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Structural characterization of virgin and irradiated nuclear graphite

The present work was performed within the framework of the **Task 3.2: Structural Changes by Irradiation and Treatment.** In fact, the changes in graphite structure by irradiation and treatment effects will determine its behaviour in repository conditions. Thus, in order to study the structural modifications and to correlate them with the long term behaviour, it was necessary to address adapted analytical methods, which help for comprehension, giving the scientific basis of the mechanism corresponding to the observed behaviour. The contribution of the *Ecole Normale Supérieure* (Ens, partner 11) in Carbowaste program concerned the structural characterization of virgin and irradiated nuclear graphite by several techniques such as Raman microspectrometry, Transmission Electron Microscopy, Scanning Electron Microscopy and X-ray Diffraction. These techniques allow to study near the atomic scale, i.e. the scale which is usually the most pertinent to understand and foresee the carbon materials properties. Actually, our research was developed on UNGG (Uranium naturel-graphite-gaz) graphite samples, in collaboration with the French partners of Carbowaste, in particular with INPL (C.E. Vaudey, N. Toulhoat, N. Moncoffre,), CEA (L. Gosmain), ANDRA (S. Schumacher, L. Petit) and EDF (L. Petit).

The ENS investigations were concretely initiated since the recruitment of Dr M.R. AMMAR (Post-doc researcher) on October 2008 (almost 1 year). Indeed, a part from the delay time to receive the irradiated samples, several administrative authorizations were required to have an access to CEA facilities in order to study them**.** Nevertheless, the ENS developed a close collaboration with the *Institut de Physique Nucléaire de Lyon* (INPL, partner 17) to characterize the structural modification of graphite by ion irradiation beam (implantation) so as to simulate neutrons effects in the nuclear reactor.

Firstly, ENS's work has been started by characterizing the virgin nuclear of Saint Laurent des Eaux, France (SLA2) by Raman microspectrometry. This technique was particularly

attractive because it has a high spatial resolution (~ 1 µm) and provides less averaged information, in comparison with X-ray diffraction (XRD). Moreover, analyses were quick, operationally straightforward, non-destructive and requiring minimal sample preparation.

Compared to a single crystal of graphite (as for the Highly Oriented Pyrolytic Graphite (HOPG)), Raman spectrum of nuclear graphite exhibited additional bands called D for "Defect" bands, which are known to be characteristic for finite crystals of graphite. The polarization of the laser spot was used to distinguish preferentially oriented from randomly oriented crystals. Our result ensured that the nuclear graphite is composed of small crystallites more or less randomly oriented in the area of the laser spot. This aspect has been confirmed by X-ray Diffraction analyses.

Raman mapping of virgin nuclear graphite was performed, using the structural parameter R_2, (D_1 area relative to the whole bands area). Compared to HOPG, virgin nuclear graphite featured a clear repartition on the defect band area. This showed the heterogeneity of the nuclear graphite, at a micrometric scale, in terms of the organization degree. This variation could be related to the composition of the nuclear graphite consisting in two main phases: the binder matrix (coal-tar pitch) and the filler particles nearly spherical (petroleum coke) heated at 2800°C. Petroleum cokes are generally the more graphitizable of the two, and this aspect could give a noticeable decrease of the defect bands in Raman spectrum. Additional experiments are now initiated by combined Raman mapping, scanning electron microscopy and optical microscopy to try to distinguish between the binder and the filler in the nuclear graphite.

Actually, prior to selecting any treatment option for irradiated nuclear graphite, a comprehensive understanding in terms of the nanostructure of raw and modified graphite was needed. Ion irradiation beam (implantation) seemed to be an effective way of the structural modification of graphite, where the structural defect could be similar to those induced by neutrons irradiations at some fluences and temperatures. Moreover, such implantation can introduce a wide range of defects in a controlled manner.

Raman analyses showed an increase of defect bands with fluence in room conditions, resulting in a disorder increase in the graphitic structure, till a complete amorphization for higher fluences characterized by an asymmetric broad single band. Compared to X-ray diffraction,

Raman microspectrometry appears as particularly sensitive to both the disorder and the amorphization, and that to very small volumes of matter (less than 0.1 μm^3).

The situation got even more interesting when we implanted the nuclear graphite at various temperatures. At high implantation temperatures (up to 600°C), the defect band in Raman spectrum decreased significantly suggesting that graphite defects recombine as fast as they form.

Transmission electron microscopy (TEM) technique turned out to be particularly interesting as well, especially its 002 lattice fringe (LF) mode that allowed a direct imaging of the polyaromatic layers profile and consequently the access to the multiscale organization in the nanometer-micrometer range. However, the observation of the nanostructural changes caused by the ion beam irradiation at the surface or near the surface (implantation depth about 1 µm) was not really or easily achievable by the conventional techniques such as hand grinding, ultramicrotomy and mechanical abrasion or ion thinning. The process which provided a great advance in the study of the ion-implanted graphite was the use of thin sections prepared by the focused ion beam (FIB) technique. In fact, its very important benefit was the easy and direct control of the choice of the area, the sample orientation according to the beam and the specimen thickness during ion milling (less than 100 nm that making it electrons transparent). By using thin sections prepared by FIB technique, we were be able to image directly, for the first time, the structural modification due to implantation at the nanometre scale; this can be considered as a great improvement in the characterization of the ion-implanted graphite.

Our results showed a drastic change of the polyaromatic layers organization at the surface, where the density of ^{37}Cl implantation was maximal. The graphite structure was strongly damaged without being completely amorphous: only short nanometer sized fringes forming small BSU (stacks of 2-3 layers) were visible and these stacks were strongly disoriented, losing the lamellar nanostructure of the virgin graphite. Geometrically speaking, such cross-linked BSUs form nanopores that could be considered as potential sites for radionuclides trapping.

The decrease of L_a, the coherent domain (BSU) diameter was also confirmed after ion beam irradiation by the measurement of the rotation moirés fringes in the 11DF dark field images, which was in perfect correlation with Raman results.

As we expected, the nanometer scale appeared extremely pertinent to explore as it was planed at the beginning within the framework of Carbowaste program, based on our knowledge in carbon materials.

Irradiated graphite studies have recently begun on G2 samples issued from the nuclear reactor of Marcoule, France. The nuclear graphite was irradiated at a temperature close to 300°C. Compared to virgin graphite characterized by a weak defect band, Raman spectrum of irradiated graphite shows a slight increase of this later. This aspect has been confirmed by TEM observations with the 002 LF mode for which the polyaromatic layers were slightly distorted. We attributed this relatively weak structural degradation of this irradiated graphite (about 4dpa) to the irradiation temperature.

Now, our experiments are in progress to study other irradiated graphite depending on their location in the UNGG reactor (which were submitted to other irradiation degrees and/or temperatures), and from other types of reactors. For this, a HRTEM image analysis will be tested to acquire more quantitative structural data.

Although our work delayed by the late recruitment of a post-doc researcher and the reception of irradiated samples, ENS's new results obtained on the graphite structure are original and promising for a better understanding of irradiated graphite structure. The degradation of the graphitic structure, that we brought to light, gives birth to a disordered nanoporous carbon which could be implied in the radionuclides trapping. Such feature appears to be crucial for the choice of a future decontamination process.

We believe that ENS's team will be able to reach what we planed to do in the structural characterization of the nuclear graphite. .