CARBOWASTE

Treatment and Disposal of Irradiated Graphite and Other Carbonaceous Waste

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- Report (WP 4 Task 2) –

REPORT ON TRITIUM ORIGIN/LOCATION AND BEHAVIOUR UNDER TEMPERATURE

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Executive summary

Deuterium has been implanted into virgin samples of Saint Laurent A2 moderator nuclear graphite. This allows simulating tritium displaced from its original structural site through recoil during reactor operation. The fluence of 5.10^{16} ions.cm^{-2} was implanted at two distinct energies, of 70 keV and 390 keV, corresponding to two distinct implantation depths respectively around 650 nm (deuterium concentration at the R_p ~3.4 at.%) and 2.8 µm (deuterium concentration at the R_p ~2.5 at.%). Then, the samples were annealed in vacuum or in argon at temperatures ranging from 600°C to 1200°C for durations varying from 30 minutes to 192 hours.

The results show that only a small fraction of deuterium is released at UNGG reactor temperatures (less than 10 at.% at 500°C). The release becomes significant for temperatures higher than 600°C and is almost totally completed for temperatures equal or higher than 1200°C. The release curves for the samples implanted at greater depth (~2.8 µm) or for HOPG, are slightly shifted to higher temperatures with respect to the samples implanted at lower depth (~650 nm), revealing the role of the interconnected pores through which molecular deuterium permeates.

The release follows two stages: a rapid step where the release occurs within a few hours (ranging from 30 minutes to around 12 hours) is followed by a much slower release step (up to around 192 hours) during which the release of deuterium saturates. The initial stage is characterized by an activation energy of 1.2 eV and might correspond to detrapping of deuterium located at crystallites edges and its diffusion at the crystallite surfaces as well as its permeation through the open pores. Compared to this “loosely” bound deuterium, the total release of deuterium located inside the crystallites and chemisorbed to carbon atoms through sp2 or sp3 bounds requires temperatures above 1100°C.

Thus, this study shows that at UNGG reactor temperatures that do not exceed around 500°C, there is no significant deuterium release in inert atmosphere or vacuum.

Revisions						
Rev.	Date	Short description	Author	Internal Review	Task Leader	WP Leader

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1. Introduction

Graphite has been used as moderator in UNGG reactors. After reactor shutdown, tritium is the predominant radionuclide in terms of radioactivity together with ^{14}C in irradiated graphite. Its half live is short (12.3 years) but this radionuclide is of major concern during dismantling as well as during the operational phase of disposal because of its mobility in the environment.

It is therefore necessary to collect information on its location and speciation as well as on its inventory in irradiated graphite in order to be able to optimize the waste management outlet.

Therefore, the Institute of Nuclear Physics of Lyon decided to study the behaviour of tritium in nuclear graphite using implanted deuterium to simulate the presence of tritium.

The work is performed in the frame of the PhD thesis of Maël le Guillou (September 2011-September 2014) and the results presented in this report have been obtained during the first year of his thesis.

2. Tritium formation and migration

In the nuclear reactor, tritium has several production routes. On one hand it can be issued from the ternary fission of ^{235}U or ^{239}Pu and on the other hand it can be formed through the neutron activation of several impurities present in concrete, cooling gas or moderator graphite.

Concerning graphite, tritium originates mainly through the neutron activation of boron and lithium through following reactions:

$$^{6}Li + n \rightarrow {}^{4}He + {}^{3}H$$

$$^{10}B + n \rightarrow 2{}^{4}He + {}^{3}H$$

$$^{10}B + n \rightarrow {}^{9}Be + {}^{3}H$$

Tritium is a low energy β^- emitter (maximum energy 18.6 keV and mean energy 5.7 keV) and decays to form stable helium that may be activated to form tritium again according to following reactions:

$$^{3}H \rightarrow {}^{3}He + e^- + \nu_e^-$$

$$^{3}He + {}^{1}n \rightarrow {}^{1}H + {}^{3}H$$

Figure 1 represents the neutron activation cross sections for lithium, boron isotopes and ^{3}He as function of neutron energy. This figure shows that, when the neutron have been

thermalised in the moderator, tritium is formed mainly through the neutron activation of lithium 6 which predominates compared to the production through boron.

