

RAPID DENSIFICATION OF CARBON AND CERAMIC MATRIX COMPOSITES MATERIALS BY FILM BOILING PROCESS

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Abstract

The Film Boiling technique is a particular Chemical Vapor Infiltration process for the densification of carbon matrix and also ceramic matrices, such as SiC, BN and SiO₂. Its particularities resides in the very high thermal gradient and high chemical precursor concentration which lead to a densification zone moving quite quickly through the piece to densify.

The influence of main parameters (temperature, pressure, composition of the precursor, control of the vapor flux) on both the microstructure of the material and the working of the process (densification rate, material yield, energy efficiency) are described. High densification rates (several mm/h), good materials characteristics (mechanical, micro-structural) and reproducibility are the main advantages of this process. For carbon precursors, graphitizable carbon matrices are almost deposited, whatever are the conditions, which is quite difficult to get with CVI. For SiC precursor, modification of the temperature process can lead to the deposition of micrometric size alternated layers of carbon and silicon carbide.

1 Introduction

Ceramic Matrix Composites (CMC) possess high toughness at high temperature, which permits them to be used in rocket motor, jet engine or thermal protection systems in the aerospace industry. Chemical Vapor Infiltration (CVI) remains the main process for CMC elaboration although other ways are studied such as Precursor Impregnation and Pyrolysis (PIP) or reaction bonding. The main drawback of CVI is its slowness which can be reduced, but only partially, by addition of thermal gradient, forced flow or pulsed flow system [1]. The Film Boiling technique is a particular Chemical Vapor Infiltration

process whose very high thermal gradient and mass transfer fluxes constitute the driving force [2]. They are induced by the vaporization of a liquid precursor, on the external surface of the porous structure to fill up. This technique presents many advantages: high densification rates (several mm/h), good materials characteristics (mechanical, micro-structural), reproducibility and relative simplicity, and possibility to get various matrices.

2 Principle of the process

The sample to densify, a carbon or ceramic fabric, is put into a reactor and immersed in a liquid (or melted) precursor. A coiled tube outside the reactor, connected to a R.F generator, is used to inductively heat the sample. If the fabric is not an electrical conductor, a carbon mandrel, acting as a susceptor, can be added. During heating, the precursor boils and the vapor enters the porous structure and gives ceramic deposit by cracking in the highest temperature area [Fig 1].

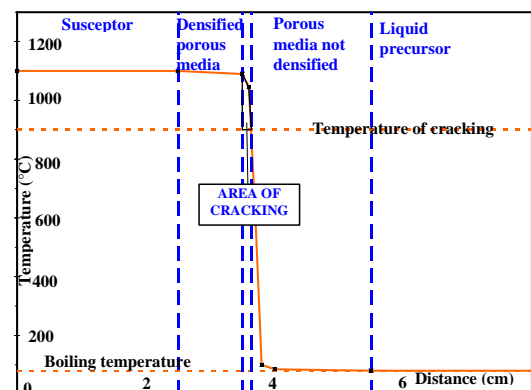


Fig. 1. Example of temperature distribution and areas in a sample (cylindrical carbon mandrel and carbon felt during densification).

Very strong thermal gradient (up to 300 °C/mm) are generated inside the fabric, due to the highly endothermic vaporization phenomena. The uncracked vapors are condensed within a cooling system above the reactor. The reaction gases are released in an extractor. The high densification rates can be explained by high precursor concentration (the pressure is 1 bar, instead of less than 0.1 bar in classical CVI process), strong convections, due to high thermal gradient, and by the fact that densification sets up from internal to external part of the sample, which avoids plugging of external porosity.

3 Carbon/Carbon composites densification

3.1 Parameters influence

The parameters that drive the process are the same as CVI but the vapour phase composition (hydrocarbon species/H₂) cannot be adjusted and chemical flux (and resident time) is difficult to control. Nevertheless the natural working of the Film Boiling leads to good results.

3.1.1 Temperature

An increase of the temperature leads, using cyclohexane as carbon precursor, to carbon yield increase and, in an exponential way, densification rate (speed at which densification front is moving through the fabric) increase (Fig. 2). Effect of temperature deposition on microstructure is described in § 3.2.

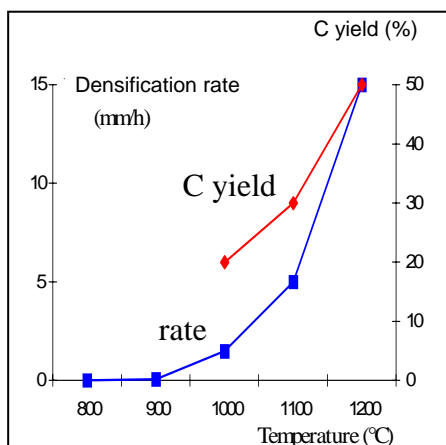
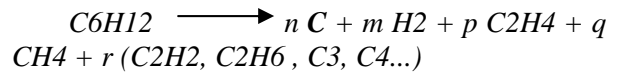


Fig.2. Densification rate and carbon yield versus temperature, with cyclohexane and for a carbon felt.

