

PYROCARBON-BASED MULTILAYER FOR HTR FUEL PARTICLES

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Introduction

The next generation nuclear plant projects are designed to develop highest-level functions and requirements. The generation IV International Forum has defined in a "roadmap" different goals in the main areas of safety and reliability, proliferation resistance, physical protection together with sustainability or economics. One of the most promising concepts, the very high temperature reactor (VHTR) has for example the capability to efficiently produce hydrogen (cogeneration mode).

The general fuel type selected for that purpose is a key element of the concept. It has already been selected based on the large background accumulated in the past. But the final design, processing and qualification are underway. The Triso-coated fuel particle is the unit in this concept. Each particle contains a kernel of uranium dioxide or uranium oxycarbide (UO_2 or UCO) of 500 to 800 μ m in diameter. The confinement barrier is managed by means of a coating of ceramic multilayer as shown on Fig. 1. They are based on the synergy of the thermo-mechanical properties of silicon carbide (SiC) and pyrocarbon (PyC), thereby improving the retention of fission products. First, the kernel is coated by a carbon buffer (95 μ m-thick) and a silicon carbide layer sandwiched between two dense pyrocarbon coatings, namely an inner pyrocarbon (I-PyC) and an outer pyrocarbon (O-PyC) layer. Each particle acts as miniature pressure vessel; a feature that is intended to impart robustness to the reactor fuel system [1]. These coated particles are introduced within fuel elements in a production reactor (pebble-bed or block-type design).

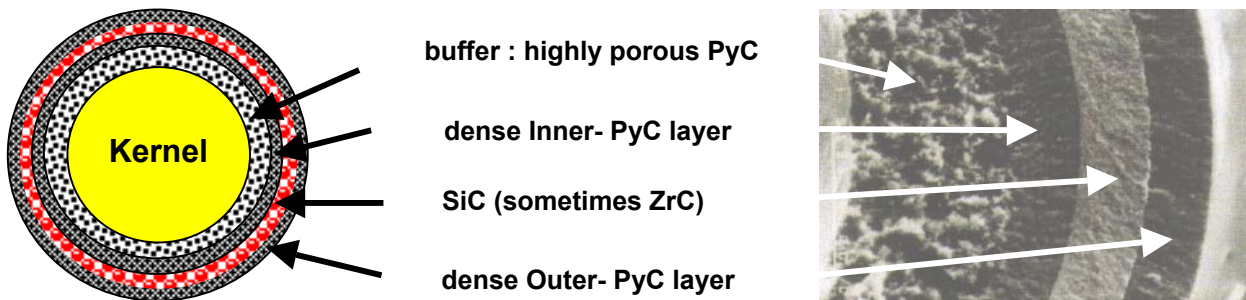


Figure 1. Triso-coated fuel particle : schematic and SEM picture of the ceramic multilayer

This multilayer is managed as a composite for strength and sealing performances : a maximum confinement to retain gases and metallic fission products is obtained under irradiation. But the composite needs to have optimal thermo-mechanical performances all along its lifetime while undergoing irreversible transformations (e.g. oxidation of the buffer, shrinkage and creeping of dense pyrocarbons, strain of SiC under the elastic limit *etc...*).

Pyrocarbon is the challenging material. It has to be deposited with two different densities. First under the form of a buffer layer with a thick and porous texture (~95µm thick with a density : $\rho \sim 1$). The role of the buffer is to provide voidage, to accommodate the gases pressure and to protect against cracking the second dense layer, the sealing layer ($\rho \sim 1.85$). This is the BISO design employed in fertile fuel particles at low irradiation temperature. BISO are easier to re-process to extract a bred fissile fuel.

In the TRISO design, an additional SiC rigid shell is managed. The inner dense pyrocarbon (I-PyC) behaves as a protection during its processing involving HCl as a product of the methyl trichlorosilane cracking during silicon carbide deposit. A second dense pyrocarbon, the outer pyrocarbon (O-PyC) is finally deposited as shown in Fig. 1.

Table 1. 5th PCRD HTR-F objective for the Triso-coated particle.

