetics of  $TiC_{1-x}$  formation. Thus, it appears important to have a more accurate approach of the coupling between heat and mass transfer in order to monitor processing conditions.

### 3 Numerical simulation of phenomena

In the present contribution, we aim to describe heat and mass transfer coupling by setting up a static model based on the following considerations.

First, the use of very high running speeds allows thermal transfer to be considered as quasi radial: that is to say, transfer phenomena are negligible in the longitudinal direction. Concerning mass transfer, filaments are considered free of  $TiC_{1-x}$  when entering the liquid bath so that carbon migrates directly from the filament surface to the liquid metal from the part immersed in the liquid bath. It is assumed that for this length, carbon flow is governed by carbon dissociation, that is to say, carbon dissolution kinetics. As soon as the carbon content in the liquid titanium close to the filament surface is high enough for inducing  $Ti_2C$  formation, the carbon transfer is controlled by diffusion flow through the  $TiC_{1-x}$  layer.

Otherwise, the time required to ensure filament wetting can be calculated from the fraction of the filament where  $TiC_{1-x}$  has not yet formed since filament wetting cannot occur directly on carbon.

#### 3.1 Equations

The studied system axisymmetry led us to use cylindrical coordinates and to perform 2-D numerical simulation. Thermal transfers were modelled by the following heat equation, taking phase change phenomena into account:

$$(\rho c)^* \frac{\partial T(t, r)}{\partial t} = \frac{\partial}{\partial r} \left( \lambda^* \frac{\partial T(t, r)}{\partial r} \right) + \frac{\lambda^*}{r} \frac{\partial T(t, r)}{\partial r} + Q(t, r) \quad (1)$$

where  $(\rho c)^*$  and  $\lambda^*$  respectively represent heat volume and thermal conductivity of the coated filamentary composite components (SiC, C, TiC, liquid Ti, solid Ti or liquid and solid Ti),  $T$  temperature,  $t$  time and  $r$  radius.  $Q(t, r)$  is a source term related to phase change phenomena [5, 6].

Carbon diffusion in liquid titanium is controlled by the following Fick equation:

$$\frac{\partial C(t, r)}{\partial t} = \frac{\partial}{\partial r} \left( D \frac{\partial C(t, r)}{\partial r} \right) + \frac{D}{r} \frac{\partial C(t, r)}{\partial r} \quad (2)$$

where  $C$  represents the carbon concentration and  $D$  the carbon diffusion coefficient in liquid Ti. The C diffusion in solid Ti is neglected because of very small C concentration gradients in the Ti solid coating and although the C diffusion coefficient in solid Ti is not negligible compared to that in liquid Ti at solidification temperatures.

### 3.2 Geometry and initial thermal conditions

For the examples of numerical simulation presented, the length of the experimental device was 2.05 m, the height of the bath was 5 cm, the forced cooling zone was 1 m, the last zone before winding was about 1 m.

The SiC filament diameter is equal to 140  $\mu\text{m}$  and its protective pyrocarbon coating is about 4  $\mu\text{m}$  thick. As previously mentioned, the liquid metal bath is maintained at 1720°C during the coating process and the initial filament temperature is 20°C.

### 3.3 Boundary conditions

In the bath, 1720°C was imposed as the temperature condition at the boundary of a domain defined by a filament surrounded by a 5 cm thick titanium tube belonging to the liquid bath. Otherwise, for reference, numerical tests corresponding to filament running speed of 2  $\text{m s}^{-1}$ , the titanium coating thickness was expected to be equal to 50  $\mu\text{m}$  [7]. The dimension of the studied domain was then equal to 124  $\mu\text{m}$  outside the liquid bath. A flux condition was imposed at the external surface of the coated filament:

$$\phi = \sigma \varepsilon (T^4 - T_\infty^4) + h(T - T_\infty) \quad (3)$$

where  $\sigma$  is Boltzman's constant ( $\sigma = 567.10^{-10} \text{ W m}^{-2} \text{ K}^{-4}$ ),  $\varepsilon$  the emissivity ( $\varepsilon = 0.4$ ),  $h$  the convection coefficient and  $T_\infty$  room temperature ( $T_\infty = 20^\circ\text{C}$ ).

