

Structural study of the nuclear graphite modified by ion beam irradiation

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Introduction

Graphite has been widely used as a moderator, reflector and fuel matrix in various types of nuclear reactors since the late 1940s. Its characteristics make it a material particularly suitable for the nuclear application. However, graphite, as well as other carbon installations, represents the greatest volume of radioactive waste at the end of the reactor's life. To date, about 250000 tonnes have been accumulated, worldwide [1]. Prior to select any treatment option for the irradiated nuclear graphite, a comprehensive understanding in terms of the microstructure of raw and modified graphite is needed, so as to provide wise decontamination processes. The ion irradiation beam (implantation) seems to be an effective way for the structural modification of graphite, where the vacancy and interstitial defects created could possibly be similar to those induced by neutrons irradiation [2]. There is a significant incentive to use ion beam irradiation to emulate the effect of neutrons damage as this technique has the potential for an easy variation of the irradiation parameters such as fluence and implantation temperature over a wide range of values, in a controlled manner. The purpose of this work is to study, by Raman microspectrometry, the microstructure of a raw and the modified nuclear graphite resulting from the 250 keV $^{37}\text{Cl}^+$ ions irradiation beam at different fluences and implantation temperatures.

Experimental

All the samples of the nuclear graphite are issued from one of the "natural uranium graphite gaz" (UNGG) nuclear reactors. They were implanted using the 400 kV ion implanter of the Institute of Nuclear Physics of Lyon (IPNL, France). Some of the samples were implanted uniformly at room temperature with a 250 keV $^{37}\text{Cl}^+$ ions beam irradiation at varying fluences ranging from 10^{12} to 10^{16} ions/cm². Others were subjected to varying implantation temperatures ranging from 200 and 600°C, using a fluence of 5.10^{13} ions/cm². The

beam currents on the samples were limited to $0.5\mu\text{A}/\text{cm}^2$ to minimize the beam heating during the ion beam irradiation.

Studies were performed in ambient conditions by using a Renishaw InVia spectrometer equipped with an Ar laser source (2.41eV/514.5nm), focused through a Leica microscope. The spectra were collected under an optical microscope ($\times 50$ objective). Raman analysis of graphite might be affected by polarization effects between the electromagnetic field of the incident laser and the graphite structure; this might enhance virtually the defect bands especially for the measurement on the graphite edge planes. These effects are rather weak with a 514.5nm wavelength [3], and to further attenuate them, we used a $\frac{1}{4}$ wavelength plate before the microscope which yields a circular polarization of the laser. Very low incident power (1-5 mW) was used to avoid heating effects [4]. Each spectrum represents the average of three measurements. Raman mapping was performed using XY motorized stage and the sampling step size was $0.5\mu\text{m}$. Raman maps were obtained by analyzing the data with Matlab program.

Beysac et al. [5] proposed to characterize the organization degree of carbon materials (natural coal, cokes and anthracite) by the structural parameter:

$$R_2 = \frac{A_{D_1}}{(A_G + A_{D_1} + A_{D_2})}$$

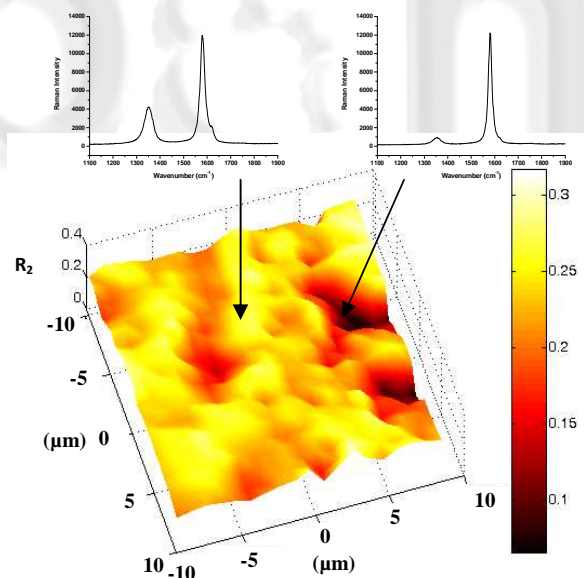


Fig.1. Raman map of the evolution of the structural parameter R_2 . Area of images $20\mu\text{m} \times 20\mu\text{m}$. Acquisition time, 60 s per point at 2 mW of laser power.

