High density Carbon/Carbon manufactured by an hybrid process, involving pitch impregnation under moderate pressures

A. Dekeyrel[1], A.Allemand[1,2], M.-A. Dourges[1], R. Pailler[1], N.Teneze[2], J.Blein[2],P.David[2]*

1 University of Bordeaux 1, Laboratoire des Composites Thermostructuraux (LCTS), UMR 5801, 3 allée de La Boétie, 33600 PESSAC (France)

2 CEA, DAM, LE RIPAULT, BP 16, F-37260 MONTS, France

* Corresponding author. E-mail : allemand@lcts.u-bordeaux1.fr

Introduction

The aim of this study is to propose a process for manufacturing high density three dimensional carbon/carbon composites. According to previous work, using moderate pressure (< 10 MPa) involves, to get high density C/C composites (1.80 g.cm^{-3}), numerous cycles of pitch densification [1]. Therefore, this study explores an hybrid process which consists in a pre-densification step before cycles of pitch densification. This pre-densification step must increase rapidly the apparent density of a raw preform. As a consequence, for the same number of pitch densification cycles this pre-densification should permit to get higher density. Film boiling chemical vapour infiltration (also called "Kalamazoo") has been used for this first pre-densification step [2] [3]. C/C composites syntheses, from two kinds of raw fabric architectures, have been done using this first step of film boiling CVI. Theoretical calculations and experimental measurements of apparent density give evidences that using a film boiling CVI step is more efficient to elaborate C/C composites under moderate pressure.

Experimental

Two kinds of raw preforms have been studied. The first one is a needled preform which will be called "No" in this paper (No referring to Novoltex® from Snecma Propulsion Solide – SAFRAN group). The second one is a 3D orthogonal fabric which will be called 3D.

Film boiling CVI is a thermal gradient technique in which a mobile densification front is created by a strong temperature gradient inside the porous preform heated by inductive effect. The mass and heat fluxes being opposite inside the sample, the precursor, liquid toluene in our study, is pyrolysed. Subsequently a high amount of C is deposed inside the preform. In this work two dwell times have been studied one short called SC and the other long called LC.

Cycles of pitch densification have been realised with M50, a petroleum pitch from Marathon-Ashland. To achieve one cycle of densification the preform is placed in an open stainless steal can filled with M50 in excess. The can is, then, placed in a specific autoclave. The heat-treatment under moderate pressure is carried out in this closed autoclave. The sample is heat-treated for 40 min at 200°C in vacuum, then,

during this temperature dwell, N$_2$ is introduced to a pressure of 5MPa. After this step of impregnation the temperature is increased to 430-440°C, temperature dwell is 6h, N$_2$ pressure is 8MPa, this step enables the mesophases to grow. Then, the temperature is slowly increased at 0.5°C.min^{-1} to 700°C, at that time pressure is 10MPa. After cooling down, the sample is taken off the autoclave. The carbonized sample is then heat-treated for 5h at 1100°C in an horizontal kiln under N$_2$. To achieve graphitisation, the sample is heat-treated for 30 minutes at 2500°C. Beyond graphitisation, this last heat treatment permits to re-open porosities and so to prepare the sample to an other densification cycle.

Material densities (called true densities) were measured by helium pycnometry (AccuPyc 1300 from Micromeritics). Porosity was also characterized by mercury intrusion porosimetry (Autopores IV from Micromeritics).

Thermal conductivity was measured by flash method. Samples are machined in the shape of small cylinders $\varnothing$=15mm H=2 mm.

Microstructures were determined by optical microscopy (OM).

Results and Discussion

"3D" samples:

Table 1 presents pore distributions after a short and a long film boiling densification. After a short one a majority of pores is still large (65µm) whereas after a long one size of pores decreases. In terms of microstructure (Fig.1) C is deposited mainly around bundle. A large crack surrounding bundle can be seen after graphitization. Table 2 shows that, film boiling enables to reach a certain density but, even after two cycles of pitch densification, the apparent density stays low.

Table 1. Open porosity, size and distribution of pores in 3D preform.

|	Open Porosity %	Pore Size µm distribution%	Apparent density g/cm^3
Raw preform	56	-	0.79
Short film boiling SC	43	65 µm (95%) Other (5%)	1.03
Long film boiling LC	31	27µm (25%) 20µm (65%) Other (10%)	1.34

Table 2. Apparent densities at each cycle of densification and gap between theoretical results and real ones.

	Apparent density (d$_a$) g/cm^3	Theoretical apparent density (Td$_a$)	d$_a$/ Td$_a$ %
SC	1.03		
First cycle M50	1.06		
Second cycle M50	1.19	1.44	83%
LC	1.34		
First cycle M50	1.38	1.59	86%
Second cycle M50	1.41	1.61	88%

Table 2 shows the theoretical apparent density which is the density expected if all the pitch inside a pore was pyrolysed.

