CARBON 73 (2014) 413–420

Available at www.sciencedirect.com

ScienceDirect

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

New advances on the thermal behaviour of chlorine in nuclear graphite

A. Blondel [a], N. Moncoffre [a,*], N. Toulhoat [a,b], N. Bérerd [a,c], G. Silbermann [a,d], P. Sainsot [e], J.-N. Rouzaud [f], D. Deldicque [f]

[a] Université de Lyon, Université Lyon 1, CNRS/IN2P3, UMR5822, Institut de Physique Nucléaire de Lyon (IPNL), 4 rue Enrico Fermi, F-69622 Villeurbanne cedex, France

[b] CEA/DEN, Centre de Saclay, F-91191 Gif sur Yvette cedex, France

[c] Université de Lyon, UCBL-IUT A, département chimie, 43 Bd du 11 Novembre 1918, F-69622 Villeurbanne cedex, France

[d] EDF/DIN/CIDEN/DIE, 154 Avenue Thiers, CS 60018, 69458 Lyon cedex 06, France

[e] Université de Lyon, Université Lyon 1, LaMCoS, INSA-Lyon, CNRS UMR5259, F-69621 Villeurbanne cedex, France

[f] Laboratoire de Géologie de l'Ecole Normale Supérieure (ENS), UMR CNRS-ENS 8538, 24 rue Lhomond, F-75231 Paris cedex 5, France

ARTICLE INFO

Article history:
Received 21 November 2013
Accepted 1 March 2014
Available online 7 March 2014

ABSTRACT

This paper deals with the thermal behaviour of ^{36}Cl in nuclear graphite used in UNGG French reactors (graphite moderated and CO_2 cooled reactors). Implanted ^{37}Cl simulates ^{36}Cl displaced from its original structural site by recoil. The implanted nuclear graphite samples were annealed in the 200–1600 °C temperature range and the 6–50 h time range. Structural modifications were followed by Raman microspectrometry. ^{37}Cl concentration depth profile evolution was determined by Secondary Ion Mass Spectrometry or by Rutherford Backscattering Spectrometry, depending on the implantation fluence. This study shows a correlation between the reordering of the graphite structure with annealing temperature and the chlorine release. It evidences also two distinct chlorine release steps with different kinetics (a rapid one followed by a much slower one) and suggests the presence of two different chlorine trapping sites. A low energy site at edge surface of crystallites (or coherent domains) and a high energy one located inside the crystallites (or coherent domains) for which temperatures higher than 1300 °C are required to allow chlorine removal.

1. Introduction

Since the mid-50's, the first commercial 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 the two main dose determining radionuclides on the long term which are ^{14}C and ^{36}Cl. The present paper focuses on the behaviour of ^{36}Cl. This radionuclide is mainly issued through the neutron activation of ^{35}Cl by the reaction $^{35}Cl(n, \gamma)^{36}Cl$, pristine chlorine being an impurity of nuclear

* Corresponding author.
E-mail address: n.moncoffre@ipnl.in2p3.fr (N. Moncoffre).
http://dx.doi.org/10.1016/j.carbon.2014.03.004
0008-6223/

graphite, present at the level of some at.ppm [1]. ^{36}Cl is a long lived radionuclide (about 300,000 years) and 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 [2,3]. The solubilization of ^{36}Cl is controlled by the water accessibility into irradiated graphite pores as well as by factors related to ^{36}Cl itself such as its chemical speciation and its location within the irradiated graphite. Both speciation and chlorine location should strongly influence its behaviour and need to be taken into account for the choice of liable management options. However, data on radioactive chlorine features are difficult to assess in irradiated graphite and are mainly related to inadequate detection limits. Therefore, in order to simulate the presence of ^{36}Cl, we implanted ^{37}Cl into virgin nuclear graphite. Ion implantation has been widely used to study the lattice location, the diffusion and the release of fission and activation products in nuclear materials [4–7]. ^{37}Cl implantation has already been used by Pipon et al. [6,8–11] in uranium dioxide and Vaudey et al. [12–14] in nuclear graphite, in order to simulate the behaviour of ^{36}Cl displaced from its original site through recoil during reactor operation.

