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Temperature effects on the behavior of carbon 14 in nuclear graphite

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ABSTRACT

The dismantling of the 1st French generation UNGG (Uranium Naturel Graphite Gas) nuclear reactors operated by the French utility, EDF (Electricité de France) will generate around 17,000 tons of irradiated graphite wastes that have to be disposed of. ^{14}C is one of the main radioactive dose contributors over 10,000 years. For the management of this waste, it is mandatory to get an accurate estimation of ^{14}C. The general aim of our work is therefore to simulate the behavior of ^{14}C in nuclear graphite and to elucidate the coupled and decoupled effects of temperature, irradiation and radiolytic corrosion that mainly influence ^{14}C behavior in graphite during reactor operation. This paper focuses on the behavior of ^{13}C implanted into nuclear graphite and used to simulate the presence of ^{14}C displaced from its original structural site through recoil during neutron irradiation. It aims at evaluating both the temperature and the disorder level of the implanted graphite structure effects on ^{13}C migration using two complementary techniques, NRA and SIMS, to evaluate the ^{13}C distribution at the millimeter and micrometer lateral scales respectively. Raman micro-spectroscopy is used to check the graphite structure evolution. The results show that ^{13}C is not released up to 1600 °C whatever the initial structural disorder level of the implanted graphite. This might be due to the fact that ^{13}C might be trapped into interstitial clusters. The extrapolation of our results to the behavior of ^{14}C shows that reactor temperatures (200–500 °C) did not induce any ^{14}C release. Moreover, as long as there is no gasification of the graphite matrix, high temperatures tend to stabilize ^{14}C into the remaining graphite structure. This fact has to be considered in case of high temperature purification of ^{14}C from irradiated graphite.

1. Introduction

The decommissioning of the six gas cooled nuclear reactors UNGG (Uranium Naturel Graphite Gas) operated by EDF (Electricité de France) in France will produce around 17,000 tons of irradiated graphite waste. These reactors were fuelled with metallic natural uranium, graphite moderated and CO_2 cooled. According to the French law of June 2006, a specific disposal must be created for this long lived-low level waste. However, other management options such as total or partial decontamination of the graphite waste are considered. These options include high temperature annealing or the use of oxidizing atmosphere for promoting selective extraction of radionuclides. ^{14}C is the major radionuclide of this waste in terms of activity. It is a long lived (T = 5730 years) b emitter. ^{14}C in irradiated graphite has two main production routes: the neutron activation reactions $^{14}N(n,p)^{14}C$ (^{14}N is mainly adsorbed at the graphite surfaces), σ = 1.19 barn (at 430 °C) or $^{13}C(n,\gamma)^{14}C$ (^{13}C is in the graphite matrix and represents 1% of the carbon atoms), $\sigma = 8.88 \times 10^{-4}$ barn (at 430 °C) [1]. The predominance of one reaction versus the other depends on the nitrogen content in the graphite. However, as the radiolytic corrosion led to the release of most of the adsorbed nitrogen (or ^{14}C issued from the adsorbed nitrogen), the remaining ^{14}C has been mainly produced through the activation of ^{13}C as evidenced by a recent paper of Poncet et al. [2]. In order to assess the radionuclide inventory calculations made by EDF, we aim at investigating the behavior of ^{14}C during

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reactor operation. Therefore, we use ^{13}C implantation into virgin nuclear graphite to simulate ^{14}C displaced from its original structural site through recoil and investigate the coupled and decoupled effects of temperature and irradiation on its mobility. This approach has already been successfully used for the study of ^{36}Cl in nuclear graphite [3–6]. The present study aims at evaluating both the temperature and the disorder level of the graphite structure effects on ^{13}C migration.

2. Experimental procedure

2.1. Sample preparation and ^{13}C ion implantation

Graphite samples were cut out from a virgin graphite block issued from the EDF UNGG Saint-Laurent A2 (SLA2) reactor. The surfaces were manually polished under ethanol with diamond pastes. The dimension of the sample surface was about 6×6 mm^2 and the thickness around 3 mm. This graphite has the same characteristics as those of the moderator stack of SLA2, with a bulk density of about 1.68 g cm^{-3} and an average porosity of about 32%, including 7% of closed pores. The samples were then annealed in high vacuum ($P \cong 10^{-7}$ mbar) at 1000 °C for 8 h to desorb most of the gaseous impurities present in the pores and also to anneal the defects induced by polishing, at least partially.

Then, $^{13}C^+$ ions were implanted at 150 keV using the 400 kV ion implanter IMIO400 of IPNL at a fluence of 6×10^{16} at/cm^2 in order to reach a maximum concentration of 5 at.% at the projected range R_p of 300 nm according to SRIM [7] and considering a graphite filler grain density around 2.2 g cm^{-3}. This concentration is necessary to distinguish the implanted signal from the pristine one which is 1.07 at.%. The implantation process generates 7.4 dpa (displacement per atom) as calculated by SRIM at the R_D. In order to study the thermal behavior of ^{13}C according to the disorder level of graphite, the implantations were performed on samples either at 15 °C or on samples heated at 600 °C. Indeed, increasing temperature during implantation favors the mobility of defects and partially reorders the graphite structure [8].

