



# Characterizing various types of defects in nuclear graphite using Raman scattering: Heat treatment, ion irradiation and polishing



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## ARTICLE INFO

### Article history:

Received 17 June 2015

Received in revised form

29 July 2015

Accepted 31 July 2015

Available online 19 August 2015

### Keywords:

Raman spectroscopy

TEM

Defects

Heat treatment

Ion beam irradiation

Polishing

Carbon

Graphite

Nuclear graphite

## ABSTRACT

Raman spectroscopy has proved to be an appropriate technique to probe defects in carbon-based materials owing to its high sensitivity, most often focused on the commonly used  $I_D/I_G$  parameter. However, this ratio may be activated by various types of defects and in a completely independent manner. Therefore, discriminating between defects is challenging. The central idea of the present work is to provide a better understanding of the Raman response to the various types of defects that may appear in nuclear graphite (carbon–carbon composite) during its manufacturing process, its operation in the nuclear reactor, or even during its preparation process such as polishing which is usually used prior to Raman characterization. This work also demonstrates the discrimination of the defect types using the combination of the  $I_D/I_G$  and FWHM(G), two structural disorder indicators evolving differently according to the type and the concentration of the introduced defects into the carbon network. The ion-beam irradiation was used here as an effective way for creating defects that could be similar to those created by neutrons in the nuclear reactor.

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## 1. Introduction

Graphite has been widely used as a neutron moderator, reflector and fuel matrix in various types of nuclear reactors since the late 1940s. Its characteristics made it a material particularly suitable for the nuclear application [1]. Consequently, graphite represents the greatest volume of radioactive waste at the end of the reactor's life. To date, about 250,000 tonnes have been accumulated worldwide [2]. This is typically the case of the French UNGG or the British MAGNOX nuclear reactors developed independently in the same period. The long-term storage or disposal of the nuclear graphite waste requires a special management strategy and the challenges for the fundamental management options are reflecting the chemical, physical and structural properties of the material itself,

its retrieval from the core and the associated inventory of long-lived radio-isotopes such as chlorine ( $^{36}\text{Cl}$ ) or carbon ( $^{14}\text{C}$ ) that result from neutron activation processes [3]. Therefore, prior to select any management option for the neutron-irradiated graphite, a comprehensive understanding of the structural properties of raw and structurally modified graphite is needed, so as to provide efficient and effective solutions [4,5].

Raman spectroscopy appears to be an appropriate technique to probe the structural modifications of nuclear graphite. It has become nowadays a method of choice and an ideal technique for characterizing all carbon-based materials due to the detailed information provided by this optical and non-destructive technique. It can probe either the structural, vibrational, mechanical or even electronic properties such as the determination of the atomic structure (zigzag or armchair of graphene edges) [6], the phonon dispersion [7], the determination of the number of graphene layers [8], as well as their stacking order [9], growth kinetics [10], doping [11], crystallite size [12,13], strain [14]. Moreover, the presence of

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any defects in  $sp^2$  carbon network leads to particularly rich and unique phenomena in their Raman spectra thereby placing this characterization technique among the most sensitive to defects in  $sp^2$  carbon matter [15–17], most often focused on the commonly used  $I_D/I_G$  parameter, namely the intensity ratio of the defect-induced D and the symmetry-allowed G bands. Recalling, the G band corresponds to one-phonon Raman scattering process at the 1<sup>st</sup> Brillouin zone center  $\Gamma$  ( $q=0$ ,  $q$  stands for the phonon wave-vector) and consists of the collective in-plane bond stretching of the polyaromatic carbon atoms ( $E_{2g}$  symmetry) [18,19]. The D  $\sim$  (1250–1400  $cm^{-1}$ ) band corresponds to the totally symmetric transversal phonon  $A'_1$  located in the vicinity of the high symmetry phonon points (K or K'). Its activation resonance process is rather quite special (intervalley Raman mode), involving peculiar electron–phonon interaction mediated by defects [17,19]. Therefore, we can imagine that the more the quantity of defects raises, the more the transitions giving rise to the D band increase and this is why the intensity ratio  $I_D/I_G$  is commonly used as an indicator of the defect density in carbon materials. However, what is extremely complex is to provide a quantitative description of the introduced defect (such as the determination of the coherent domain diameter, point defect density....) based on the unique  $I_D/I_G$  parameter, because the commonly used D band may be activated with various types of defects and in a completely independent manner. This is why the effect of disorder on the electron and phonon properties in carbon-based materials should systematically be probed both in the momentum space and in the real space (i.e. STM, TEM, AFM) in order to provide an accurate correlation between the two spaces.

The central idea of this paper is to provide a better understanding of the Raman response through the various types of defects that may appear in the nuclear graphite during its manufacturing, after its surface preparation and upon ion-beam irradiation. The latter has extensively used to understand the structural modification of many materials [20–26] and was used here as an effective way to explore the key parameters responsible for the possible structural damages of graphite in nuclear reactors and also for creating defects that could be similar to those created by neutrons. Indeed, neutron irradiation induces collision cascades and thus many atomic displacements (dpa). In order to emulate defects induced by neutrons, the samples have been irradiated with  $^{37}Cl$  ions at energy of 250 keV and at different fluences and temperatures. The advantage of using  $^{37}Cl$  is also to simulate the presence of  $^{36}Cl$ .