The ratio between real apparent density and theoretical is more or less the same never mind the cycle (impregnation yield was 100%). Those results enable to think that the pitch is expelled from the pore during heat treatment in autoclave. This phenomenon takes place both in pores size of 65µm and 20µm.

Fig.1 OM of a 3D preform after short calefaction
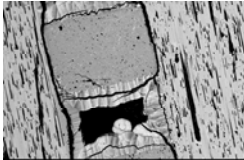
"No" samples

Figure 2 presents apparent density versus the cycles of densification for needdled preform No with (No-cal-M50) and without calefaction densification (No-M50). It can be seen that film boiling permits to reach rather high density (1.60) in a first step. Then, after four cycles of densification the density reaches 1.80 which was our aim. The sample without pre-densification exhibits a density of 1.70 after four cycles of densification. The dash curves show theoretical calculation of density using the same approch as 3D. Figure 3 represents for each step the volume filled. Using film boiling enables to fill rapidly a large amount of the empty volume. After that, the cycles of pitch densification are not as efficient as in No-M50. In fact in the case of needled preform, the weaker the volume to fill is the weaker the densification is. Conclusion can be the same as the 3D : when pores are getting smaller because of previous densifications the pitch is exuded because of gaz pyrolyses pressure during heat treatment.

In terms of microstructure figure 4 shows that No-50 exhibits large pores (Fig4b) which enables to think that a fifth cycle can be efficient. This one could decrease the porosity to 18% whitch is still higher than No-cal-M50 after four cycles (14%).

Fig. 2 Apparent densities (real and theoretical) versus number of densification cycles for raw preform and pre-densified preform
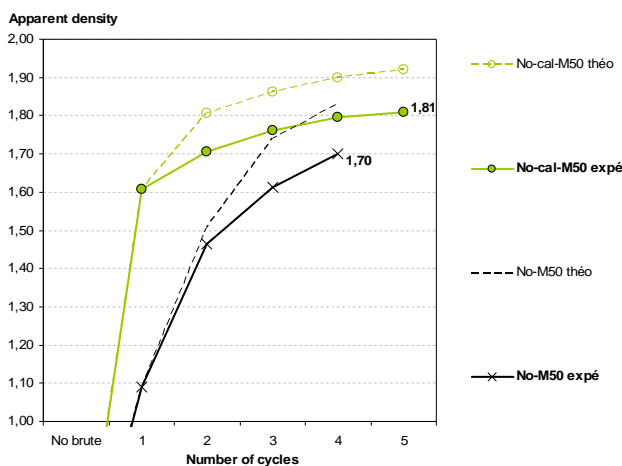

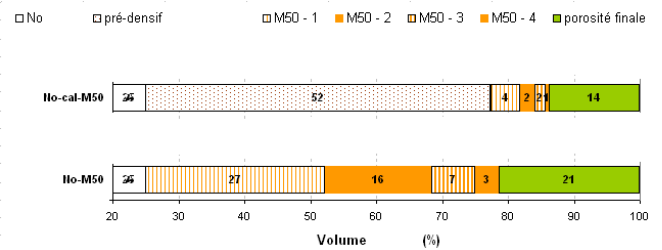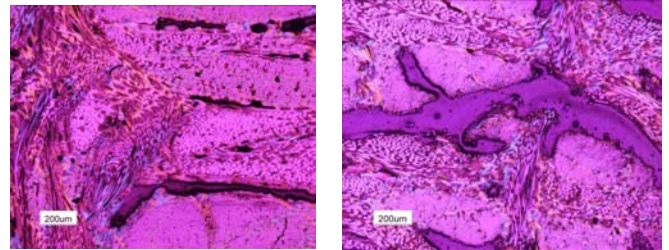**Fig. 3** Volume proportion which filled each step of densification.

Fig.4 : Microstructures of No preform after all the steps of densification a) with film boiling b)without film boiling

The microstructure of No-cal-M50 exhibits small and closed porosities (Fig4a) which tend to think that an other densification cycle will be unefficient. This is corroborated by figure 2 where a density dwell is reached by No-cal-M50. The thermal conductivity of these two samples has been measured. It is 55 W/m/K for No-M50 and 25 W/m/K for No-cal-M50. This result is unexpected because whereas the density of No-cal-M50 is higher its conductivity is lower. Two reasons can explain such a result: the first one is the fact that carbon from film boiling exhibits large cracks which often surround bundles (theses large cracks drastically decrease the thermal conductivity if they are orthogonal to the heat flux), the second one can be the organization of the carbon from calefaction. TEM study has shown two kinds of carbon organization around bundle one is highly anisotropic and the other is more isotropic.

Conclusions

This study has permitted to show that using film boiling as pre-densification enables to reach the density aim of 1.80 but just with needled preform after four cycles of pitch M50 densification. On the other hand, with 3D preform, pre-densification by film boiling did not manage to reach such an high density. This comes from the fact that pitch is exuded from pores during heat treatment. Pore architecture is of first interest for densification.

References
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