2.2. Heat treatments

After implantation, the graphite samples were annealed respectively at 500, 1300 or 1600 °C for 3, 7 and 6 h. Depending on the annealing temperature, different setups were used. At 500 °C, the annealing was performed under vacuum ($P \sim 10^{-7}$ mbar) in a silica tube placed in a tubular Pekly ETF 30–50/15-S furnace. At 1300 °C, an alumina tube was used, placed into a tubular Nabertherm RHTH 120–150/18 furnace. In this case, the annealing was performed under 2% hydrogenated argon flux in order to prevent any oxidation of the samples. At 1600 °C, a Setaram Setsys Evolution system was used and the samples were annealed in a platinum–iridium sample holder placed into an alumina tube under a 5.0 argon flux.

2.3. Depth profiling analysis of implanted ^{13}C

Two profiling techniques were used in order to determine the ^{13}C distribution profiles. The $^{13}C(p,\gamma)^{14}N$ nuclear reaction was used to measure the carbon profile at the millimeter lateral scale. At this scale, the one millimeter sized incident beam probed a representative piece of nuclear graphite material (made of infra-millimeter-sized coke filler grains and binder components, including macropores). The experiments were carried out with the 4 MV Van de Graaff accelerator of IPNL. The excitation function of this reaction presents a resonance at 1748 keV (FWHM = 75 eV, σ = 360 mbarn). Using steps of 2 keV from 1740 to 1780 keV, the 9.17 MeV gamma rays (I = 86%) produced by this reaction were detected with a Canberra Ge(Li) detector. The excitation curves were processed using the SPACES software [9] to extract the ^{13}C concentration profile. Taking into account the beam energy resolution and the energy straggling, the depth resolution of this technique ranges from 20 nm (at the surface) to 50 nm (at 600 nm depth).

In order to study the carbon distribution at a micrometer lateral scale, Secondary Ion Mass Spectrometry (SIMS) experiments were carried out with a Cameca® IMS 6f facility. The primary beam was chosen to be O_2^+ to ionize ^{13}C atoms. The primary beam current was about 32 nA. Craters of 40×40 μm^2 surface were made as far as possible in coke filler grains (corresponding to the less porous components) and the central 8 μm diameter area of the craters was analyzed. The mass resolution $M/\Delta M$ was set to 650 to avoid a major polyatomic interference due to $^{12}C^1H$. SIMS analysis provides a chronogram which represents the number of detected ^{13}C ions as function of sputtering time. To convert SIMS chronograms into depth profiles, two conversions were applied. Firstly, to correlate sputtering time and depth, the crater's mean depth was measured by optical interferometry using a Neox 3D interferometer of Sensofar. Secondly, to convert the intensity signal to concentration, the pristine ^{13}C signal was used as an internal standard. The depth resolution is around 40 nm at 800 nm depth.

2.4. Structural analysis

Furthermore, we investigated the graphite structure by using Raman micro-spectroscopy to evaluate the structural disorder level before and after implantation and annealing. Studies were performed in ambient conditions by using a Renishaw INVIA spectrometer equipped with an Ar laser source, focused through a Leica microscope. The Rayleigh scattering component was removed by a Notch filter, and the Raman scattered light was dispersed by a holographic grating with 1800 lines/mm and detected by a CCD camera. The spectra were collected under microscope (×50 objective) using the 514.5 nm wavelength (2.41 eV). A very low incident power (1–5 mW) was used to avoid heating effect. Due to the heterogeneity of nuclear graphite samples made of grains and binder, the analyses were made, as far as possible, on the coke filler grains in which the crystallites are preferentially oriented parallel to the sample surface. These zones were checked under optical microscope and appear the most reflective.

3. Results

3.1. Effect of the sample temperature during implantation

The influence of sample temperature during implantation on the ^{13}C mobility as well as on the graphite structure evolution was studied. Fig. 1 represents the ^{13}C concentration profiles on the samples implanted at 15 and 600 °C obtained by (a) NRA (at the millimeter scale) and (b) by SIMS (at the micrometric scale). Considering the NRA profiles, the area of the profile corresponding to the sample implanted at 600 °C is calculated to be around 10% lower than the area of the profile corresponding to the sample implanted at 15 °C. This is due to the fact that the implantation temperature induces a loss of ^{13}C during the implantation process. Considering SIMS data, for each implantation temperature, around 20 profiles were measured on 20 different coke grains from six different samples. For the samples implanted at 15 °C, the profiles are dispersed in function of depth due to local textural heterogeneities. However, the areas of the different profiles are almost equal (not shown here). Therefore, we averaged the different profiles and represented a mean profile (black squares, average of around 20 profiles) as well as its envelope defined by the dashed black lines. This envelope reflects mainly the dispersion of the profiles

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