## 2. Experimental

### 2.1. Sample preparation

A series of anthracene-based cokes with different structural orderings as well as highly oriented pyrolytic graphite (HOPG), natural graphite (Ceylon from Sri Lanka) and amorphous carbon were taken here as reference materials. The nuclear graphite samples (pile grade) used in the present study are issued from one of the “Natural Uranium Graphite Gas” (UNGG) nuclear reactors (Saint Laurent des Eaux) (SLA2). These samples were irradiated with  $^{37}Cl^+$  ions using the 400 kV ion implanter IMIO400 of the Institute of Nuclear Physics of Lyon (IPNL, France). Some of the samples were uniformly implanted at room temperature with energy of 250 keV at varying fluences ranging from  $10^{12}$  to  $10^{16}$  ions/cm<sup>2</sup>. Others were subjected to varying irradiation temperatures ranging from 200 to 600 °C, using a fluence of  $5 \cdot 10^{13}$  ions/cm<sup>2</sup>. The beam current on the samples was close to or lower than 1  $\mu A/cm$  [2] in order to minimize the beam heating during the ion-beam irradiation. The defects induced by polishing process could be studied using nuclear graphite samples polished with 1  $\mu m$  diamond particles.

### 2.2. Characterization

Vibrational Raman studies were performed in ambient conditions by using a Renishaw Invia Reflex spectrometer equipped with an Ar<sup>+</sup> laser source (2.41 eV/514.5 nm). The spectra were collected under a Leica DM2500 optical microscope ( $\times 50$  objectives/N.A. = 0.75). Very low incident power ( $\sim 1$  mW) was used to avoid heating effects or a possible modification of the local structural organization [27,28]. Each spectrum represents the average of three measurements. The quantitative Raman parameters were obtained from the deconvolution of Raman spectra by the fitting procedure using a linear baseline and Lorentzian function.

Some other complementary techniques were used. In order to reveal the distribution of the different constituents of the virgin nuclear graphite, i.e., binder, filler as well as the types and distribution of porosity within its microstructure, polarized optical microscopy was used. The nuclear graphite nanostructure was investigated using TEM JEOL 2011 microscope operating at 200 kV. The material was directly imaged combining the dark field (11DF) mode and the 002 Lattice Fringe mode (often called “high-resolution” mode). The latter has undergone nowadays a considerable progress enabling to achieve a quantitative description of the  $sp^2$  carbon nanostructure [29–31]. For TEM observations of virgin nuclear graphite, the samples were finely ground in an agate mortar and then they were suspended in pure ethanol solution prior to be deposited on Lacey TEM grids and air dried. For the observation of the nanostructural changes induced by the ion-beam irradiation at the surface or near the surface, ultrathin sections prepared by focused ion-beam technique were used enabling an optimal comparison of Raman spectroscopy and Transmission Electron Microscopy results [26].

## 3. Results and discussions

### 3.1. Characterizing the formation of nuclear graphite

Generally, graphite may be manufactured using various processes involving temperature [12,13,17,32,33], pressure [34], or catalysis [35]. If we consider here the only effect of temperature, graphite can be manufactured from graphitizable carbons by a graphitization process using polyaromatic structures (or precursors) more or less ordered according to the manufacturing technique used [36]. These polyaromatic precursors may consist for example of amorphous carbons (with more or less high  $sp^3$  content) generally in the form of coatings, polymers (with high heteroatom content) [37], or graphitic-like carbons (with high  $sp^2$  content) such as pyrocarbons [38] or those produced from a resolidification of plastic phase giving rise to the so-called “semi-coke” [39–41]. This latter is typically the “standard” process industrially used for a mass production of graphite as it is the case of electrodes or nuclear graphite manufacturing. The industrial transformation into graphite requires high temperature treatment  $\sim 2800$ – $3000$  °C passing through carbonization stage (up to  $\sim 1500$  °C), pre-graphitization stage ( $\sim 1600$ – $2100$  °C) and eventually graphitization stage ( $\sim 2100$ – $3000$  °C) [39–41].

The nuclear graphite is an industrial carbon–carbon composite obtained after a heat treatment between 2500 °C and 3000 °C of a blend of petroleum coke grains and pitch-based binder. This graphitization process is usually carried out in the presence of purifying agents (NaF, MgF<sub>2</sub>, Cl<sub>2</sub>, etc.) in order to obtain the nuclear grade graphite with extremely low impurity content [42].

In order to understand the formation and the final structure of the nuclear graphite, anthracene based-coke (one of the graphitizable carbons) with various heat treatments is used as a reference. [43] Fig. 1 displays Raman spectra of this reference carbon material

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