Film Boiling Chemical Vapor Infiltration of C/C Composites: Influence of Mass and Thermal Transfers[1]

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Abstract

The "Film boiling" Chemical Vapor Infiltration (CVI) process is a rapid densification one developed in particular for the elaboration of carbon/carbon composite materials. In order to optimize this new thermal gradient process, we have carried out several studies, on one hand, about the nature of the complex chemical reactions in a confined medium, and on the other hand, relative to the role of heat and mass transfers inside the preform. We show in this study that the introduction of a permeable sheath around the preform leads to hybrid liquid/gas CVI process which presents the advantages of very high densification rates associated with a moderate input energy.

Keywords: chemical vapor infiltration (CVI) process, c/c composite, pyrocarbons

1. Introduction

The current development of carbon/carbon composite materials is limited by the economical and technical constraints. During the last decade, new processes have been investigated to obtain improved composite materials. As underlined by Golecki [1], these new rapid infiltration techniques are at different stages of technological achievement. It is therefore interesting to compare them with the standard isothermal/isobaric Chemical Vapor Infiltration (CVI) process.

The main advantages for this old process is a good control of the external parameters in large furnaces where a great number of complex preforms are densified together; moreover a good matrix quality is obtained with a selected type of anisotropic pyrocarbon microstructures, in particular the so-called rough laminar (RL) one, associated with a low residual porosity [2]. The main drawback is a very long processing time with a rather low overall precursor efficiency. It turns out that new more effective methods have been developed to increase the densification efficiency, while keeping a valuable final composite.

These new techniques are based either on a thermal gradient or a pressure gradient or even a mixture of them [1]. In particular, a thermal gradient technique coupled to an in-situ vaporized liquid precursor which is a film boiling CVI-type method has been proposed then developed [3]. As compared to the isothermal process, a mobile densification front is created by a strong temperature gradient inside the porous preform because the heater is located inside it. At the opposite of the classical process where the competition between the chemical reactions and the mass transport inside the whole porous medium is always present, for this new process the two phenomena are spatially separated [4]. Indeed in these "cold wall" reactors, this is a new class of out of equilibrium systems with a reactive front which is time and space dependents [5] as also encountered for example in atmospheric re-entry of missiles, or in gaseous combustion with a flame front.

This chemical effect is related with the mass uptake but also the thermal transfers of gases and liquids inside the porous preform. It turns out therefore that the control of both thermal and mass transport which are coupled with the local chemical reactions occurring both in surface and in volume, are fundamental to understand and to optimize the so-called "Kalamazoo" process [2]. This is the work that we are presenting here, using two different sheaths around the preform for controlling these exchanges between the boiling liquid and the preform itself [6].

2. Experimental: Reactor and Parameters

In the boiling film technique, the heated porous substrate is immersed into a liquid hydrocarbon as, for example,

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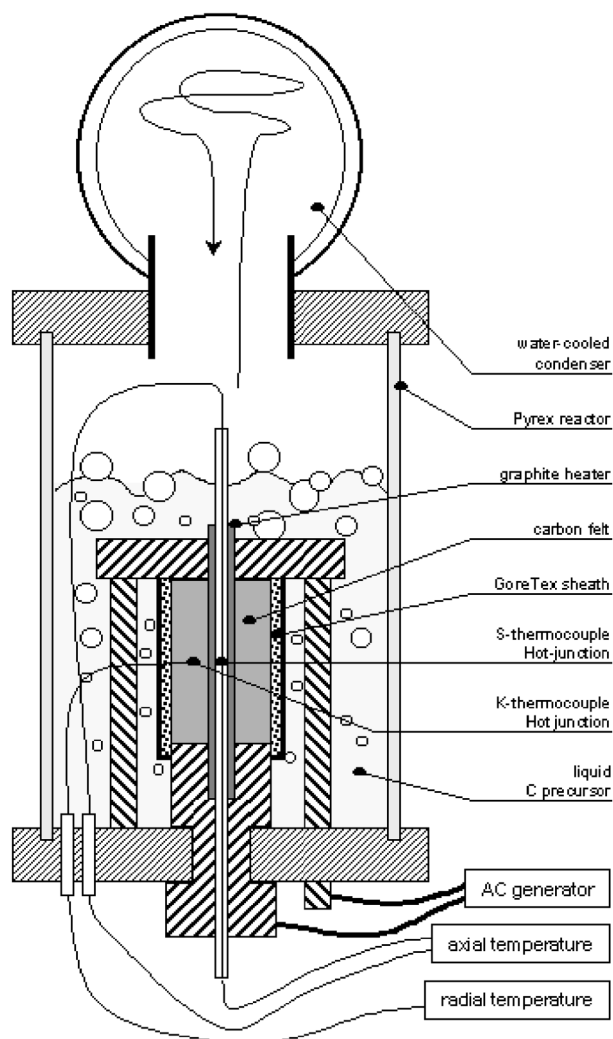
Fig. 1. Experimental set-up.