One of the main factors that determine ^{36}Cl behaviour during reactor operation is the nuclear graphite temperature. Previous results have been obtained by Vaudey et al. [12–14], on the temperature effects on implanted ^{37}Cl behaviour in moderator graphite issued from the Saint-Laurent A2 French reactor (noted SLA2) for annealing times ranging up to around 10 h. They have shown that chlorine is released according to a two-step mechanism. The release starts at temperatures as low as 200 °C and reaches around 20% after some hours at around 500 °C, i.e. maximum UNGG operating temperature. However, it does not exceed 30% after some hours at 800 °C. The first kinetic step is almost athermal and has been attributed to the release of accessible chlorine located close to interconnected open pores or weakly bound chlorine (as for instance oxychlorides). The second step has been related to the very slow release of less accessible chlorine located inside the graphite matrix and more strongly bound to carbon (organic chlorine) [12–14]. These results are in agreement with those of Clayton et al. [15] who observed a maximum ^{36}Cl release around 50% after 27 h annealing at 500 °C in graphites from Advanced Gas cooled Reactors (AGR).

The present work has two main goals: to study the thermal behaviour of ^{37}Cl during longer times up to 50 h and to characterize the chlorine behaviour during thermal treatment at higher temperature (1300–1600 °C) in view of purifying the irradiated graphite waste from ^{36}Cl during a high temperature annealing in a non-oxidizing atmosphere.

2. Experimental

2.1. Sample preparation

Samples were prepared from virgin moderator nuclear graphite of the SLA2 UNGG reactor. This kind of graphite was manufactured from petroleum coke grains (Lima) blended with coal tar pitch. Shaped blocks were formed by extrusion of the blend. They were heat-treated up to about 2800 °C (graphitization treatment) and polycrystalline graphite was obtained. Blocks were impregnated one time with pitch, rebaked and regraphitized in order to increase the density to 1.68 g cm^{-3}. The difference with crystalline graphite (density = 2.265 g cm^{-3}) is mainly due to internal porosity (at the interfaces between the filler grains and the binder, and within the graphitized components themselves). As a result of mixing of several carbon components (themselves frequently texturally heterogeneous), this material is structurally heterogeneous at a nanometric scale. It presents a complex multiscale organisation. It can thus be locally more or less anisotropic and not completely graphitized. The micrometer sized coke grains, formed by several more or less oriented crystallites themselves formed by a stacking of graphene planes, are usually the most graphitized constituents. The samples were cut along the spinning axis. As a consequence, the sections contain grains preferentially oriented perpendicularly to the surface [13]. The section surfaces (around 1 cm^2) were polished using diamond pastes ranging from several micrometers down to one micrometer. Polishing is required for achieving subsequent RBS or SIMS analyses. However, as polishing is known to induce defects [16], the samples were afterwards annealed at 1000 °C during 8 h under secondary vacuum in order to anneal these defects as much as possible [12]. So-prepared sections are now ready for implantation.

2.2. ^{37}Cl implantation

^{37}Cl ions were implanted using the 400 kV ion implanter of the Institute of Nuclear Physics of Lyon (IPNL, France). Target samples were cooled to 15 °C during implantation. In order to study the effects of the chlorine concentration and the structural ordering level of the graphite, 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 theoretical concentration, at the projected range (called Rp), around 40 ppm. This value, calculated using the Stopping and Range of Ions in Matter SRIM software 2008-04 [17], is of the same order as mean chlorine concentrations measured in nuclear graphite. This fluence allows limiting the amount of displaced atoms estimated by SRIM 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 theoretical concentration at the Rp estimated around 1at.%. It simulates locally enriched chlorine zones or "hot spots". It allows obtaining a high disorder level of around 10 dpa, inducing a noticeable structural disorder in the graphite samples. Both implantations result in nearly Gaussian profiles with Rp centered around 210 nm.

2.3. Sample annealing

After implantation, two types of annealing treatment were performed. In order to explore the long term behaviour of ^{36}Cl during reactor operation, samples were annealed at temperatures ranging from 200 to 1100 °C during 8, 30 and 50 h under either argon 5.0 flow or vacuum in two different furnaces (Thermolyne Furnace 21100 and Pekly ETF 30-50/15-S).