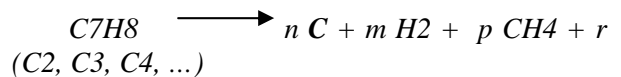
3.1.2 Precursor

Aromatic compounds allow higher densification rate and higher carbon yields than cyclohexane. The global reactions, determined weighing the samples, measuring the by products gaz flowrate and analysing their composition by Gaz Phase Chromatography, are, for cyclohexane and toluene, these ones:



$$1 < n < 3, 1.5 < m < 3, 1 < p < 2, 0.6 < q < 0.8, r < 1$$

$$n, m, p, q, r = f(T, P)$$



$$5 < n < 6, m \sim 2, p \sim 1, r \sim 1$$

The carbon yield for toluene, is above 70 %, instead of less than 10 % for CVI.

3.1.3 Pressure

The densification rate increases with an increase of the pressure (Fig. 3), which is due to a higher vapor concentration.

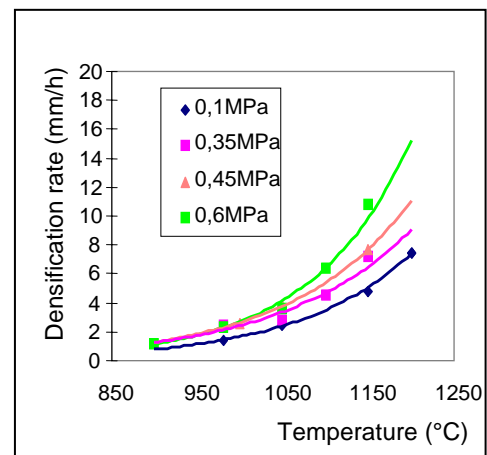


Fig.3. Densification rate versus pressure, with cyclohexane and for a 2.5 D fabric.

3.1.4 Vapor flux modification

The vapor flux can be partially adjusted using a filter, surrounding the sample. It decreases the

thermal gradient, leading to a larger cracking area, which, for the same maximal T, both enhances the densification rate and decreases (down a factor of 10, for small samples) the energy consumption [2].

3.2 Characteristics of the materials

Polarized light optical microscopy was used to determine the nature of the deposited pyrocarbon (rough or smooth laminar, isotropic, etc.) and to visually assess the nature of the matrix. Fig. 4 shows large conical growth areas, distorted Maltese crosses, high optical contrasts. According to the classification [3], the deposited pyrocarbons are rough laminar (and thus should be graphitizable) in the temperature range 900-1200°C.

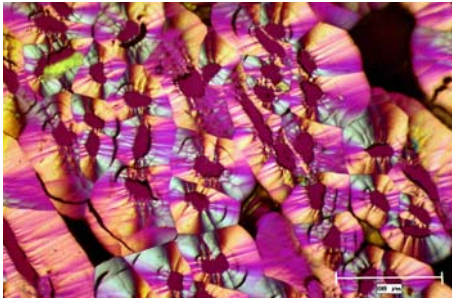


Fig.4. Polarized light optical micrography of a C felt/C synthesized at 1000 °C.

An X-ray powder diffraction study of C felt/C composites has been carried out in order to show the influence of the synthesis temperature and of the HTT. The studied parameters are d_{002} (interlayer spacing along the c-direction), Lc (crystallite size along the c-direction) and the evolution of γ_{11} (band with HTT (Table 1). Because of the low fiber volume fraction (< 6 %), the contribution of the fibers (which are not graphitizable) is negligible.

T synthesis (°C)	900	1000	1100
As prepared			
d_{002} (Å)	3.477	3.480	3.474
Lc (Å)	20	20	30
After 2h at 2450°C/Ar			
d_{002} (Å)	3.367 ₅	3.367 ₆	3.367 ₄
Lc (Å)	900	790	700
After 2h at 2700°C/Ar			
d_{002} (Å)	3.356 ₇	3.357 ₇	3.357 ₂
Lc (Å)	> 1500	> 1500	> 1500

Table 1. X-Ray diffraction results

There is no significant difference when changing fabric type, pressure, or vapor flux, in a quite wide domain.

The mechanical properties and behavior for brakes, determined on quite large samples (Fig. 5), are similar to those of CVI C/C.



Fig. 5. C/C brake (diameter 40 cm) densified by Film Boiling process.

4 Ceramic matrix composites

The main disadvantage of Film Boiling, in comparison with classical CVI, is the limited choice of the composition of the vapor which will be cracked. For CVI, numerous gaseous precursors exist (or can be synthesized in situ with, for example, reaction of a metal and a halogen), and the composition of the gases to be cracked can be adjusted in any proportion, just by mixing them with controlled flow rates ratio. With Film Boiling, the composition of the vapor is limited by existing chemical compounds. Other difficulties come from that the precursors, as organo-metallic compounds, are often costly, not stable in air or moisture conditions, and sometimes toxic, which need the use of a glove box around the densification apparatus.

