Nuclear Instruments and Methods in Physics Research B xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb

Ion irradiation to simulate neutron irradiation in model graphites: Consequences for nuclear graphite

N. Galy [a,b], N. Toulhoat [a,c], N. Moncoffre [a,*], Y. Pipon [a,d], N. Bérerd [a,d], M.R. Ammar [e], P. Simon [e], D. Deldicque [f], P. Sainsot [g]

[a] Université de Lyon, Université Lyon1, CNRS/IN2P3 (IPNL), 4, rue Enrico Fermi, F-69622 Villeurbanne cedex, France
[b] EDF DP2D Lyon, France
[c] CEA/DEN – Centre de Saclay, F-91191 Gif-sur-Yvette cedex, France
[d] Université de Lyon, UCBL IUT Lyon 1, département de chimie, 43, boulevard du 11 novembre 1918, F-69622 Villeurbanne cedex, France
[e] CNRS, CEMHTI UPR3079, Université d'Orléans, CS90055, F-45071 Orléans Cedex 2, France
[f] Laboratoire de Géologie de l'Ecole Normale Supérieure, Paris, UMR CNRS ENS 8538, 24 rue Lhomond, F-75231 Paris cedex 5, France
[g] Université de Lyon, Université Lyon 1, LaMCoS, INSA Lyon, CNRS, UMR5259, France

ARTICLE INFO

Article history:
Received 8 December 2016
Received in revised form 22 May 2017
Accepted 23 May 2017
Available online xxxx

Keywords:
Graphite
HOPG
^{14}C
Raman microspectrometry
HRTEM

ABSTRACT

Due to its excellent moderator and reflector qualities, graphite was used in CO_2-cooled nuclear reactors such as UNGG (*Uranium Naturel-Graphite-Gaz*). Neutron irradiation of graphite resulted in the production of ^{14}C which is a key issue radionuclide for the management of the irradiated graphite waste. In order to elucidate the impact of neutron irradiation on ^{14}C behavior, we carried out a systematic investigation of irradiation and its synergistic effects with temperature in Highly Oriented Pyrolitic Graphite (HOPG) model graphite used to simulate the coke grains of nuclear graphite. We used ^{13}C implantation in order to simulate ^{14}C displaced from its original structural site through recoil. The collision of the impinging neutrons with the graphite matrix carbon atoms induces mainly ballistic damage. However, a part of the recoil carbon atom energy is also transferred to the graphite lattice through electronic excitation. The effects of the different irradiation regimes in synergy with temperature were simulated using ion irradiation by varying Sn(nuclear)/Se(electronic) stopping power. Thus, the samples were irradiated with different ions of different energies. The structure modifications were followed by High Resolution Transmission Electron Microscopy (HRTEM) and Raman microspectrometry. The results show that temperature generally counteracts the disordering effects of irradiation but the achieved reordering level strongly depends on the initial structural state of the graphite matrix. Thus, extrapolating to reactor conditions, for an initially highly disordered structure, irradiation at reactor temperatures (200 – 500 °C) should induce almost no change of the initial structure. On the contrary, when the structure is initially less disordered, there should be a "zoning" of the reordering: In "cold" high flux irradiated zones where the ballistic damage is important, the structure should be poorly reordered; In "hot" low flux irradiated zones where the ballistic impact is lower and can therefore be counteracted by temperature, a better reordering of the structure should be achieved. Concerning ^{14}C, except when located close to open pores where it can be removed through radiolytic corrosion, it tends to stabilize in the graphite matrix into sp^2 or sp^3 structures with variable proportions depending on the irradiation conditions.