cyclohexane. The most advantageous shape is a cylindrical reactor as presented in Fig. 1. The cylindrical carbon preform (Φ=20 mm, L=45 mm) is made of ex-cellulose carbon felt disks (RVC 2000 from Le Carbone Lorraine company) with an apparent density of 0.1. These disks are stacked around a central graphite rod (Φ=3 mm) resistively heated by Joule effect; the electrical current is provided by an usual low tension generator. The reference temperature of the sample is measured inside the axial channel of the heating rod with an S-type thermocouple located at the middle height of the preform; moreover a few thermocouples can be inserted in the preform itself to follow the radial thermal gradient during the densification process.

For these experiments, we have wrapped the preform with a thin permeable sheath of PTFE membrane (GoreTex cloth from W.L. Gore & Associates. USA) that can suffer temperatures up to 260°C. The permeability of one layer is around 1 Darcy. Several layers of Gore-Tex can be realized to control all the exchanges.

Alternatively, we have used Pyrex glass cylinders fitting the diameter of the sample and drilled with peripheral holes of various sizes to control the amount of matter exchange.

The process parameters are divided into three different classes as already analyzed [2]. They are respectively geometrical and energetic, hydrodynamical and chemical factors that are coupled together. In our previous studies using a bench reactor as described above and presented in Fig. 1, we have mainly investigated the chemical conditions. As it has been pointed out by Hüttinger [7], then checked in a full series of experiments, an overall reaction model which considers two classes of reactions is recognized. They are respectively the homogeneous gas phase reactions in volume and the heterogeneous surface reactions; under standard conditions, the first ones are promoted with an increasing residence time, and the so-called maturation effect which controls the different types of pyrocarbon microstructures [8]. One advantage of the film boiling technique is to promote these heterogeneous surface reactions giving rise to a better carbon yield. In our previous experiments we have demonstrated the influence of different liquid precursors, as cyclohexane, benzene, toluene and chlorobenzene, on both the pyrocarbon yield (up to 50% for aromatic compounds) and the type of deposited microstructure [4]. We have also investigated the catalytic CVI process by adding ferrocene to the organic precursor [9]. An important increase of the densification rate has been observed, as demonstrated by the decrease of the apparent activation energy deduced from the Arrhenius law. However the deposition mechanism and the associated type of microstructures are completely modified by the catalyst with the presence of multiwall nanotubes and soots, inside a rather amorphous matrix which does not present valuable mechanical characteristics.

Indeed, it turns out that to optimize the whole process and to control therefore the densification front, the key hydrodynamic parameters have also to be rationalized. Pursuing our research we have introduced a sheath (PTFE membrane or glass tube) around the preform to control both the mass and thermal transfers.

To analyze the effect of a such controlled barrier, we have examined the following responses:

i) the total power which is necessary to run the reactor,

ii) the pyrocarbon mass uptake and the rate of the associated densification front,

iii) the matrix quality, i.e. the type and the distribution of deposited pyrocarbon microstructures.

