BENCH REACTOR FOR FAST DENSIFICATION PROCESSING OF CARBON-CARBON COMPOSITE MATERIALS

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Introduction

The densification of high temperature composite materials such as carbon-carbon composites is usually produced by a vapor phase (or boiling liquid) route. The conventional way is accomplished by isothermal and isobaric chemical vapor infiltration (CVI). More recently, many attempts have been made, using a very steep thermal gradient inside the carbon substrate, which gives significantly reduced processing times. Among these new techniques, the film boiling process [1] leads to a fast densification of a thermally conductive carbon fibrous preform.For a better knowledge of this process, we have developped a laboratory cold-wall reactor with an internal resistive heater which allows us to experiment different parameters as temperature, substrate nature, liquid carbon precursor...

Experimental

Set-up: (fig 1)
The cylindrical (2 cm in diameter) sample is built with several carbon felt discs (*Carbone Lorraine* RVC 2000) stacked around an axial tubular graphite resistor. Temperature is measured at the center of the sample with an S-type thermocouple.
The thermal gradient inside the carbon felt, is obtained between the graphite rod, heated by Joule effect up to 1300°C, and the carbon precursor bath at its boiling temperature.

Characterizations :
Here are presented extensive experiments driven on cyclohexane as main carbon precursor up to 1300°C for a standard duration of 30'.
In this first step, we are dealing with the process kinetics and the characterization of the matrix by optical microscopy, He pycnometry and Xray diffractometry.

Results and discussion

Densification rate:
We are looking for the relation between the deposition rate (in µm/h) around the carbon filaments previously presented [2], and the densification rate (in mm/h) of the sample in the bulk.
Optical micrography of a polished cross section of the sample shows, from the measure of deposit thickness around the carbon fibers,(fig 2) a radial densification profile, obtained here from cyclohexane after 30' at 1250°C. Two areas can be separated apart a "densification front line":

- right, a progressing densification area where further deposition occurs around individual fibers.
- left, a densified area where further deposition occurs only inside remaining large open pores.

The deduced densification rate can be sketched for different temperatures (fig 3), from which curve, following a pseudo-Arrhenius law (reaction temperature beeing assumed constant, at least close to the center), we can compute:

- an apparent activation energy: Ea ~ 340 kJ mol^{-1}
- an inclusive reaction constant: k ~ 3.2 10^{12} mm h^{-1}

Microstructure:
Due to the superposition of pyrocarbon laid at progressively increasing temperatures around each carbon fiber, the recognition of the usual microstructures (Smooth Laminar, Rough Laminar, Isotropic) is tricky at low displayed temperatures. Nevertheless, micrographic observation of S.L. pyrocarbon at lower temperature and R.L. over 1250°C is in agreement with the measured densities.
After heat treatment (5 h at 2500°C), the segregation between graphitizable R.L. pyrocarbon and ungraphitizable S.L. is here also enforced, as checked by Xray diffraction.

Comparison of the experimental processes
Two different set-up of different sizes have been used under the general title of "film boiling process" :

- "bench reactor", resistive heating, 2cm samples
- micro-reactor, resistive heating,1mm samples [2]

This technique is based on a moving reactive hot frontier with a steep densification profile (fig 2).
A bulk densification front is moving through the porous substrate in this process at sensible speed (cm/h), in agreement with the deposition rate on the fibers themselves, as in-situ observed with the micro-reactor [2].
A simple model allows us to connect these two quantities and then to define the moving radial thermal gradient [3].
It turns out that a slow temperature decrease associated to the heating mode is present and not fully controlled in this type of reactor. This last result is different from what we get from a pilot installation where an inductive heating is used [1]. But in both cases, the fundamental characteristic is a reactive hot wall with a progression controlled by the competition between heterogeneous surface reactions and mass/heat tranfers through the porous medium [3].

Conclusion

The benefit is here the simplicity and the versatility of the experimental set-up which makes also possible the complete densification in a less than 3 h. single run of representative samples. It thus opens widely the field of research to many kind of precursors and porous substrates for the preparation of new carbon/carbon (and related) composite materials.

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References

[1] Bruneton E, Narcy B & Oberlin A. Carbon 1997; 35:1593-1611.