1. Introduction

Nuclear graphite has found widespread use in many areas of nuclear technology based on its excellent moderator and reflector qualities. Thus, since the sixties, several first generation commercial nuclear reactors using natural uranium fuel, CO_2-cooled and graphite moderated were built. Many of these reactors are now being decommissioned and over 250000 tons of irradiated graphite waste are waiting for management all over the world. Neutron irradiation of graphite results in the production of radionuclides such as ^{14}C, ^{36}Cl or ^{3}H, these radionuclides being a key issue for the management of the irradiated graphite waste. In case of disposal, a particular attention is paid to ^{14}C due to its long half-life ($T \sim 5730$ years) and as it is a major contributor to the radioactive dose and might be dose determining at the outlet [1]. Thus, what-

* Corresponding author.
E-mail address: moncof@ipnl.in2p3.fr (N. Moncoffre).

http://dx.doi.org/10.1016/j.nimb.2017.05.056
0168-583X/

ever the management option (purification, storage or disposal), a previous assessment of the radioactive inventory has to be made. This work aims at gaining information on ^{14}C location and speciation in the irradiated graphite. The goal of this paper is to elucidate the effects of neutron irradiation on ^{14}C behavior and on graphite structure modification using ion irradiation. ^{14}C has two main production routes: i) transmutation of nitrogen ($^{14}N(n,p)^{14}C$) where nitrogen has been mainly adsorbed at the surfaces of the irradiated graphite during maintenance procedures; ii) activation of carbon from the matrix ($^{13}C(n,\gamma)^{14}C$). Significant quantities of ^{14}C and ^{14}N have been depleted during reactor operation mainly through radiolytic corrosion at the gas/graphite interfaces. Thus, the remaining ^{14}C results mainly from ^{13}C neutron activation of the carbon matrix [2,3]. In order to get more insight into both ^{14}C behavior and graphite structure modification as well as to elucidate the impact of neutron irradiation, we carried out a systematic investigation of ion irradiation and its coupled effects with temperature. The process of fabrication of graphite results into a complex multiscale organization with locally more or less anisotropic and not completely graphitized zones. At the atomic scale, it is composed of stacked graphene layers forming the basic structural units or coherent domains termed as crystallites when the stacking is quasi perfect. From the nanometer to micrometer scales, crystallites are more or less parallel one to each other within "orientation domains" forming pore walls. At a larger scale, the texture is characterized by around 80% micrometer sized filler coke grains that are blended with pitch-based binder grains and displays multisized inter-granular micrometer sized pores (around 25% open pores and 7% closed pores) [4,5]. Thus, for simplification purposes, Highly Oriented Pyrolitic Graphite (HOPG) was used as a model material system representative of the nuclear graphite coke grains. Moreover, in order to study the influence of a preexisting initial disorder on graphite behavior under irradiation, the samples were implanted with ^{13}C (allowing simulating the presence of ^{14}C) at different fluences. This allows inducing a high or a low disorder into the graphite matrix which is representative of the multiplicity of the structure states already present in nuclear graphite. It also allows simulating structural differences resulting from early neutron irradiation in high or low flux regions of the reactor. Then, the samples were ion irradiated to simulate neutron irradiation. Ion-beam irradiation has been effectively used to simulate neutron irradiation effects [6,7]. The collision of the impinging neutrons with the graphite matrix carbon atoms induces mainly ballistic damage. However, a part of the recoil carbon atom energy is also transferred to the graphite lattice through electronic excitation [8]. Therefore we simulated the effects of the different irradiation regimes coupled with temperature using ion irradiation by varying Sn(nuclear)/Se(electronic) stopping power. Thus, the samples were irradiated with different ions of different energies at various facilities using dedicated irradiation cells. The structural modifications were followed by Raman microspectrometry and High Resolution Transmission Electron Microscopy (HRTEM).

