PYROCARBON INFILTRATED BY PULSE-CVI

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INTRODUCTION

Pulse chemical vapor infiltration (P-CVI) was developed to study infiltrated pyrocarbon (PyC) texture in model pores with various diameters (Fig 1) [1-3]. At each cycle or pulse, the reactor was first evacuated at residual pressure (P ~ 0.5 to 1 10^{-1}kPa) and for a large part the sample porosity too. After a stay of 2.5s under primary vacuum the reactor was filled in with the source gas: propane up to the nominal pressure. Then the reactor was maintained closed during a more or less long time, t_R, the residence time ; t_R is easily controlled in a wide range of time, typically from 0.2s to 120s. The pulse was ended by the vacuum stage. The next pulse was then managed in the same way.

In this process the experimental parameters controlling the quality of the infiltration are temperature and pressure as known for I-CVI, but also **residence time** which is a key parameter in P-CVI.

In this work infiltrated carbon is characterized by its optical texture regarding T, P and t_R.

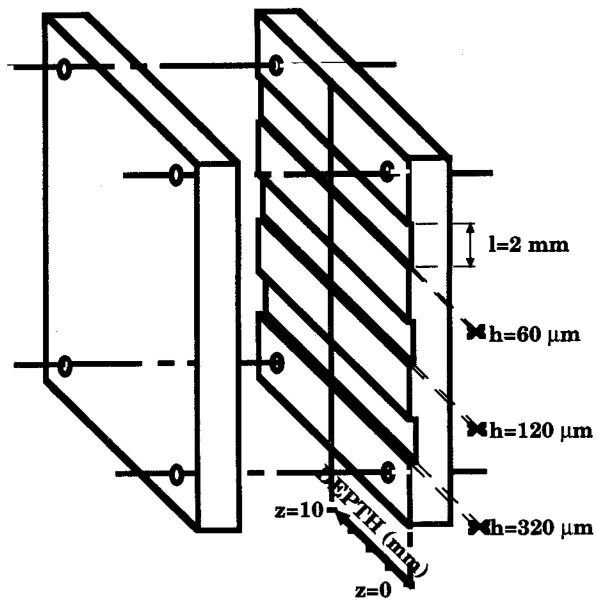

Fig. 1 Schematic of the model pores.

EXPERIMENTAL

After infiltration, the graphite bloc (Fig 1) was sawn along the pore axis z and optical microscopy measurements were performed on polished longitudinal sections. The extinction angle, Ae, was measured on a MeF3 Reichert-Jung microscope equipped with polarized light. The extinction angle is indirectly a measurement of the reflecting power of PyC. This measurement sums different variations up : i.e. mainly the intrinsic bireflectance (depending on structure) convoluted by the misorientation of crystallites along the anisotropic plane (nanotexture). The extinction angle Ae is obtained in cross polars by rotating the analyzer of the microscope "as for a compensator" [4]. Then, this angle depends on the amplitude of the beam transmitted parallel to the anisotropic plane regarding the normal direction; the larger the angle Ae, the higher the anisotropy. The following correspondence between Ae and the classical textural classification can be done in the case of low-temperature pyrocarbons:

rough laminar	18°	≤	Ae		
smooth laminar	12°	≤	Ae	<	18°
dark laminar	4°	≤	Ae	<	12°
isotropic			Ae	<	4°

RESULTS

Three different Ae profiles were observed along the pore depth (h=60µm), depending on residence time at a pressure, P=1 kPa (Fig. 2)

(i) For a short residence time, t_R=0.5 s, a flat profile was observed with a poor PyC-texture (but not isotropic) : Ae=12°. The deposit is homogeneous all along the pore .

(ii) For an intermediate residence time, t_R=5 s, the texture at the entrance of the pore (z=0 mm) is improved up to the best value : Ae=20°. Inside the pore, a gradient is appearing : Ae=14° at the middle of the pore. The profile exhibits a bell-like shape (half). For a residence time of 10 s, this gradient is a little bit minimized (Ae=15°).

(iii) For longer residence times the profiles get worst concerning the texture. When t_R=30 s, the texture inside the pore (for 5mm<z<10mm) turns rapidly into a dark laminar (12°). The flat profile with the homogeneous but poor texture is observed again for very long durations, e.g. t_R=60 s.