[2] Rovillain D, Trinquecoste M, Bruneton E, Derré A, David P, Delhaès P. Extended abstracts, Eurocarbon'98 Strasbourg (France): AKK-GFEC, 1998; 455-56.

[3] Rovillain D. Procédés de densification rapide et caractérisation de composites carbone-carbone. Université Bordeaux I. Thèse, 1999

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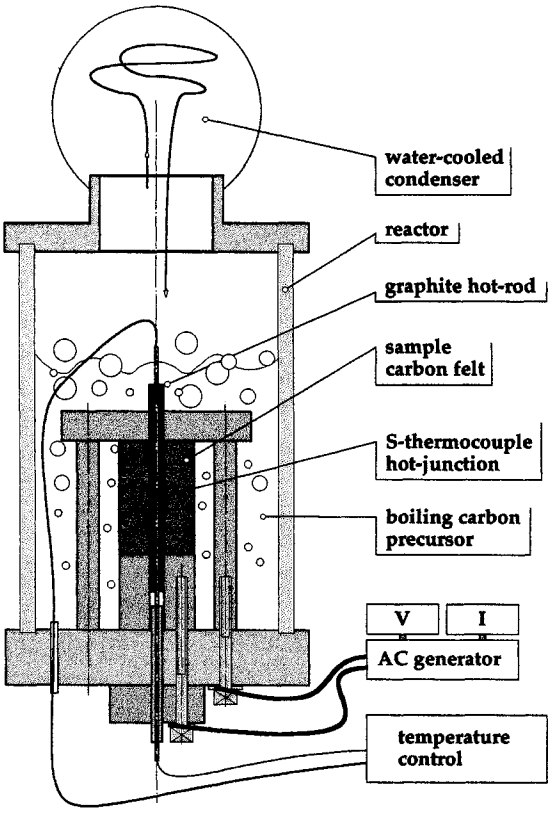

Fig. 1: Experimental set-up

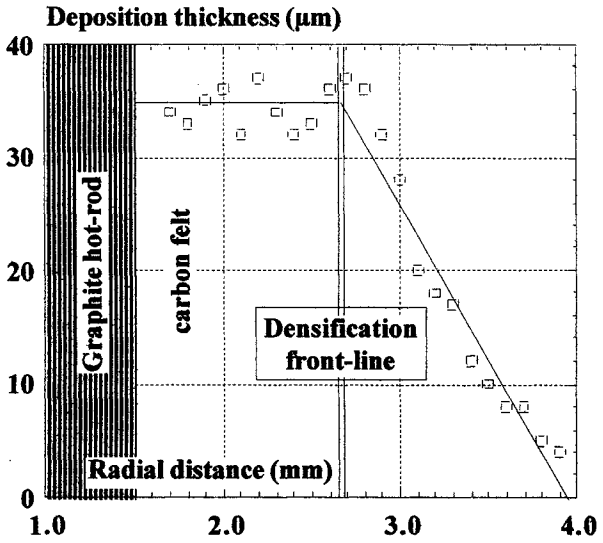

Fig. 2: Radial densification profile (from cyclohexane, 30' at 1250°C)

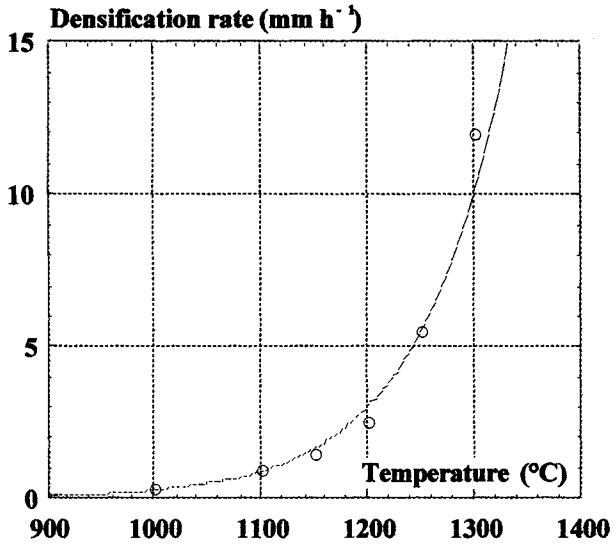

Fig. 3: Densification of a carbon felt (from cyclohexane)