4.1 C/SiC and SiC/SiC composites

C/SiC and SiC/SiC have been developed for rocket and jet engines and thermal protection systems. They present the advantage to sustain high temperature in oxidizing atmospheres. Methyltrichlorosilane (MTS, CH_3SiCl_3) is used in CVI to get SiC matrices, but it is necessary to mix it with hydrogen to get stoichiometric SiC without C [4]. The pyrolysis at 1300 K of MTS by Film

Boiling, gives homogeneous deposition with a 2.0 density (3D SiC/SiC) for a relatively thick sample (Fig 6). Chemical analysis gives a composition $Si/C = 0.9 \pm 0.2$ and α and β phases are detected by X-ray diffraction.

For temperature above 1350 K several deposits are obtained (with proportions of Si varying from 10 to 40 weight %) as showed in Fig. 7 for a 3 DSiC preform. The reaction must be, assuming that the main reaction gases are silicon chloride and hydrogen:

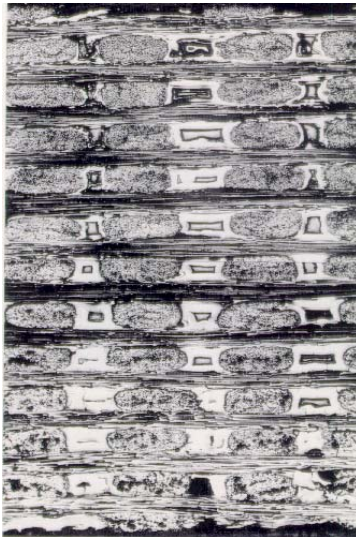
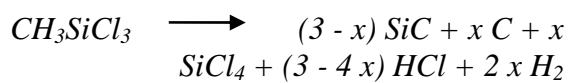


Fig. 6. Optical photomicrograph of a 3D SiC/SiC (8 mm thick) densified using MTS at 1300 K.

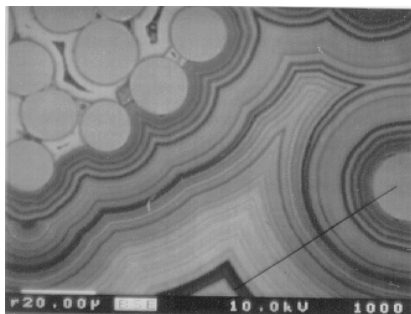
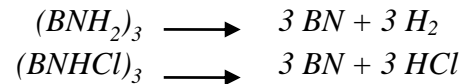


Fig.7. Optical photomicrograph of a 3D SiC/SiC densified at 1350 °K (detail)

4.2 C/BN composites

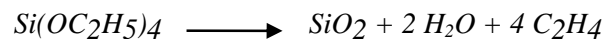
Boron Nitride densification is feasible by Film Boiling but is also more delicate than these of carbon or oxides. Two precursors, borazine $(BNH_2)_3$ (Bp: 25°C) and trichloro-borazine $(BNHCl)_3$ (Bp : 200°C) can lead to boron nitride by the decomposition reactions:



The main problem lies in the sensibility to hydrolysis of these precursors and of the densified products. In order to avoid it, they have to be treated at high temperature (2000°C). The densified carbon felts (at 900°C) present characteristics similar to those of carbon densification. The porosity is about 15 %, density is 1.7 and polarized light micrography reveals Maltese crosses and growth cones, characteristic of a rough laminar structure type. Transmission electron microscopy shows the orientation of the structure and permits the determination of the crystallites dimensions: $L_a = 50-100$ nm, $L_c = 10-20$ nm. RX gives an average d_{002} value of 3.37 Å (theoretical: 3.33 Å).

4.3 C/SiO₂ composites

Tetraethoxysilane (TEOS, $Si(OC_2H_5)_4$) can be used as silicon dioxide precursor. It is often used in sol-gel processes and needs less precautionary measures than BN or SiC precursors. It gives SiO₂ by the reaction [4]:



The boiling point of TEOS is 439 K and its behavior is quite similar to the one of cyclohexane during the Film Boiling process. The cracking starts up for a temperature of about 1000 K (instead of 1150 K for cyclohexane) and the densification rate is 1 mm/h at 1300 K. Only SiO₂ is deposited up to 1330 K, but, for higher temperatures, SiO₂ and C are obtained. The final densities are about 1.7 for densified felts and 1.5 for 3DC preform. The densification of the cavities (for 3D) is very good in the first mm of the sample (part exposed to the highest temperature) but is weak in the external part,

due to the limitation of temperature necessary to get SiO₂ without C.

5 Conclusion

Film Boiling process presents the important advantages to be very fast and to allow densification of large samples. For carbon, graphitizable deposits are obtained in a quite large domain. This process allows the densification of ceramic matrices different from carbon, with densification rates similar to these of carbon. Nevertheless, the control of matrix composition (SiC, SiO₂) limits the range of temperature process and leads to lower densities in the case of 3 D fabrics, for thick samples (>3-4 mm). Future work will focus on deposition of ultra-refractory carbides.

References

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