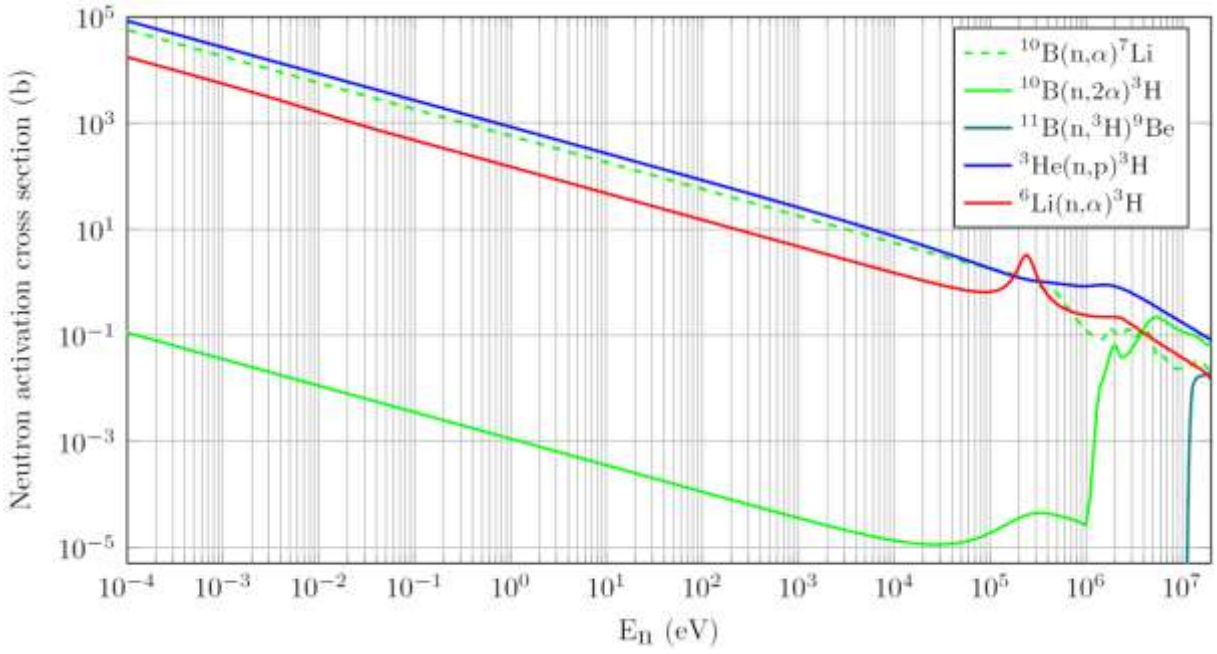


Figure 1: Neutron activation cross sections for boron 10 and 11, lithium 6 and helium 3 [ENDF-AIEA, 2012]

The recoil energy of tritium is around 2.7 MeV and this results in its displacement out of its original structural site.

The behaviour and migration mechanisms of hydrogen isotopes have often been investigated in the literature related to nuclear fusion for hydrogen storage purpose. The isotopes are generally absorbed or implanted into graphite and their thermal desorption is studied.

The location, migration, trapping sites and the absorption enthalpies of hydrogen isotopes in graphite strongly depend on its graphitization degree, i.e. on graphite structure itself as well as on the disordering level induced by irradiation [Atsumi 2002, Atsumi 2003, Atsumi&Tauchi 2003, Suda et al. 2007]. Schematically, the retention of hydrogen decreases when the graphite is well graphitized. On the opposite, it increases for higher concentration of carbon dangling

bonds, i.e. for irradiated graphite (and consequently graphite with smaller crystallites) or oxidized graphite.

Thus, on the basis of thermal desorption studies of hydrogen or deuterium, Atsumi et al. [Atsumi 2002, Atsumi 2003, Atsumi&Tauchi 2003] determined that thermal desorption occurs in a temperature slot ranging roughly from 700 K to 1100 K. They have identified two main migration paths for hydrogen isotopes respectively corresponding to molecular diffusion through the open pores on one hand and within the coke grains (along the crystallite surfaces) on the other hand. In both cases, hydrogen isotopes migration is subjected to sequences of trapping and detrapping. In the case of isotropic graphite manufactured by Toyo Tanso or graphite manufactured by Union Carbide, the activation energy of the apparent diffusion process of hydrogen isotopes along the grains and on the crystallite surfaces has been calculated to be 1.3 eV.

Moreover, two main trapping sites have been identified corresponding to carbon dangling bonds located at the crystallite surfaces or located between the graphene planes. The hydrogen isotopes may be on one hand covalently bound at edge surfaces of crystallites with an enthalpy of 2.6 eV. On the other hand, they can be bound to dangling carbons of clusters inside crystallites at higher energy trapping sites of 4.4 eV.
The amount/availability of each site should therefore strongly depend on the disordering level of graphite, i.e. on the "irradiation history".

Other authors [Suda et al. 2007] report on similar desorption temperature ranges for implanted deuterium with two main desorption peaks at 900 K and 1050 K. The peaks were attributed to be sp3 hybrid orbital type C–D bond and σ type C–D bond of sp2 hybrid carbon, respectively.

Thus, there is a general agreement among the authors according to which 1) desorption of hydrogen isotopes does not occur at temperatures lower than 700 K and desorption is completed around 1300 K and 2) hydrogen isotopes bind to carbon on at least two distinct trapping sites: a) in the crystallite on one hand, at dangling bonds or at cluster loop edges and b) at the surface of crystallites on the other hand. The relative proportion of each site and the energy distribution strongly depend on the irradiation conditions over the reactor life (ion or

neutron energy, dose, temperature…). Moreover, the relative amount of hydrogen/deuterium atoms bound to sp2 carbon with respect to those bound to sp3 carbon also depends on implantation (or irradiation) temperature because temperature tends to reorder the graphite structure : above 300°C, C–D bond of sp2 hybrid carbon dominate whereas below 300°C, the C–D bond of sp3 hybrid carbon dominate [Suda et al. 2007].

3. Samples

Virgin nuclear graphite samples from the SLA2 EDF reactor moderator have been used as well as Highly Oriented Pyrolitic Graphite (HOPG) samples. The open porosity was measured to be around 25% and the closed porosity is around 7.4%.

The samples have been cut into small 0.2 cm thick rectangular blocks (~ 0.5 x 0.9 cm^2), polished to the nearest micrometer using diamond paste diluted in ultra-pure ethanol, and pre-annealed at 1000°C during 8 h in order to remove some of the polishing defects. Afterwards, the samples have been implanted with deuterium allowing simulating the activated tritium displaced through recoil. The implantation have been carried out at the 400 kV IMIO ion implantor at IPNL at one fluence, $5x10^{16}$ $ions.cm^{-2}$ which results in a maximum deuterium concentration around 4 at.% at the maximum projected range (R_p). Two implantation energies have been chosen for the SLA2 EDF reactor moderator samples: respectively 70 keV and 390 keV, and the implantation energy of 70 keV was chosen for the HOPG samples. On each implanted sample, the implantations resulted in two deuterium peaks at respective depths of 650 nm and 2.8 µm and respective deuterium concentrations at the maximum implanted depth (R_p) of 3.4 at.% at and 2.5 at.% (Figure 2, SRIM calculations). These two depths have been chosen in order to evaluate the impact of the proximity of the surface on deuterium migration. After that, the samples have been annealed between 200 and 1200 °C. The annealing duration has been varied from 30 minutes to 192 hours in order to reveal the thermal behaviour of deuterium. Annealing was performed under vacuum or in inert gas (argon) using Thermolyne, Pekly or Nabertherm furnaces.