The authors found it to be less variable than the intensity ratios of individual bands, especially in highly disordered carbon. Indeed, the use of this parameter seems to be suited for Raman mapping in order to avoid any contribution of the fluorescence phenomenon. Figure 2 displays the Raman mapping of the virgin nuclear graphite using the structural parameter R_2 featuring a large variation of the defect bands. Firstly, the parameter R_2 varies from 0.25 to 0.35 in almost all the analyzed area probably due to the random orientation of the crystallites. Then, the parameter decreases significantly (less than 0.1) at specific zones. This variation showed the heterogeneity of the nuclear graphite, at a micrometric scale, in terms of the organization degree. Actually, the decrease of the defect band could be related to the composition of the nuclear graphite consisting in two main phases: the coal-tar pitch binder phase and the petroleum coke filler phase which were blended then heated at 2800°C. Petroleum cokes are generally the most graphitizable, and this aspect could give a noticeable decrease of the defect bands in Raman spectrum.

Ions implantation enjoys the benefit of high doses rates resulting in the accumulation of high doses in short times. It is also very efficient at producing dense cascades, similar to those produced by neutrons [2]. At room temperature, Raman spectrum, in the 800- 3400 cm^{-1} region, shows significant changes, consisting in the intensity increase of D_1 and D_2 bands relative to the G band, till a complete amorphization for higher fluence. For the ion-irradiated graphite, we point out that the possible sp^2 - sp^3 transition induced by the ion beam irradiation also increases the intensity ratio. Compagnini et al. have already observe this aspect, and assumed the coexistence of two different sublattices in the irradiated graphite [6]. A particularly interesting finding occurred when we implanted the nuclear graphite at varying temperatures. At high implantation temperatures (up to 600°C), the defect bands in Raman spectrum decrease significantly suggesting that graphite defects could recombine as fast as they form.

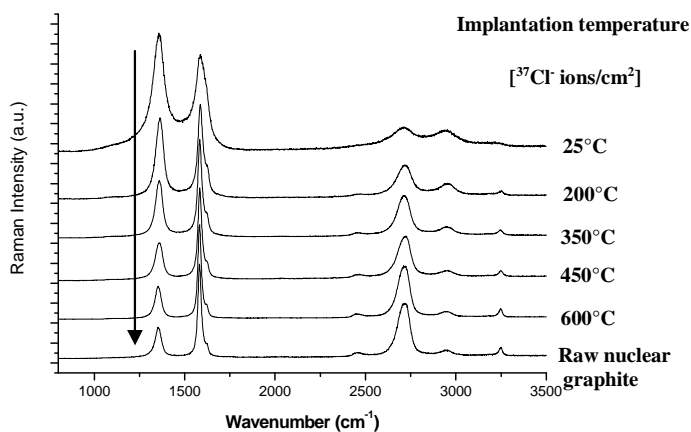


Fig.2. Raman spectra of raw nuclear graphite and ion-irradiated graphite using 250 keV Cl^+ ions at a fluence of 5.10^{13} ions/ cm^2 and at varying temperatures

Conclusions

This work assesses the structural modification of the nuclear graphite upon ion beam irradiation by Raman microspectrometry. The graphite becomes more and more disordered, then amorphized after a certain dose of implantation. The implantation temperature turned out to be a real key parameter that induces the structural modifications in the nuclear reactor.

Acknowledgment

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References

- [1] Fachinger J., Von Lensa W., Podruhzina T., Nuclear Engineering and Design 238 (2008) 3086–3091.
- [2] Was G. S. Fundamentals of Radiation Materials Science: Metals and Alloys. Springer, 2007
- [3] Tan P., Dimovski S., Gogotsi Y. *Phil. Trans. R. Soc. Lond. A* 362, (2004), 2289-2310
- [4] Everall N.J., Lumsdon J., Christopher D.J. Carbon 29 (1991) 133-137
- [5] Beyssac O., Goffé B., Petitet J.P., Froigneux E., Moreau M., Rouzaud J.N. Spectrochim Acta A. 59 (2003) 2267-2276
- [6] Compagnini G., Baratta G. A., Cataliotti R.S., Morresi A., J. Raman Spectrosc. 26 (2005) 917