2. Experimental

2.1. Sample preparation and implantation

HOPG is obtained from SPI Supplies (West Chester, US) through Neyco SA (Paris, France). We received the HOPG samples as 1 mm thick 10×10 mm^2 plates. The samples were annealed at 1000 °C-1200 °C for 8 h in high vacuum ($P \cong 10^{-7}$ mbar) in order to desorb most of the gaseous impurities. Then, they were implanted, using rastering mode, parallel to c axis with ^{13}C at room temperature (RT) under vacuum either using the 400 kV ion implanter IMIO400 of the Institut de Physique Nucléaire of Lyon (IPNL, Villeurbanne, France) or the 200 kV ion implanter EATON 200MC of the ICube laboratory of the University of Strasbourg, France. The implantation flux was in the $2–3 \times 10^{12}$ ions cm^{-2} s^{-1}range. In order to create a highly damaged structure, a batch of samples was implanted with ^{13}C at the energy of 150 keV and a fluence of 6×10^{16} at. cm^{-2}. It allows on one hand creating a strong disorder generating around 7 dpa at the projected range R_p (at a depth around 300 nm) as calculated by SRIM [9] assuming a density of 2.2 g cm^{-3} for HOPG using the Quick Kichin-Pease model and assuming a carbon displacement energy of 28 eV. On the other hand, in order to create a lower disorder level, we implanted another batch of samples with ^{13}C at the energy of 150 keV and a fluence of 4×10^{14} at. cm^{-2}. This allows creating around 0.02 dpa. Knowing that after around 11.3 years of full power operation at a fluence of 3.4×10^{21} n cm^{-2} around 2.6 dpa are created into graphite [4], the lower implantation value might correspond to the very early operation stage while the higher amount is of the same order, even if higher, as that achieved at the reactor operation breakdown. In order to enable the nanometer scale characterization of the structural defects by HRTEM along the implantation depth before and after irradiation (see next paragraphs), ultrathin sections were cut perpendicularly to the sample surfaces. The ultrathin sections were manufactured using the Focused ion Beam (FIB) technique which was shown to be relevant to prepare such implanted graphite samples [10]. The sections were cut to a depth around 3 μm, a length around 10 μm and a thickness below 0.1 μm. Such ultrathin sections are electron transparent and allow using the High Resolution mode of TEM. This preparation method, which is well described in [11], was performed with a FEI Strata DB 235 dual beam FIB at the Institut d'Electronique, de Microélectronique et de Nanotechnologie (IEMN, Université Lille 1, France). A thin layer of platinum was deposited on the samples beforehand, aiming to protect the HOPG surfaces from Ga^+ ion implantation during the milling process. The HOPG thin sections were afterwards transferred to TEM lacey grids.

2.2. Sample irradiation

The irradiations were carried out using different ions and ion energies. The aim was to try to decouple electronic excitations and ballistic effects as far as possible in order to be able to study their impact independently. Depending on the irradiation device, the samples could be heated up to 500 °C or even 1000 °C during irradiation. The irradiations were performed with carbon, argon, helium, sulfur or iodine ions using different irradiation devices: i) the 400 keV IMIO ion implantor or the 4 MV VDG accelerator (IPNL, Villeurbanne, France) for 400 keV or 600 keV C^+ ions and 800 keV Ar^+ ions, ii) the 15MV Tandem (IPN, Orsay, France) for 100 MeV S^{9+} ions or 200 MeV I^{13+} ions, iii) the cyclotron accelerator (CEMHTI, Orléans, France) for 15.7 MeV He^+. During irradiation, samples were kept at room temperature (RT) or annealed at different temperatures. Table 1 resumes the irradiation conditions. Depending on the irradiation facility, different irradiation cells allowing sample heating were used. The cell used for irradiations carried out in vacuum with the 4 MV VDG and the 15MV Tandem accelerator facility has been fully described by Marchand et al. [12]. The cell used for the irradiations at the cyclotron facility allows sample heating up to a temperature of 500 °C and a contact with a gas simulating the UNGG gas (mainly CO_2). Thus, according to the ion energy and mass, irradiations were performed on pre-implanted samples, on one hand in domains where nuclear energy loss dominates, leading to displacement of atoms via elastic scattering collisions. This was the case for irradiations carried out with carbon or argon ions that produced respectively around 1 to 4 dpa in the implanted zone. These values are in the same order of magnitude as those achieved in reactors. On the other hand, irradia-

Please cite this article in press as: N. Galy et al., Ion irradiation to simulate neutron irradiation in model graphites: Consequences for nuclear graphite, Nucl. Instr. Meth. B (2017), http://dx.doi.org/10.1016/j.nimb.2017.05.056