3. Results and Discussion

For each experiment carried out at 1100°C, we have determined the used energy under stationary conditions and the pyrocarbon mass uptake, as presented in Fig. 2. We
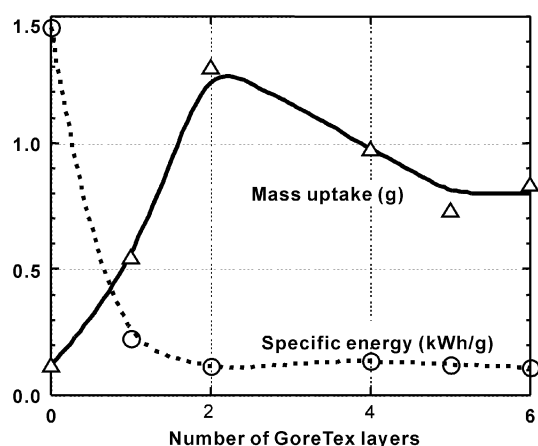
Fig. 2. Mass uptake and total dissipated energy versus the number of GoreTex sheaths (0 to 6 layers).
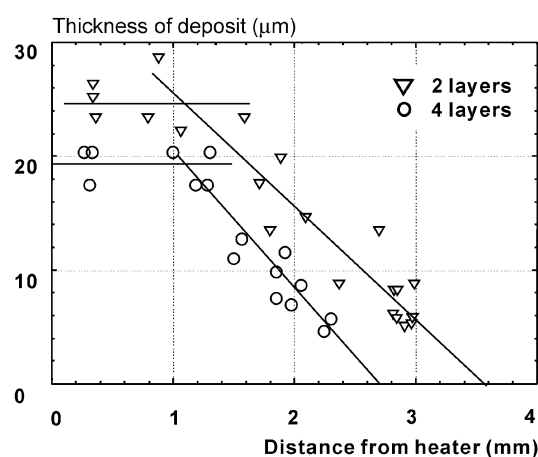

Fig. 3. Radial densification profiles determined from optical microscopy pictures for 2 and 4 GoreTex layers.

immediately observe a decrease of the energy necessary to run the reactor as soon as one layer of GoreTex is wrapped around the preform. In parallel, the total mass uptake is going through a maxima for two GoreTex layers then decreases slowly. It turns out immediately that the used power per gram of deposited pyrocarbon is decreasing in presence of this barrier, indicating an improved energetical efficiency of the reactor.

To get a better insight, we have estimated the densification rate and its profile by examining the optical micrograph of a radial cross-section of the partially densified felt. A polished surface of these samples observed by polarized light optical microscopy between crossed polarisers shows both the type of microstructure related to the optical anisotropy through its Maltese cross, and its mean thickness measured around single filaments at different radial distances [3, 4].

We can thus determine both the densification rate from the thickness of the densified zone and the associated densification profile (Δe) as shown in Fig. 3. Compared to the

Table 1. Influence of the number of GoreTex layers under the deposition rate Vd, the deposition profile Δe and the specific deposition energy

Number of GoreTex layers	0	1	2	4	5	6
Vd (mm.h^{-1})	0.6	2.5	4.0	3.2	2.8	2.3
Δe (mm)	1.3	1.6	2.1	2.0	2.3	2.8
Specific energy (Wh.g^{-1})	1460	225	115	135	125	110

previous results [4] obtained without GoreTex layers, we can deduce that the densification speed is increased but with a modified thermal profile: all these results are reported in Table 1.

A maximum of deposition rate (Vd), for two cloth layers, is measured in agreement with the optimized mass uptake. When the number of GoreTex layers is still increasing, the mass exchange is reduced with the diminishing layer permeability because of the presence of a diffusion barrier between the reservoir and the preform.

We have also observed the type of deposited pyrocarbon which is quite reproducible, in this series of experiments. This is representative of a rough laminar microstructure which is the graphitable one, interesting for most of the applications [2]. On the micrographs, we detect also some residual closed micro porosities that we do not estimate quantitatively but which are related with these high densification speeds.

To get a better control on the process, we have examined the radial thermal gradient thanks to the inserted thermocouples at different distances from the axial graphite heater inside the preform [9]. In presence of at least one layer of Gore-Tex, the temperature rise starts immediately inside the preform. This schematic model, presented in Fig. 4, is considering that the process is controlled by two fixed extreme temperatures: the deposition temperature (T_D) and the boiling point (T_B) of the precursor. Several parts are recognized with specific functions at a given deposition time:

− part I: the graphite heater and the already densified preform at an almost constant temperature T_D, usually 1100°C,

− part II: the reacting front where the chemical reactions are occurring, associated with a temperature gradient between T_D and T_P (minimum pyrolysis temperature) as revealed by the densification profiles,

− part III: the porous preform where the heat and mass exchanges in the gas phase are located; they are dependent of the selected type of preform which only plays the role of a thermal exchanger,

− part IV: the biphasic zone at the precursor boiling temperature (T_B) where the carbon precursor is present in both liquid and gas phases inside the porous preform.