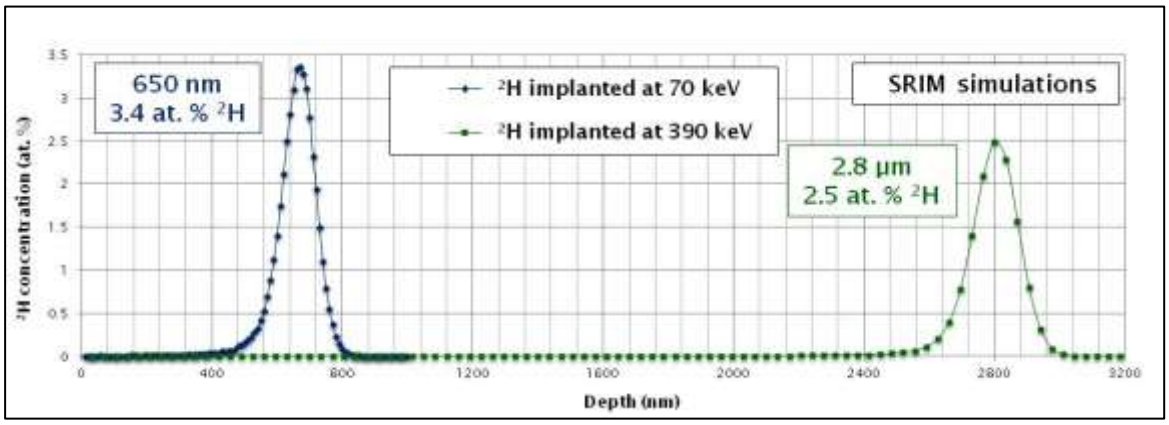
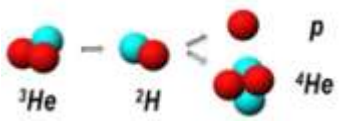


Figure 2: SRIM simulations corresponding to both deuterium implantation energies

4. Deuterium analysis

Deuterium profiles have been analysed before and after annealing using Nuclear Reaction Analysis (NRA) at the 4 MV Van de Graaff accelerator at IPNL. The $^{2}H(^{3}He,p)^{4}He$ nuclear reaction was used.



At a detection angle of 135°, the maximum cross section is of 60 mb.sr^{-1} at 630 keV and FWHM is around 700 keV. The protons produced by this reactions have an energy around 13 MeV and result in an isolated peak at high energy (or high channel number) well separated from the carbon peaks of the matrix. They have been detected with a surface barrier detector covered with a 23 µm thick Mylar foil in order to stop the backscattered particles (Figures 3 and 4). The incident beam diameter was around 1 mm^{2}.

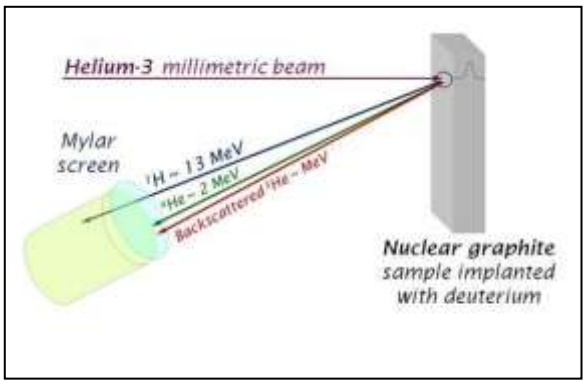


Figure 3: Experimental device

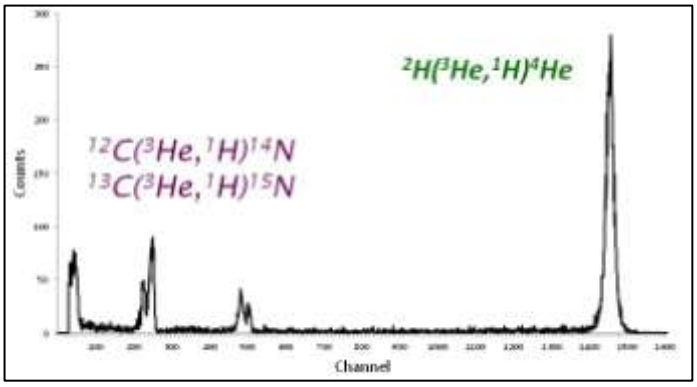


Figure 4 : Spectrum of the reactions on carbon and deuterium

5. Results and discussion

5.1 Samples implanted at 70 keV (~650 nm)

The annealing has been performed on the different samples from 200°C to 1200°C from 30 minutes to 192 hours.

Figure 5 shows the evolution of the deuterium spectra after 4h annealing at temperatures ranging from 200°C to 1200°C. The annealing results in a decrease of the peak areas. This implies that the main process driving the migration of tritium is release through the graphite porous structure. The release begins at 600°C and is completed at 1200°C.

