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Ion irradiation of ^{37}Cl implanted nuclear graphite: Effect of the energy deposition on the chlorine behavior and consequences for the mobility of ^{36}Cl in irradiated graphite ☆

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ABSTRACT

Graphite is used in many types of nuclear reactors due to its ability to slow down fast neutrons without capturing them. Whatever the reactor design, the irradiated graphite waste management has to be faced sooner or later regarding the production of long lived or dose determining radioactive species such as ^{14}C, ^{3}H or ^{36}Cl. The first carbon dioxide cooled, graphite moderated nuclear reactors resulted in a huge quantity of irradiated graphite waste for which the management needs a previous assessment of the radioactive inventory and the radionuclide's location and speciation. As the detection limits of usual spectroscopic methods are generally not adequate to detect the low concentration levels (<1 ppm) of the radionuclides, we used an indirect approach based on the implantation of ^{37}Cl, to simulate the presence of ^{36}Cl. Our previous studies show that temperature is one of the main factors to be considered regarding the structural evolution of nuclear graphite and chlorine mobility during reactor operation. However, thermal release of chlorine cannot be solely responsible for the depletion of the ^{36}Cl inventory. We propose in this paper to study the impact of irradiation and its synergetic effects with temperature on chlorine release. Indeed, the collision of the impinging neutrons with the graphite matrix carbon atoms induces mainly ballistic collisions. However, a small part of the recoil carbon atom energy is also transferred to the lattice through electronic excitation. This paper aims at elucidating the effects of the different irradiation regimes (ballistic and electronic) using ion irradiation, on the mobility of implanted ^{37}Cl, taking into account the initial disorder level of the nuclear graphite.

1. Introduction

Since the mid-50's, the first nuclear reactors, carbon dioxide cooled, graphite moderated using natural uranium as fuel, have been built. Their operation resulted in a huge quantity of wastes and therefore, around 250,000 tons irradiated graphite and other related carbonaceous wastes (issued from UNGG, MAGNOX, AGR and also from HTR or RBMK) have been accumulated over the world. Many of these reactors are now being decommissioned and the various management options (treatment, disposal...) need to take into account two main dose determining radionuclides on the long term which are ^{14}C (T = 5730 years) and ^{36}Cl ($T \sim$ 300,000 years). In order to choose appropriate management options for these wastes, it is necessary to know the location and the speciation of the contaminating radionuclides because these features will strongly influence the properties of the irradiated graphite with respect to the radionuclide's retention or release. The detection limits of usual spectroscopic methods are generally not adequate to detect the low concentration levels (<1 ppm) of the radionuclides in the irradiated graphite. Therefore indirect approaches may be used, based on the incorporation of stable or radioactive isotopes. For example concerning hydrogen isotopes (H, ^{2}H or ^{3}H), gas permeation or implantation has often been used

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to simulate and study their incorporation or release in carbon used as plasma facing material for fusion devices [1–10].

Ion implantation was successfully used to gain information on the thermal behavior of radionuclides such as ^{14}C, ^{36}Cl and ^{3}H or their precursors and indirectly, on their location and speciation in the nuclear graphite after reactor shutdown [11–16]. However, while the above mentioned studies show that temperature is one of the main factors that has to be considered regarding the structural evolution of nuclear graphite and the impurities mobility, the impact of irradiation as well as the synergetic effects of irradiation and temperature have also to be considered. In particular, neutron irradiation causes mainly displacement damage when neutrons impinge on the crystal lattice whereas gamma irradiation of the cooling gas favors radiolytic corrosion of graphite.