This phenomenon called "calefaction" in free space (Nukiyama's model) is rather unstable in a porous media but effective to transport heat and mass [10].
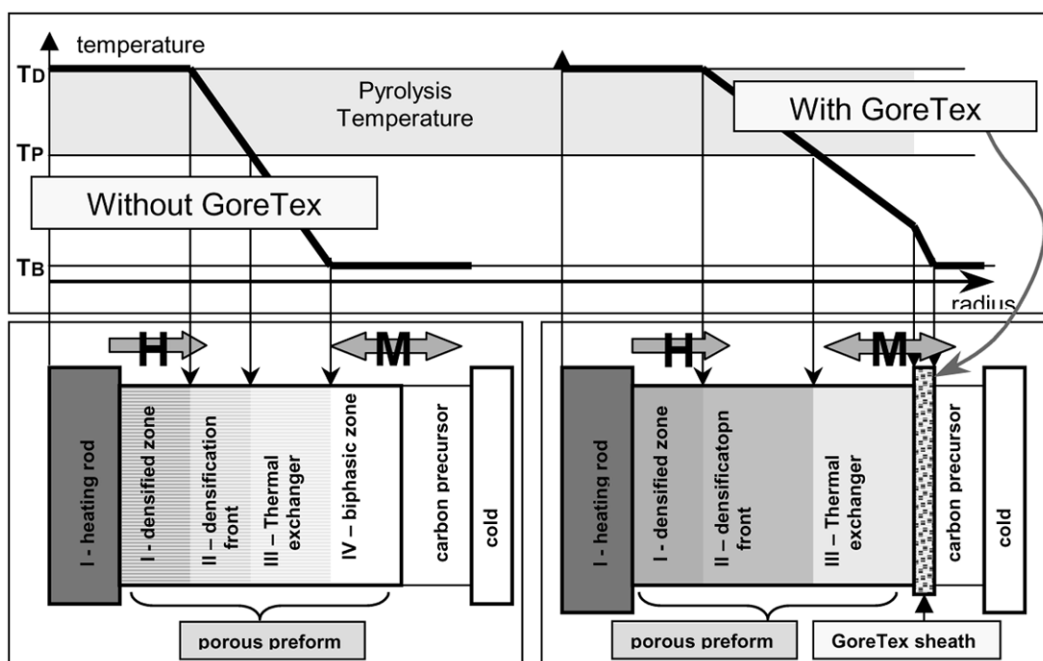
Fig. 4. Sketch of the radial temperature gradients in standard process (without GoreTex) and for the modified one (with a GoreTex sheath).

However, in presence of a thermal barrier (Fig. 4b), this zone IV is disappearing, the gas phase is only penetrating inside the preform because the calefaction effect is happening only inside the reservoir. It follows that the thermal gradient is modified, and also the related consumed energy, as actually observed experimentally (see results in Table 1).

As plotted in Figs. 4, the modelization process is based upon the presence of these several defined zones. It appears that the width of the reacting zone is larger in presence of a barrier than without it, as shown experimentally by the extension of the deposition profile Δe (see Fig. 3). As long as the mass transfer is controlled by Fick diffusion process and the associated concentration gradients [4] the deposition mechanism appears more effective than in presence of a steeper thermal gradient. Its complete control would be interesting in particular by comparison with the ultimate situation which is the standard isothermal process, i.e. when the thermal gradient is suppressed.

To summarize the results, as shown in Fig. 2, we have two defined regimes: for one or two layers of GoreTex, we are in presence of a thermal barrier that stabilizes mainly the calefaction effect outside the preform. Then for a larger number of layers, we have a diffusion barrier which controls the mass exchange between preform and precursor reservoir, and therefore the whole process. We can note that complementary experiments using perforated glass tubes have qualitatively confirmed these results.

4. Conclusion

With the introduction of a permeable sheath around the preform, we have shown that we can improve the efficiency of this fast deposition technique, giving a better carbon yield with less used energy [6]. In fact, this is a kind of mixed gas/ liquid CVI process in the sense of a liquid phase is used as a reservoir, but only the gases are penetrating inside the preform, to reach the hot surface as in classical CVD process.

Concerning the matrix quality, it is necessary to analyze and control it fully under these experimental conditions [11]. For that purpose, it is also necessary to understand and to modelize the local conditions [12] which are concerning the chemical reactions coupled with the hydrodynamical and thermal parameters inside an evolutive porous preform. These recent studies allow us to optimize and control this new process before industrialization.

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