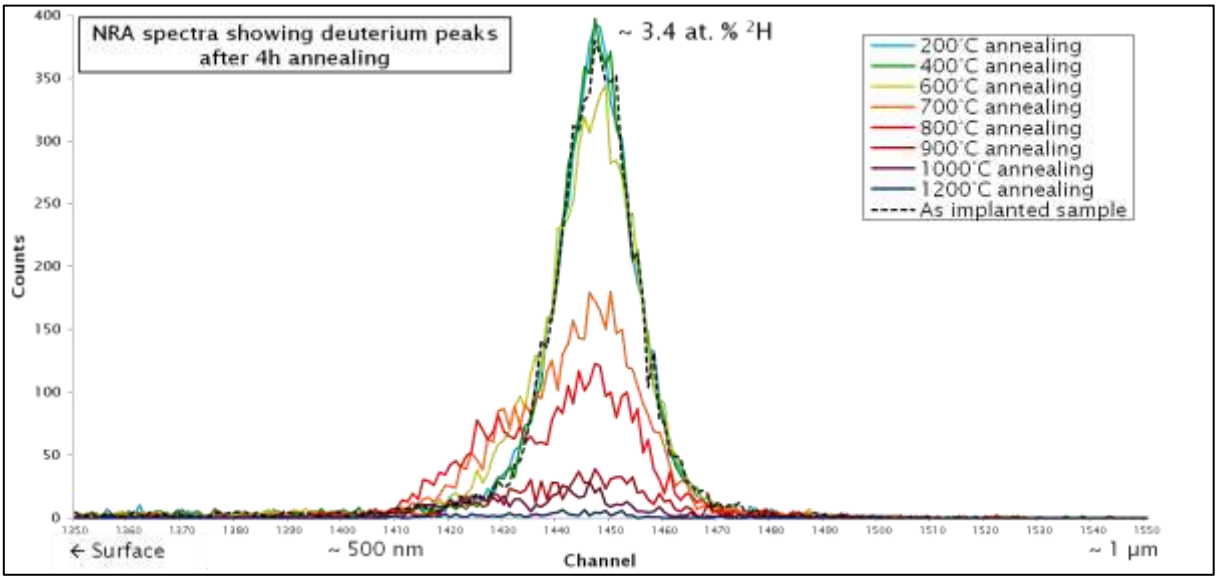


Figure 5: NRA spectra of deuterium in SLA2 nuclear graphite implanted with ^{2}H at 650 nm (70 keV) and $5x10^{16}$ $^{2}H^{+}$ cm^{-2} before and after annealing in argon from 200°C to 1200°C during 4hours

A slight diffusion towards the sample surface resulting in peak width enlargement is also observed. However, due to the resolution of the technique around 150 nm and considering the peak FWHM around 400 and 500 nm, the diffusion phenomenon cannot be quantified.

A major effect of the annealing temperature is evidenced on Figures 6 and 7. These figures gather the data of the deuterium releases in function of temperature for increasing annealing durations (Figure 6) and the releases in function of annealing time for increasing temperatures (Figure 7).

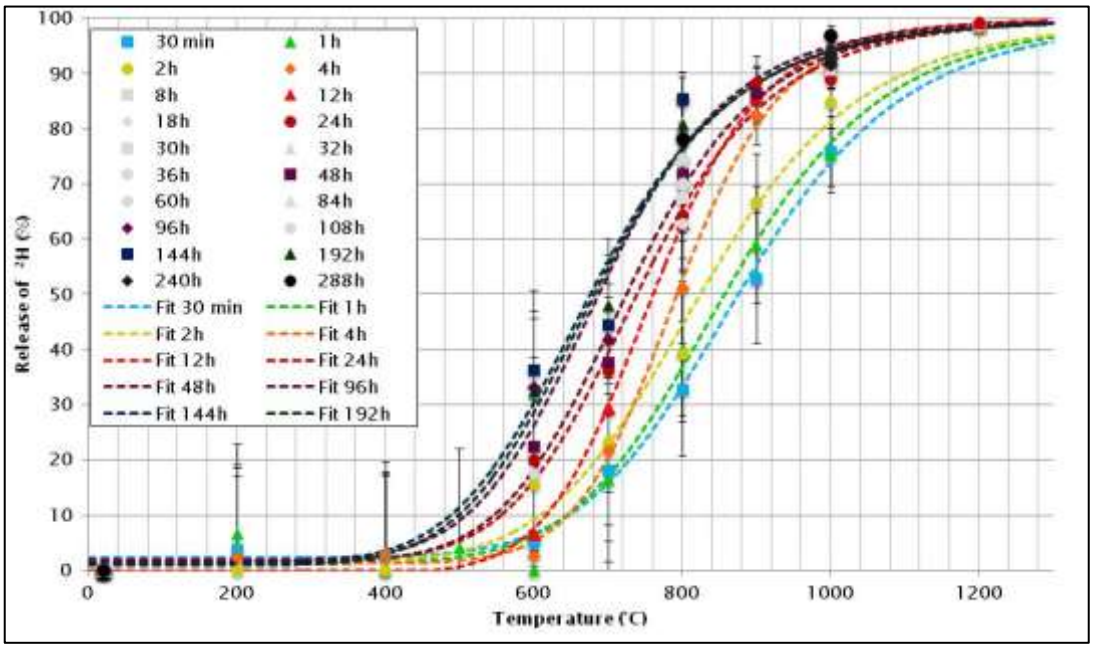


Figure 6: Deuterium release curves in function of annealing temperature for different durations for the SLA2 samples implanted at 70 keV