UO₂	PyC (buffer)	I- & O-PyC dense	SiC
500 ± 40 µm	95 ± 20 µm	40 ± 10 µm	35 ± 7 µm
≥ 10,4 g/cm ³	≤ 1,05 g/cm ³	1,9 g/cm ³	≥ 3,18 g/cm ³
D _{max} /D _{min} ≤ 1,1		BAF ≤ 1,06	100% beta
defective particles ratio ≤ 5. 10 ⁻⁶			
heavy metal contamination U ≤ 10 ⁻⁷			

On the processing point of view, silicon carbide is easily controlled by the fluidized bed CVD process from methyl trichlorosilane diluted in dihydrogen (CH₃SiCl₃-H₂) at 1500°C up to 1650°C. Pyrocarbon is much more difficult to control.

This paper focuses on the main challenges in question regarding the structure and processing of this thermostructural multilayer composite : the isotropy and the texture of the pyrocarbon deposit. Finally, it points out the main issues still to be solved in this area.

Results

(i) Assessment of pyrocarbon isotropy

One challenge in this technology is the control of a perfect isotropic deposit of the pyrocarbon. It is the key for an optimal sealing together with an optimal behavior under irradiation. The anisotropy has a strong influence on the shrinkage and swelling behavior of the PyC layers¹ under fast neutron irradiation.

The BAF is an index measured by XRD techniques to ascertain the isotropy of the deposit. It was first developed by Bacon for nuclear graphite [2] (Bacon Anisotropy Factor). The BAF expresses the anisotropy of a carbon under the form of the ratio of the CTEs parallel and perpendicular to the deposit, at 400°C. Bacon postulated that the in-service behavior under irradiation is in first approximation that of the thermal expansion at 400°C. Values of the BAF increase from unity (ideal isotropic material) to higher values as the preferred orientation of the graphene layers increases. The setup can be a problem. In the case of thick deposit, it is easy to drill a fine rod to be measured in transmission [3]. In the case of thin deposit around a kernel, Bokros has proposed to sample the deposit on a flat graphite discs introduced in the same time as the spherical particles [4] in the coater. The experimental data are recorded from the 002 Debye-Scherrer ring under the form of $I(\phi)$ vs ϕ . The intensity $I(\phi)$ depends on the amount of graphene planes distribution (normal) above the deposition plane normal (ϕ). The BAF is then drawn from the experimental data as follow :

$$BAF = \left(\frac{\sigma_{\perp}}{\sigma_{\parallel}} \right)_{400^{\circ}C} = 2 \frac{\int_0^{\pi/2} I(\phi) \cdot \cos^2 \phi \cdot \sin^2 \phi \cdot d\phi}{\int_0^{\pi/2} I(\phi) \cdot \sin^3 \phi \cdot d\phi}$$

Different experimental setups have been proposed from that time in order to draw the data directly from the particles [5]. Pluchery [6] has proposed an original setup and compared data obtained on the discs and on the particles. He came to the conclusion that the BAF values measured on coated particles and those determined from coated discs that are manufactured simultaneously are not equivalent [7]. Afterwards, most of the BAF's values were drawn from optical measurements.

Optical indexes have been developed to measure the anisotropy by reflected polarized light. As most of the physical properties, light reflection intensity varies with the absorption of the crystal, which is more important for the rays perpendicular to the basal planes. When measured at 545nm the reflection parallel and perpendicular to the planes of graphite are 32% and 9%, respectively (see Fig. 2).

This property is used to evidence any anisotropy in the deposit. The English Dragon project or French CEA have developed the DAR index [8] (Degree of Anisotropy by Reflectance).

$$DAR = R_{90^{\circ}} / R_{0^{\circ}}$$

with $DAR = (1 + \gamma + BAF) / (2 + \gamma BAF)$,
 and $\gamma = R_{min} / R_{max} = 0.21$

The measurement is obtained by rotation of the analyzer (without polarizer), parallel to the deposition plane (0°) or at 90° . The window size is a square of : $25\mu\text{m}$, $15\mu\text{m}$ or $3.9\mu\text{m}$. In USA at GA, the index was the OAF^9 (Optical Anisotropy Factor). The photometry is the same except that the polarizer is rotated (without analyzer) parallel or perpendicular to the deposit. Also, an oil objective is used.

$$OAF = R_{90^\circ} / R_{0^\circ}$$

with $BAF \sim 1 + 0.77 (OAF-1)$

Oak Ridge National Laboratory [¹⁰] and Jülich KFA [¹¹] developed also an index named OPTAF for Optical Anisotropy Factor :

$$OPTAF = R_{min} / R_{max}$$

The optics is more complicated for OPTAF. A continuous measurement is done under cross-polars with the rotation of the sample (in oil). OPTAF is the ratio of the minimal and maximal reflectance values (disregarding the deposit plane).

