CATALYTIC CHEMICAL INFILTRATION FOR CARBON/CARBON
COMPOSITE MATERIALS
FABRICATED BY THE BOILING FILM PROCESS

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Introduction
The Chemical Vapor Infiltration (CVI) process for making composites are divided in two general classes. The classical isothermal isobaric process and the more recent fast densification techniques based on a thermal (or pressure) gradient. In particular, the so-called “boiling film technique” where the heated fibrous preform is immersed in a liquid hydrocarbon has been developed [1]. A well known result is a very high densification rate associated with a higher yield giving rise to a good matrix quality for the deposited anisotropic pyrocarbon (so-called smooth or rough laminar microstructures) [2]. One of the known effective factors to improve the carbon deposition is the catalytic effect using transition metals. We have explored this way for CVI process using this technique of cold wall reactor.

Experimental
A small bench reactor with a central resistive heating for the cylindrical preform (carbon felt RVC 2000 from Le Carbone Lorraine Company) is used [2] (fig. 1). The preform is immersed in the liquid precursor: cyclohexane mixed with ferrocene (0.1 to 5% in weight). For different deposition temperatures \( T_D \) (900 to 1200°C) we have examined the kinetics of mass uptake which is associated with the deposition process (fig. 2). Then in a second step, we have examined at different scales the quality of the matrix by optical microscopy under polarized light, the local iron concentration by Electron Probe Micro Analysis (EPMA), then the nanostructure by Transmission Electron Microscopy (TEM).

Results and discussion
- The presence of iron inside the precursor allows us to work at a lower \( T_P \) and with an increased rate of mass uptake which is optimized for 0.5% in weight of ferrocene (fig. 2).
- The morphology of deposited pyrocarbons is strongly modified and an apparent isotropic microstructure is observed by optical microscopy (see table 1).
- The EPMA has demonstrated that the deposition of this “isotropic” phase is correlated with the presence of iron (a higher decomposition rate of ferrocene induces the morphological change, i.e. the recovery of the anisotropic pyrocarbon when all the ferrocene has been consumed).
- The TEM images on a given sample (fig. 3) show the presence of iron containing nanoparticles but also carbon particles and nanotubes.

These observations indicate a completely different mechanism for the carbon deposition. This argument is confirmed by a lowering of the apparent activation energy determined from a classical Arrhenius plot of the mass uptake.

The deposition mechanism is strongly modified as evidenced by the change of the radial thermal gradient. It can be interpreted with a model for particle-vapor codeposition [3] which implies the formation of small particles inside the gas phase.

Conclusion
Using this fast densification process we have evidenced a catalytic effect which leads to a better infiltration efficiency. However the mechanical quality of the obtained matrix has to be improved for C/C composite applications. Concerning the CVI mechanism, we have shown that this film boiling technique is based on the presence of a moving reacting front controlled by the coupling between thermal and concentration gradients.

References
Table 1: Matrix microstructures under various experimental conditions

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Figure 1: Experimental set-up with the axial temperature profile

Figure 2: Mass uptake / catalyst concentration

Figure 3: TEM of a composite sample (T_D: 1100°C, ferrocene in cyclohexane: 5 w%)