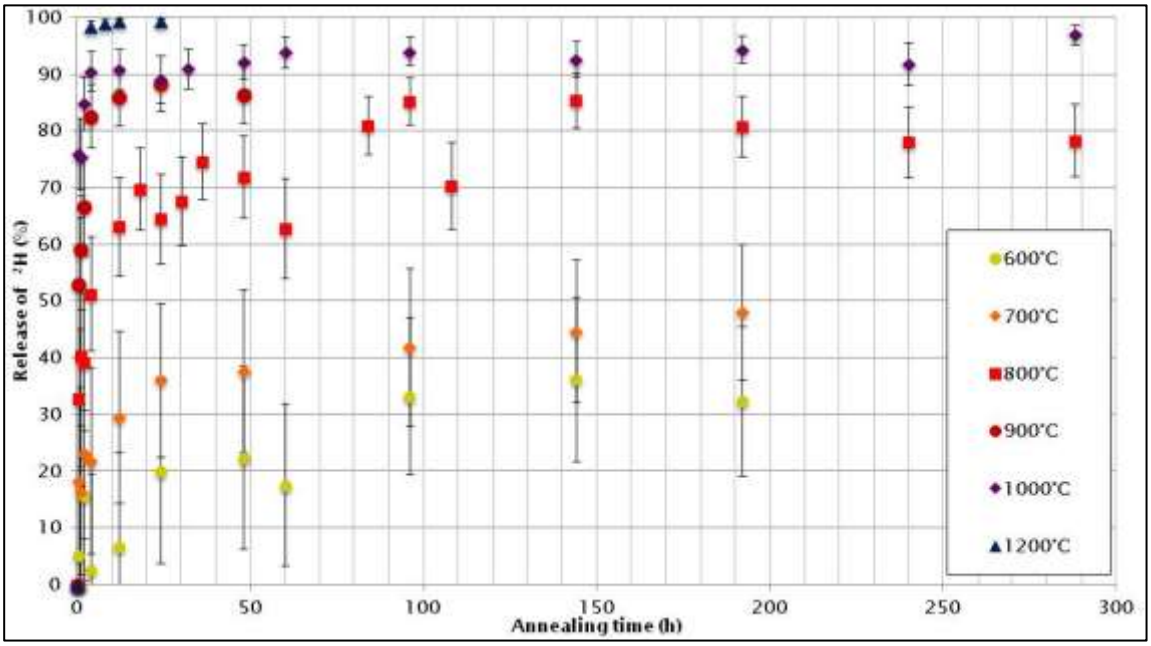


Figure 7 : Deuterium release curves in function of annealing time at different temperatures for the SLA2 samples implanted at 70 keV

5.2 Samples implanted at 390 keV (~2.8 µm)

We have compared the data obtained for samples implanted at greater depth (~2.8 µm) to the fits of the data obtained for the samples implanted at around 650 nm. The results are presented in Figures 8 and 9 gathering the data of the deuterium releases in function of temperature for increasing annealing durations (Figure 8) and the releases in function of annealing time for increasing temperatures (Figure 9). The data at this implantation depth are scarcer, nevertheless the figures show that the release kinetics seem to be similar to those obtained on the samples implanted at 650 nm. However, the released deuterium amounts are almost twice lower for similar annealing times. This is probably due to the fact that when samples are implanted at greater depth, the accessibility of deuterium to the surface via the interconnected pores is reduced compared to samples implanted at lower depth.

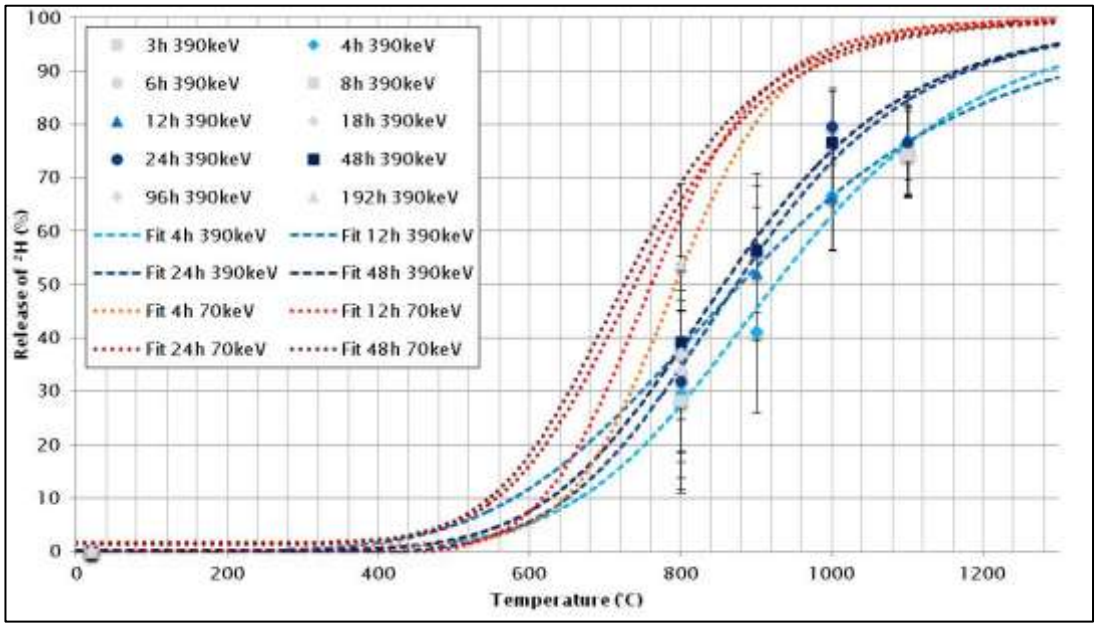


Figure 8: Deuterium release curves in function of annealing temperature for different durations for the SLA2 samples implanted at 390 keV compared to the samples implanted at 70 keV