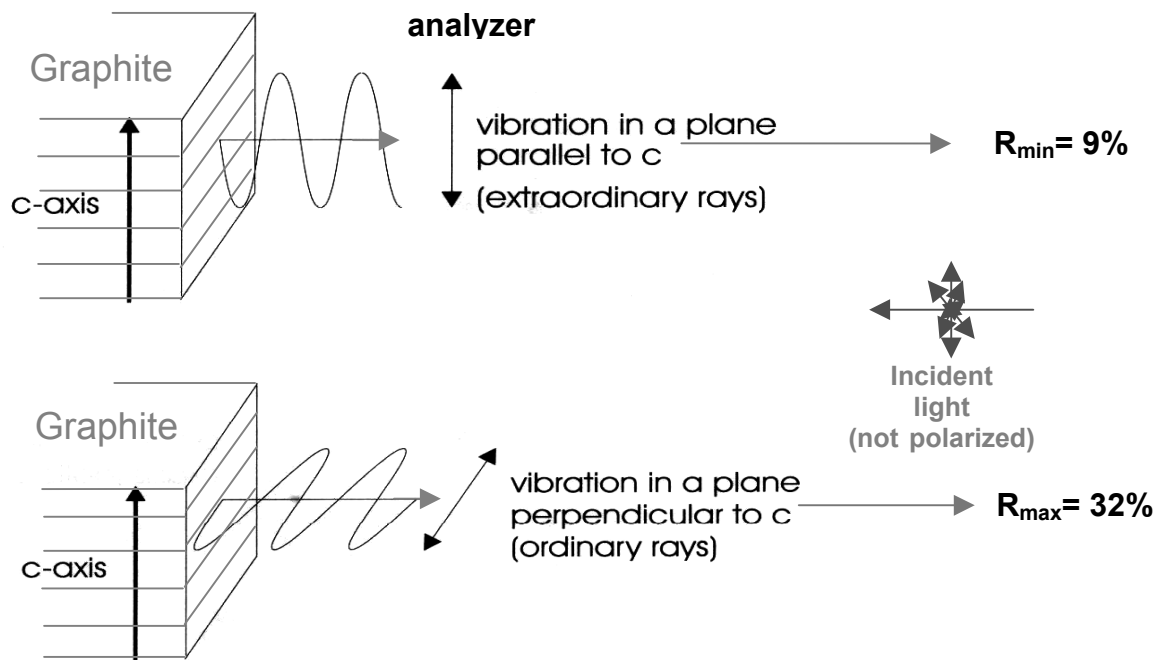


Figure 2. Anisotropy of the reflection of light on a cross section of graphite monocrystal ($\lambda = 545\text{nm}$).

Most of the BAF values produced, are in fact directly measured by optical microscopy on the particles. D.W. Stevens [¹²] from GA has developed in the seventies a model and the

apparatus known as the SMP (Synchronous Micro-Polarimeter) to access different indices as BAF_{DOM} or BAF_{XTL} much more precise than the regular one. This protocol using ellipsometry was never qualified.

(ii) Density and gas-tight : pyrocarbon structure and texture

Density of graphite is $\rho=2.26$, whereas the specification for pyrocarbon in the HTR coating is $1.6 < \rho < 1.9$ for the dense pyrocarbon. Specifications result from a balance : a tight and dense pyrocarbon exhibits some anisotropy [13]. In other words, $\rho \sim 1.9$ is the highest density that can be obtained while keeping the carbon tight and perfectly isotropic in the same time. Porosity is closed in this case.

The grade of pyrocarbon developed for the buffer is different : $\rho \sim 1$. In this case the highest porosity is sought after. The isotropy is easily kept in this case. Density is normally obtained by a sink-float technique. The PyC fragments are observed sinking in a column of liquid possessing a known density gradient. The density obtained this way is not a bulk density (geometric density), the liquid penetrates the open porosity and thus this value takes in account only the closed porosity. In the case of dense pyrocarbon, most of the porosity is closed. In the buffer, the bulk density is typically 50% of that of the anisotropic pyrocarbon. Contrarily to the previous one, it is said in the literature that half of the porosity is open in this case.