Pressure and residence time were fixed at 3 kPa and 10s, respectively. Temperature was then allowed to vary in the 900-1150°C range. Profiles of the extinction angle, Ae, are plotted in Fig. 3 for different temperatures.
(i) At 900°C the CVD deposition (z=0mm) yields smooth laminar PyC (Ae=17°). The Ae profile decreases along the pore. (ii) 950-1000°C. Profiles are flat with the highest anisotropy (Ae=20°) all along the pore, small or large. **This deposit mechanism is pore-size-insensitive : that means achieving infiltration of dense carbon whatever the pore diameter** (tested). (iii) 1050°C-1150°C. In the 60 mm pore, the aspect ratio of the pore is such that the rate is diffusion-limited : 50°C is sufficient to get out of the window (compared to 100°C for the 320 μm pore). The profile recovers the bell-like shape. As the temperature increases the gradient is increasing too. In the middle of the pore (z=10mm), Ae is equal to 15° at 1050°C, 13° at 1100°C and finally 11.5° at 1150°C.

In short, a strong effect of residence time was pointed out (during the diffusion stage) on PyC-anisotropy inside the porosity. At low temperature, residence time can be managed to achieve the right completion of gas phase reactions in order to get a highly dense carbon. A set of peculiar conditions were found (950< T<1000°C, P=3 kPa) with a residence time of t_R=10 s, for which the highly ordered texture infiltrates deep inside the porosity.

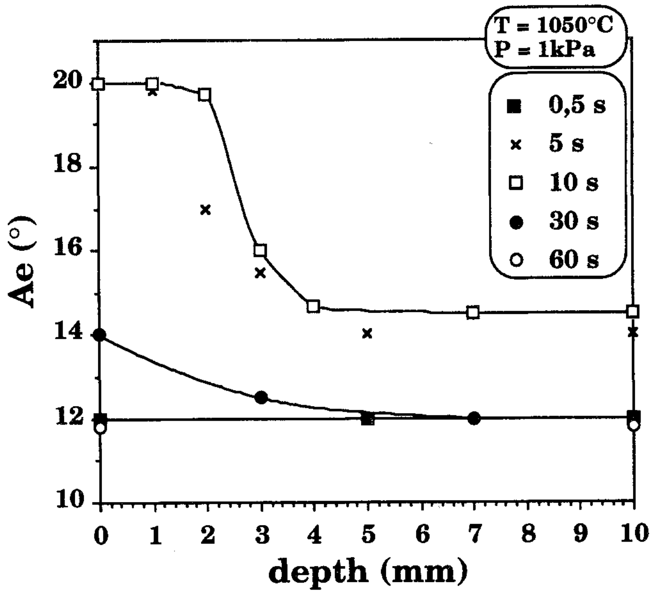

Fig. 2 Pyrocarbon texture profiles (Ae) along the 60 μm model pore as a function of t_R at P = 1kPa.

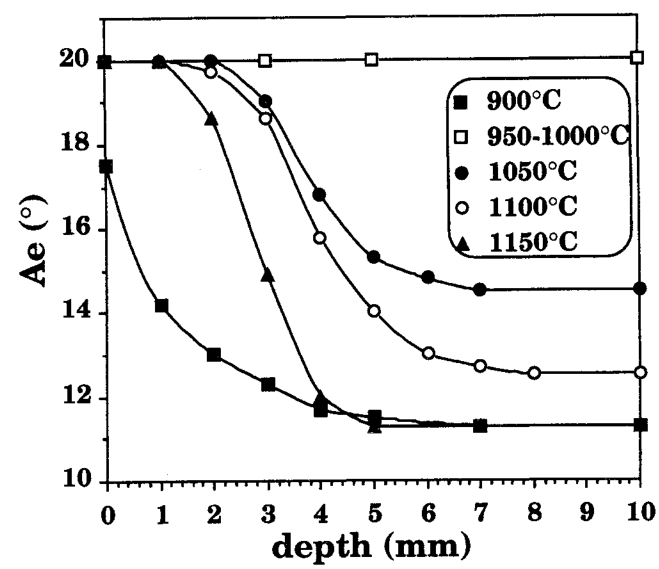

Fig. 3 Pyrocarbon texture profiles (Ae) along the 60 μm model pore as a function of T (t_R=10s and P=3kPa).

CONCLUSIONS

The comparison of the infiltration within the different pores has shown that two deposition mechanisms are existing with a continuum in-between. One was favored by very low or very long residence time (heterogeneous reactions). In this case infiltration was pore-size-insensitive with an homogeneous texture in-depth (but the anisotropy was never found very high). The second one is supposed to occur by diffusion and "condensation" of higher molecular weight species (resulting from homogeneous reactions). The deposited carbon is then characterized by a texture gradient: texture is highly anisotropic at the entrance of the pore and less and less organized in depth (pore-size-sensitive). In-between these two extremes (intermediate t_R), it was possible to combine the interest of the heterogeneous mechanism with a gentle "maturation" (homogeneous reactions). That was obtained at low pressure and low temperature. This way, a highly anisotropic pyrocarbon was infiltrated without gradient.

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ACKNOWLEDGEMENTS. This work has been supported by SEP (through a grant given to P.D).