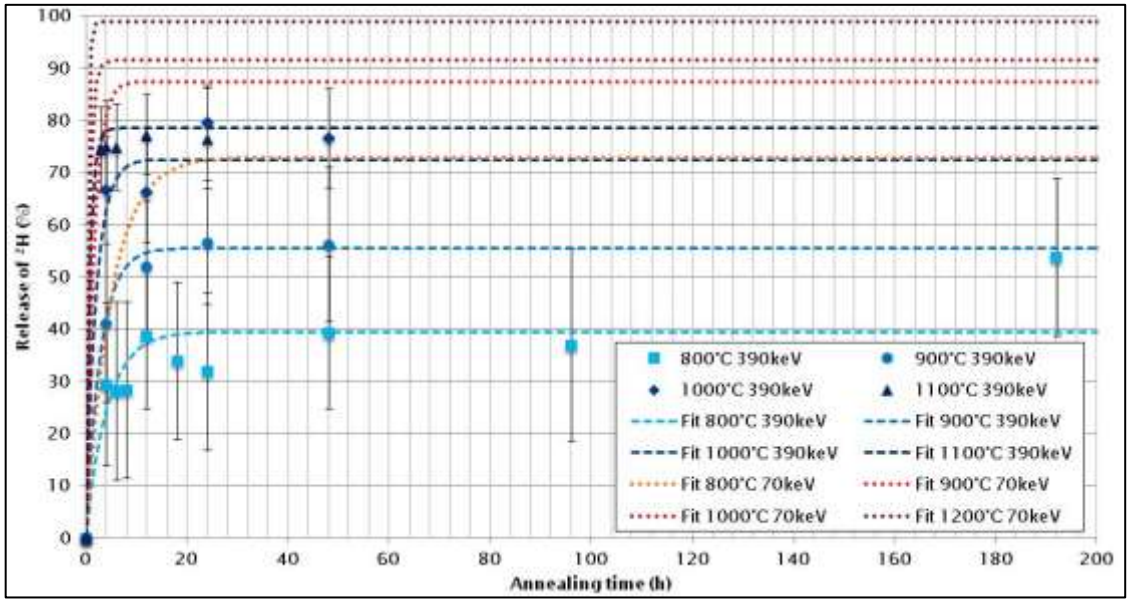


Figure 9: Deuterium release curves in function of annealing time at different temperatures for the SLA2 samples implanted at 390 keV compared to the samples implanted at 70 keV

5.3 HOPG samples

The fits of data of deuterium release obtained on the HOPG samples implanted at 70 keV are represented in Figure 10 together with those obtained for the SLA2 samples implanted at both energies. The deuterium release in the HOPG sample is only slightly lower than in the 390 keV implanted SLA2 sample, despite its non porous structure and the low level of damages induced by the implantation process (far less than 1 dpa). This is probably due to the fact that the implantation process cracks the surface and creates short cuts favoring deuterium release.

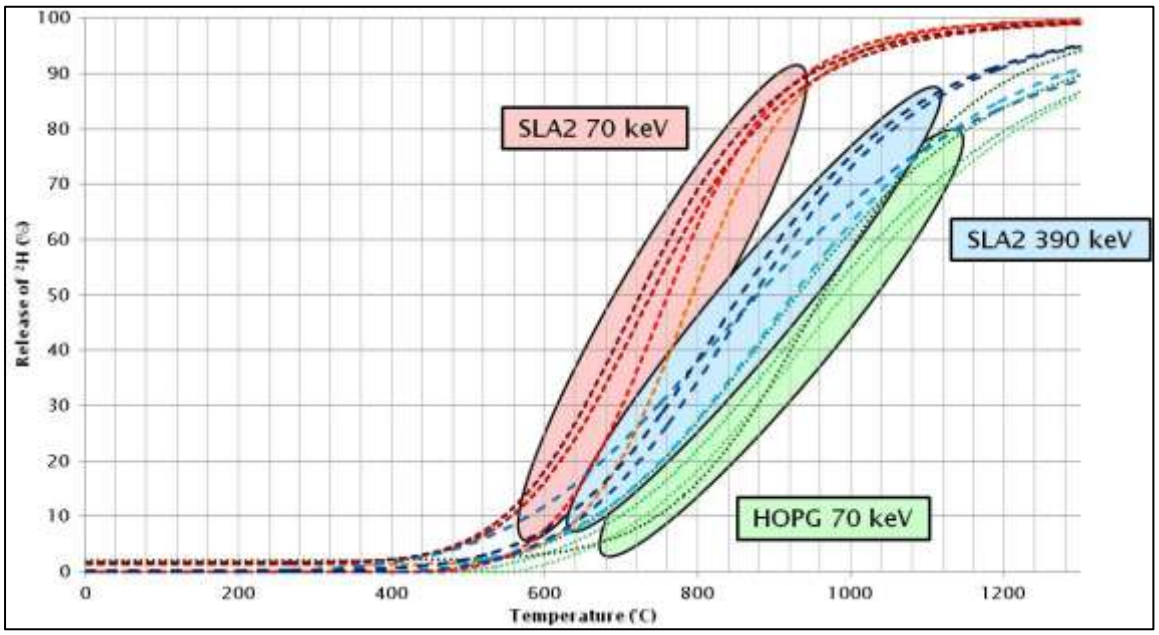


Figure 10: Comparison of the deuterium release curves and trends in function of annealing temperature for different durations for the SLA2 samples respectively implanted at 390 keV and 70 keV and for the HOPG samples implanted at 70 keV

5.4 Modeling of the release and comparison with the literature data

For all the samples and at any temperature, the data evidence two major release stages with distinct kinetics. At each annealing temperature, an important and rather rapid step where the release occurs within a few hours (ranging from 30 minutes to around 12 hours) is followed by a much slower release step (up to around 192 hours) during which the release of deuterium saturates.

First stage :

Using the results obtained at 70 keV for which we have the most data and according to Fick's law, the release of deuterium of the first stage can be modeled using the equation:

$$\frac{\partial C(x,t)}{\partial t} = -k.C(x,t)$$

Which solving gives the following equation:

$$\frac{C_T}{C_0} = \exp(-k.\Delta t)$$

Where C_T (in ppm) is the atomic deuterium concentration present in a sample annealed at a temperature T, C_0 (en ppm) the atomic concentration of deuterium present in an as implanted sample, the kinetic release constant k in s^{-1} and the annealing time Δt in s.