The main program in this area concerns the characterization of the texture of pyrocarbon by means of TEM analysis. PyC's texture is guided by a scaling transition at few tens of nanometers in relation with the spheroid diameter. (It is typically the scale of TEM investigation.) When observed by TEM contrasted bright field, those pyrocarbons show different crystallinities. This is well visible in Fig. 3 (top). Pyrocarbon can be dense but not really isotropic ($DAR=1.34$ while $D < 1.10$ is required); this was observed on flat graphite discs introduced among the spherical particles. The dense PyC ($\rho \sim 1.85$) deposited on the spherical particles (Fig. 3, middle) is highly crystallized too. More porosity appears as inter-particle pores (closed). This PyC is clearly 'composite' : seeds are concentric whereas the outer zones appear as 'coatings'. Contrast inside the carbon exhibits some variations related to the cycles of the particles during the coating. In the buffer (down in Fig.3), the pyrocarbon is deposited in different conditions. Structure and texture are different. Structure is not as dense as that of the inner PyC. Texture is highly concentric. The 'coating' still exists but is less abundant.

The challenge in processing these materials is to develop at long range, a bulk isotropic material, starting with sp^2 hybridized carbons. This was mainly developed by pioneers as J. Bokros [14] by chemical vapor deposition (CVD) in fluidized bed. To understand the deposition mechanisms, we propose to represent the growth process as in Fig.3 with the comparison of the two models proposed by Harvey *et al* [15] and Kae [16], based on TEM works. CVD growth in fluidized bed is proposed to be regarded as a competition between two different mechanisms, the homogeneous growth as spheroids that further deposit onto the surface and the direct growth of carbon onto the surface (heterogeneous growth).