Concerning cooling, it was assumed from information available in the literature, that for conditions of natural convection, the related convection coefficient is about 10  $\text{W m}^{-2} \text{ K}^{-1}$  while it is supposed to reach 300  $\text{W m}^{-2} \text{ K}^{-1}$  when forced convection is applied.

The dissolution phenomenon before any  $\text{TiC}_{1-x}$  formation was represented by a constant carbon flow  $\phi_0$ , according with numerical results and experimental results. As soon as  $\text{TiC}_{1-x}$  began to form, the carbon flow is controlled by TiC thickness which increases during the process.

### 3.4 Numerical model

For all numerical tests, filament running speeds were maintained under 3 m/s, which enabled  $\text{TiC}_{1-x}$  formation in any case and consequently, ensures the Ti liquid route coating feasibility. Using higher filament running speeds requires improvement of filament wettability by liquid titanium [8, 9].

Although the metal coating is not pure Ti, lack of phase diagrams related to Ti alloys-C led us to use the Ti-C phase diagram as a support for determining the relation between solidification temperatures and carbon concentrations in liquid Ti alloys. Besides, according to data available, thermodynamic values related to various alloys could be used. The carbon diffusion coefficient is fixed in the liquid titanium at  $D_{C/liqTi} = 5 \cdot 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$  in the vicinity of the Ti melting temperature. In  $\text{TiC}_{1-x}$ ,  $D_{C/TiC}$  diffusion depends on temperature according to literature results and can be synthesized by the following relation:

$$D_{C/TiC} = 6.1 \cdot 10^{-16} T_s - 5.4 \cdot 10^{-13} \quad (4)$$

where  $T_s$  is the liquidus temperature ( $^{\circ}\text{C}$ ).

The numerical simulation makes use of the Finite Volume Method and deals with both the resolution and coupling of conservation equations (1) and (2) in which the solute rejection at the solid-liquid interface is taken into account. Indeed, the solidification brought about by the cooling system placed at the external surfaces, leads to carbon rejection in the liquid at the liquid/solid interface with a partition coefficient  $k$  under one ( $k = 0.3$ ). The carbon concentration in liquid at the rejection interface is uniform over the whole interface and is defined by an arbitrary thickness  $dr$  which was chosen to be the space step. A mass balance enabled us to compute the amount of carbon received from the adjacent control volume, which is dependent on the solid fraction in the control volume  $V_i$  where the liquid/solid interface is.

Concerning the formation of  $\text{TiC}_{1-x}$  at the filament/liquid Ti interface, a mass balance at each time step allowed us to simulate the evolution of the TiC thickness:

$$D_{C/TiC} \frac{C_1 - C_2}{e + \Delta e} \Delta t = D_{C/liqTi} \frac{\Delta C}{\Delta z} \Delta t + (C_2 - C_3) \Delta e \quad (5)$$

where  $C_3$  is the carbon solubility limit,  $\frac{\Delta C}{\Delta z}$  the carbon concentration gradient in the liquid at the liquid/filament interface,  $\Delta t$  the time step,  $e$   $\text{TiC}_{1-x}$  thickness at time  $t$  and  $\Delta e$  the increase in TiC thickness during the time step ;  $e + \Delta e$  was used rather than  $e$  in equation (5) in order to damp the numerical oscillations related to  $e$  growth.

#### 4 Numerical results

Numerical simulations [10] have been shown that temperature distribution in liquid Ti surrounded filament can be considered as quasi uniform in the same filament section while carbon concentration gradients are very significant. Carbon concentration is higher in the liquid titanium close to the filament surface due to the carbon dissociation. Thus, carbon diffuses into the titanium towards the external surface of liquid coating and carbon concentration decreases from the filament surface towards the outside. . According to the phase diagram (figure 2), moving from the filament/ liquid Ti interface towards the external surface corresponds to a decrease in liquidus temperature, down to  $1648^{\circ}\text{C}$  (the eutectic temperature). In a second part, the liquidus temperature increases from the eutectic temperature up to a temperature close to  $1670^{\circ}\text{C}$  (Ti melting temperature) at the external surface where the carbon concentration is near zero. When carbon transfers give rise to significant increases in liquidus temperature, the real temperatures meet those of solidification

and  $TiC_{1-x}$  precipitates. The  $TiC_{1-x}$  front progresses from the  $Ti_2C$ /liquid Ti interface towards the external surface of the Ti coating.