At each temperature, the release constant k has been calculated as the slope of the straight line in the diagram representing the evolution of the logarithm of the ratio C_T/C_0 as function of different annealing times as shown in figure 11 for the temperature of 900°C:

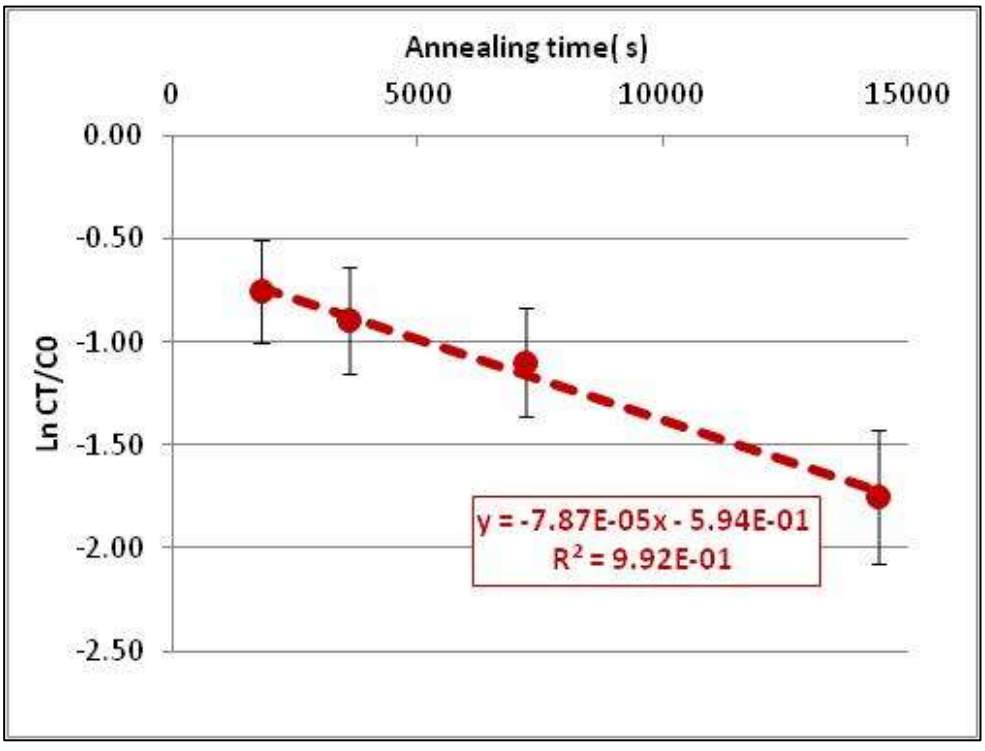


Figure 11: : Evolution of the logarithm of the relation C_T/C_0 as a function of the annealing times at a temperature of 900 °C for a SLA2 sample implanted at 70 keV

Finally, the release activation energy could be estimated from the Arrhenius Law:

$$k = k_0 \exp\left(-\frac{E_a}{k_B.T}\right)$$

where, the release constant, k, is in s^{-1}, the initial release constant, k_0, in s^{-1}, the activation energy, E_a, in eV, the Boltzmann constant, k_B = 8.65x10^{-5} eV K^{-1} and the annealing temperature, T, in K.

The Arrhenius plot (Figure 12) enabled us to calculate an activation energy around 1.2 eV for the initial rapid release stage.

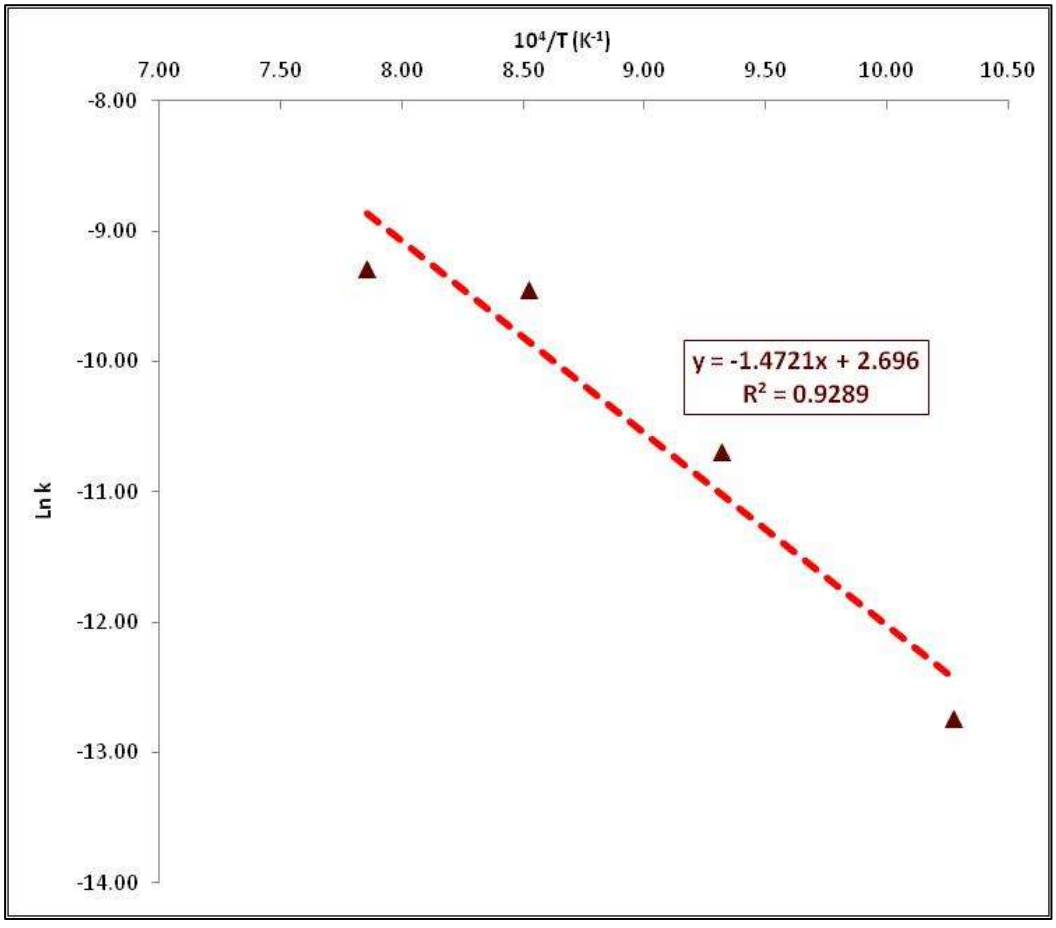


Figure 12: Arrhenius diagram of the deuterium release for the SLA2 samples implanted at 70 keV