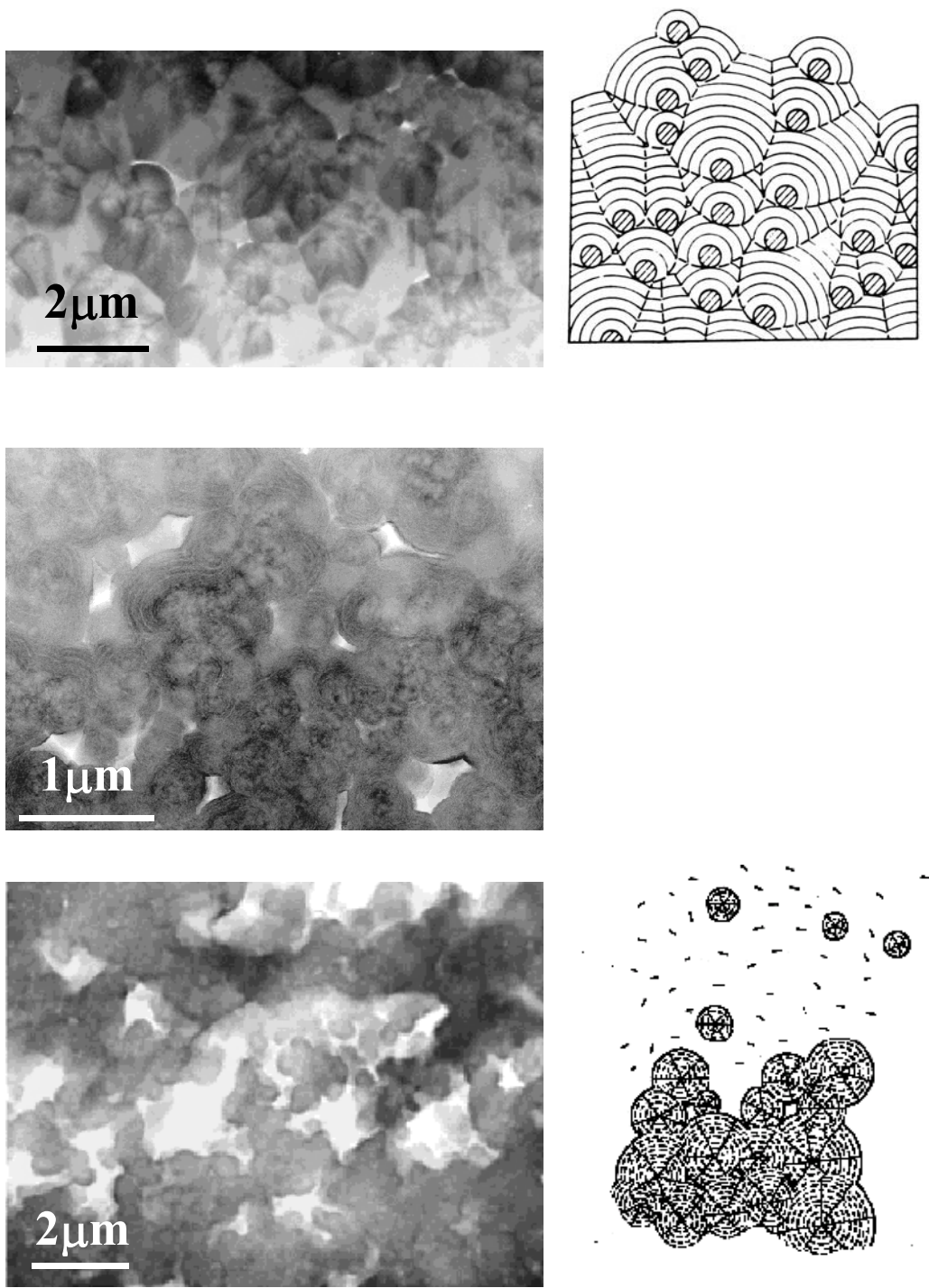


Figure 3. TEM brightfield of the different isotropic pyrocarbons textures : I-PyC as deposited on flat discs (DAR = 1.34 (top, with speculative deposit model), I-PyC as deposited on simulacra kernel with a DAR =1.01 (middle, model : intermediate of two others) and buffer pyrocarbon with a density of $\rho \sim 1$ (down with its growth model)

If most of the growth takes place as aerosol in the gas phase, the resulting texture is mostly concentric with an isotropic long-range orientation. On the contrary, the direct deposits tend to be much more oriented (anisotropic fraction). This phenomenon is well appearing in the case of flat supports. The direct deposit increases the anisotropy (Fig.3 top). In the buffer, the homogeneous growth under the form of spheroids is predominant : texture is isotropic. Dense PyC (I-PyC or O-PyC) results from a good balance between the 2 mechanisms. Distribution of this latter fraction is of the utmost importance to understand the in-service behavior (e.g. re-crystallization or creep under radiation). Quantification of structure and texture is the next step [17]. The relationships with processing are evident : for example high coating rates result in very isotropic pyrocarbon (BAF<1.1) but with somewhat greater porosity.

During the initial development in the seventies, authors have shown that texture was very versatile by using methane as precursor [18]. Afterwards, buffer was usually deposited with acetylene (C₂H₂) diluted in argon at 60 to 85% (at 1250 to 1300°C) whereas dense pyrocarbon is obtained with propylene (C₃H₆) or a blend of acetylene and propylene diluted at 20 to 40% in argon (1300°C). In counter part the deposit could easier turn to permeable. Only some of the isotropic textures were seen to be together dense and impermeable to fission products. The control of processing in term of structure and properties of pyrocarbon is absolutely necessary : optical microscopy, transmission electron microscopy, X-ray diffraction , density, etc...

Concluding remarks

Progress in the modeling of the ceramic multilayered coatings around the fuel kernels is based on a better understanding of the multilayer structure and especially that of pyrocarbon. It was emphasized in this review that carbon growth results from a competition of two different mechanisms. Crystallinity, anisotropy and heterogeneity of pyrocarbon have to be studied especially for the fraction issued from the direct growth onto the surface. Because this fraction is the “anisotropic” component, it is suspected to be the “weaker link” that controls the open porosity (nanoparticle diameter, isotropy threshold) or the creep resistance and also the shrinkage under radiation at high temperature (especially off-normal conditions). The elastic modulus and strength (in temperature) also rely on crystallinity (L_2 , L_c , d_{002}) and anisotropy.

It is finally necessary to control the role of the interfaces between the different sublayers. Debonding results from the differential swelling in neutron flux at high temperature, this is well known in SiC/PyC/SiC composites. This phenomenon is enhanced by the presence of a sealcoat on the buffer [19].

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