When filaments come out of the liquid bath, thermal transfer occurs by radiation and by natural convection or by forced convection in the cooling device and allows Ti surface temperature decreases quickly. Consequently, solidification of quasi-pure Ti starts at the external surface of the Ti coated filament and progresses towards the filament/matrix interface. The solidification phenomena induce a discontinuity of C concentration and temperature gradient at liquid/solid interface.

Finally, liquid Ti coatings are able to solidify following two distinct growing solidification fronts. The solidification front which grows first is related to  $TiC_{1-x}$  formation. The second front is related to Ti solidification from the coating external surface. This second solidification phenomenon is enhanced by the cooling system which operates when the coated filament emerges from the liquid bath (figure 3).

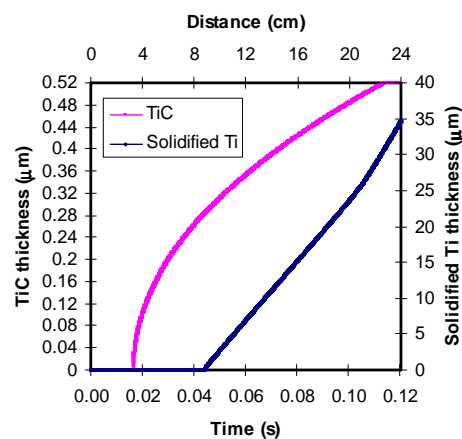
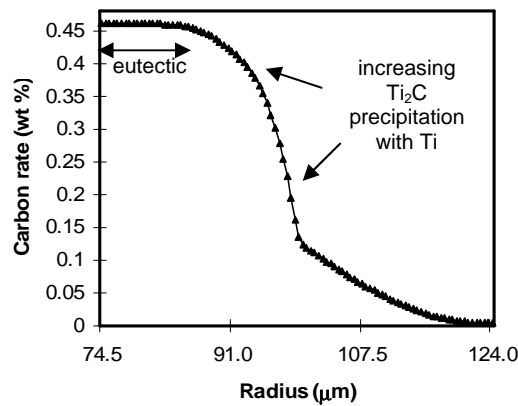


Figure 3. Evolution of the two solidification fronts ( $h = 300 \text{ Wm}^{-2}\text{K}^{-1}$ ,  $V = 2 \text{ m s}^{-1}$ )

## 5. Experimental validation of the model

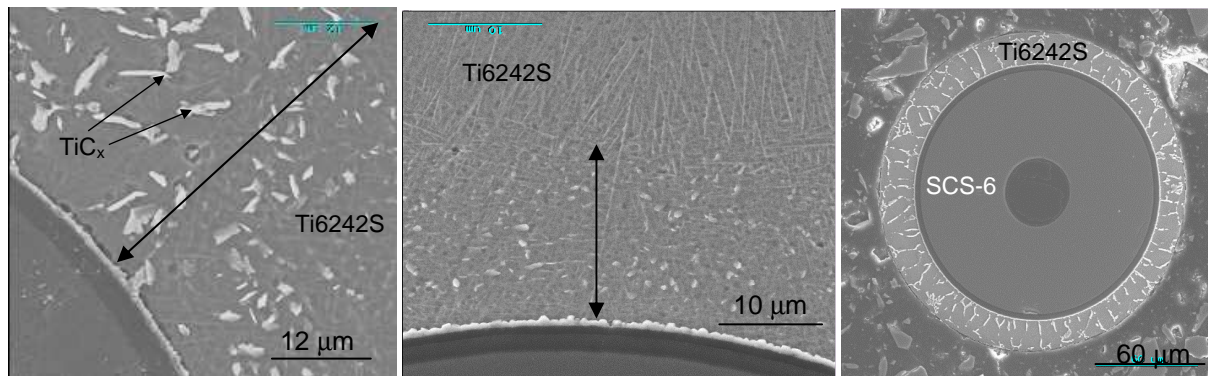
During the growth of the two solidification fronts, the C concentration in the liquid in contact with the  $TiC_{1-x}$  interphase decreases while that in contact with the Ti coating which has already solidified increases outside of the liquid boundary layer related to carbon rejection. When the temperature of the liquid Ti in contact with the solidification front reaches the eutectic temperature, that is to say, when the C concentration in the liquid at the interface reaches the eutectic concentration, further solidification leads to co precipitation of both Ti and  $Ti_2C$  phases (figure 4).