The present paper focuses on the effects of irradiation in synergy with temperature on the mobility of ^{37}Cl (simulating ^{36}Cl) implanted into nuclear graphite. ^{37}Cl implantation has already been used to simulate the presence of ^{36}Cl displaced of its original structural site by recoil. Previous papers devoted to the thermal behavior of chlorine [11–14] have put in evidence the relationship between the stepwise restructuration of graphite during annealing and different ^{37}Cl release steps. They have also shown that the ^{37}Cl release rates do not exceed around 30 at.% of the initial contents at reactor temperatures of 500 °C and that temperatures higher than 1200 °C are necessary to release all ^{37}Cl. Two distinct chlorine trapping sites with two distinct enthalpies have been identified: a low energy trapping site at edge surface of crystallites (or coherent crystallographic domains) and a high energy one located inside the crystallites (or coherent crystallographic domains). Thus, extrapolating the results to ^{36}Cl and considering the only effects of temperature, more than 60% of the initial ^{36}Cl should still remain in the irradiated graphite at reactor shutdown. Chlorine speciation has also been studied on virgin nuclear graphite samples using XPS and XANES [12,13]. Oxychlorides and organic chlorine bound to carbon have been identified. However, due to the thermally labile character of oxychlorides, most of chlorine should be bound to carbon. Pichon et al. [17] have studied the behavior of ^{36}Cl in irradiated graphite carrying out leaching experiments. Their results show a fast and high release of ^{36}Cl in solution whatever the leaching solution (pure or lime water), a great part being released in the first month and the residual part being slowly leached. Thus, they suggest the presence of two kinds of chlorine: a labile fraction present in the macroporosity on one hand and a fraction located in the microporosity or closed porosity on the other hand. This latter fraction would be less accessible to water, diffuse more slowly and therefore be released with much lower kinetics. ^{36}Cl is highly soluble in water and mobile in concrete and clay. Consequently, in case of long term disposal, it might generate a significant dose peak at the outlet after water ingress into the disposal site. The release of ^{36}Cl might impact the biosphere because of the high soil to plant transfer factor of chlorine [18,19]. The solubilization of ^{36}Cl is controlled by the water accessibility into irradiated graphite pores as well as by factors related to chlorine itself such as its chemical speciation and its location within the irradiated graphite. These properties need to be taken into account for the choice of appropriate management options. The aim of the present work is to simulate the effects of neutron irradiation using ion irradiation. The displaced carbon atoms mainly loose their energy through ballistic collisions but, for high energy neutrons (as high as 10 MeV) electronic excitation can also be transferred to the carbon lattice. Thus, it can be calculated that the electronic stopping power (S_e) of graphite for carbon ions with energies ranging from 2.84 MeV to 0.284 MeV range from 1600 to 700 keV/μm but the ranges in UNGG's are generally around or lower than 700 keV/μm. Thus, in this paper we irradiate ^{37}Cl implanted graphite samples using different ions and ion energies to explore the chlorine behavior in different irradiation regimes.

2. Experimental

2.1. Sample preparation and implantation

The detailed experimental procedure has already been published and the details can be found in Blondel et al. [14]. The samples were prepared from virgin moderator nuclear graphite of the SLA2 UNGG reactor manufactured from petroleum coke grains (Lima) blended with coal tar pitch. The material has a density around 1.68 g/cm^3, is porous and is structurally heterogeneous at a nanometric scale. The fraction of open pores varies from 19% to 25% whereas the fraction of closed pores is in the range 6–7%. It presents a complex multiscale organization, locally more or less anisotropic and not completely graphitized. The micrometer sized coke grains are usually the most graphitized constituents. The samples were cut along the spinning axis. As a consequence, the sections contain grains rather preferentially oriented perpendicularly to the surface. The sample surfaces (around 1 cm^2) were polished using diamond pastes ranging from several micrometers down to one micrometer. The samples were afterward annealed at 1000 °C during 8 h under secondary vacuum in order to anneal the polishing defects as much as possible. ^{37}Cl ions were implanted at room temperature at the 400 kV ion implanter of the Institute of Nuclear Physics of Lyon (Villeurbanne, France) or at the 200 kV implanter of the I CUBE laboratory (Strasbourg, France). Implantations result in nearly Gaussian-like profiles with a projected range Rp centered at a depth around 210 nm as calculated by the SRIM software [20]. The implantations were performed at 250 keV at two different fluences: (i) a low one (5×10^{13} at. cm^{-2}), noted LF, corresponding to a maximum ^{37}Cl concentration, at the projected range (Rp), around 40 ppm. This fluence allows limiting the amount of displaced atoms estimated by SRIM [20] around 0.025 dpa (displacement per atom) (ii) a high one (2×10^{16} at. cm^{-2}), noted HF, corresponding to a maximum ^{37}Cl concentration at the Rp estimated around 1 at.%. It allows obtaining a high disorder level of around 10 dpa, inducing a noticeable structural disorder in the graphite samples.

2.2. Sample irradiation

The irradiations were carried out using different ions and ion energies. The aim was to couple or decouple electronic excitations and ballistic effects. Moreover, depending on the irradiation device, the samples could be heated up to 500 °C or even 1000 °C during irradiation. The irradiations were performed in secondary vacuum with helium, iodine or carbon ions using different irradiation devices (i) the 4 MV VDG accelerator of IPNL for the 900 keV He^+ and 7.5 MeV He^{2+} irradiations, (ii) the 15 MV Tandem of IPN at Orsay for the irradiations with ~200 MeV I^{13+}, (iii) the IMIO 400 kV accelerator of IPNL to irradiate with 400 keV C^+ ions. During irradiation, samples were kept at room temperature (RT) or annealed at different temperatures. Table 1 summarizes the irradiation conditions.

Depending on the irradiation facility, different irradiation cells were used. The cell used for irradiations carried out at the Tandem facility with iodine at high temperature has been fully described by Marchand et al. [21]. Let us just remind that to ensure the sample heating, the sample holder consists in a pyrolitic boron nitride plate with an enclosed tungsten resistance able to heat the sample up to 1200 °C through Joule effect. A C thermocouple (Tungsten–5% Rhenium vs. Tungsten–26% Rhenium; 0–2320 C) is used to measure the target temperature. Moreover, the sample