During the co precipitation, the fraction of  $Ti_2C$  in the carbon poor alloy increases gradually up to the fraction of  $Ti_2C$  in the eutectic, which is reached when the carbon transfer boundary layer in front of the growing solid/liquid interface has disappeared. The width of the co precipitation and eutectic areas illustrated in figure 5 depends on processing conditions. Thus, the right balance between the evolution in widths measured on micrographs and that of the related widths, obtained by numerical simulation for the same processing conditions (figure 6), has been considered as a satisfying argument for validating the model and numerical simulation.

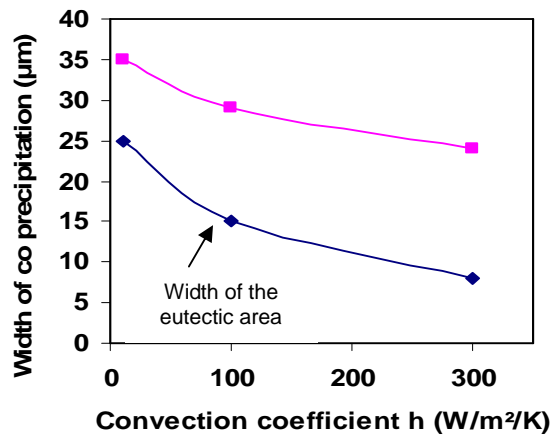


**Figure 4.** Carbon weight concentrations in filament cross section when the metal coating is completely solidified ( $t = 0.1698$  s) ( $h = 300 \text{ Wm}^{-2}\text{K}^{-1}$ ,  $V = 2 \text{ m s}^{-1}$ )

In addition, both the numerical simulation and micrographic observations have shown that for rather low filament running speed for which only  $12 \mu\text{m}$  of Ti coating can be obtained ( $V = 1.7 \text{ m s}^{-1}$ ), nearly all the Ti coating is bi-phased and has a composition close to that of the eutectic.



**Figure 5.** SEM observations of the co precipitation area at the interfacial zone for two different conditions of convection:  
 a - argon convection ( $h = 10 \text{ Wm}^{-2}\text{K}^{-1}$ ,  $V = 3 \text{ m s}^{-1}$ )  
 b - helium convection ( $h = 100 \text{ Wm}^{-2}\text{K}^{-1}$ ,  $V = 3 \text{ m s}^{-1}$ )  
 c - argon convection ( $h = 10 \text{ Wm}^{-2}\text{K}^{-1}$ ,  $V = 1.7 \text{ m s}^{-1}$ )



**Figure 6.** Influence of the Ti/Ti<sub>2</sub>C co precipitation area width vs conditions of convection ( $V = 3 \text{ m s}^{-1}$ )

This validation shows that the physical phenomena involved in processing have been taken into account correctly and the simulation can be used to point out the influence of various processing parameters.

## 5. Conclusion

The physical phenomena occurring during the processing of filamentary composites using an original liquid route have been modelled. The simultaneous numerical resolution of the equations of heat and mass transfer has allowed these phenomena to be simulated thanks to coupling and enables the influences of various mechanisms and parameters to be highlighted. First of all, it has been shown that carbon transfer from the filament to the liquid titanium coating plays a crucial role by controlling liquidus temperatures and  $TiC_{1-x}$  formation. The experimental validation of the numerical simulation has placed a prediction tool at our disposal to optimize the processing conditions particularly through the filament running speed and forced convection amplitude.

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