It is interesting to note that this activation energy value is close to the value of 1.3 eV stated by Atsumi et al. [Atsumi&Tauchi 2003] for hydrogen migration in nuclear grade graphites

manufactured by Toyo Tanso. According to these authors, this activation energy value could result from a molecular diffusion process where "hydrogen species might migrate, for instance, in a sequence of dissociation and recombination resulting from an interaction with the outer surface of a crystallite to derive the activation energy" and subsequent permeation through open pores (cf Figure 13 exctracted from [Atsumi 2003]).

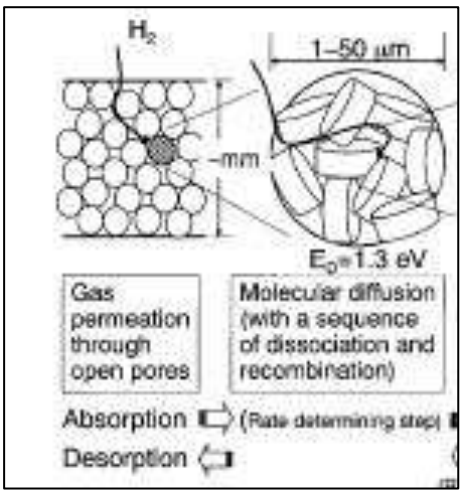


Figure 13: Schematic representation of the migration of hydrogen by molecular diffusion at the surfaces of crystallites and through the open pores taken from [Atsumi 2003]

Second stage :

As mentioned above, the release of deuterium during this stage is almost null at any temperature. This means probably that the remaining deuterium is trapped at sites requiring higher energies (i.e. higher temperatures) to be detrapped. The remaining deuterium is most probably located inside the crystallites and chemisorbed to carbon atoms through sp2 or sp3 bonds [Atsumi 2003, Stojkovic et al. 2003]. The thermal activation of these sites may begin from 700°C (cf Figure 5 where the slight widening of the deuterium peak might be at least partly due to the diffusion of deuterium from these sites). However, temperatures higher than 1100°C or 1200°C are generally necessary to lead to total deuterium release.

We compared the data for 70 keV deuterium implanted SLA2 samples annealed for one hour to the data of Sawicki et al. [Sawicki 1989] who carried out isochronal annealing of tritium implanted nuclear graphite at a fluence of 5.10^{15} ions.cm^{-2} and an energy of 40 keV (depth ~500 nm) where the temperature was kept constant for 40 minutes. We added our data (red

spots) obtained at respectively 800, 900, and 1000°C in Figure 14 extracted from [Sawicki 1989] representing the data from their own work (mentioned as "this work") together with the data from other papers. This figure shows that the retention curve obtained for our data on deuterium lies close to the curves obtained by Sawicky et al. for tritium implanted at 5.10^{15} ions.cm^{-2} on one hand, and Doyle et al. [Doyle 1981], and Braun et al.[Braun&Emmoth 1984] on the other hand for the retention of deuterium at respectively 10^{15} and 5.10^{16} ions.cm^{-2}. The curves obtained by other authors on deuterium implanted at higher fluences (ranging from 5.10^{17} to 10^{19} ions.cm^{-2}) are shifted to lower temperatures. The comparison of all these data shows that:

- Deuterium has a behaviour similar to that of tritium,
- for a given temperature, the released amount depends on the initial quantity of deuterium: the higher the implantation fluence, the lower the release temperature. This has been explained by the authors by the fact that, saturation fluence is reached for high energy sites with respect to deuterium retention. Deuterium is thus trapped in lower energy sites and therefore more easily released.

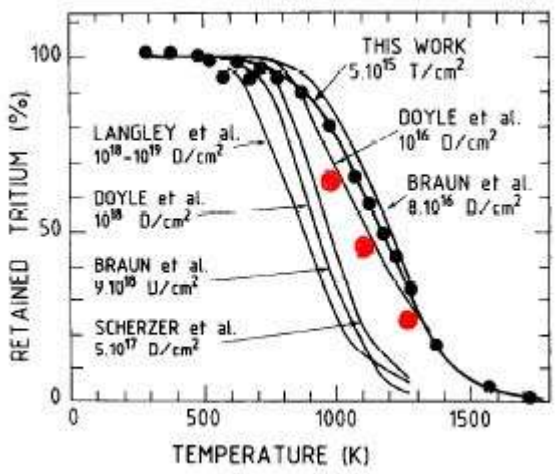


Figure 14: Amount of retained tritium in implanted nuclear graphites compared to other literature data on deuterium release (from [Sawicki 1989]) and comparison to our present work (red dots) on deuterium

6. Conclusion

In order to elucidate the thermal behaviour of tritium in nuclear graphite, we have implanted deuterium into nuclear graphite samples from SLA2. The fluence of 5.10^{16} ions.cm^{-2} was implanted at two distinct energies, of 70 keV and 390 keV, corresponding to two distinct implantation depths respectively around 650 nm (deuterium concentration at the R_p ~3.4 at.%) and 2.8 µm (deuterium concentration at the R_p ~2.5 at.%). Then, the samples were annealed in vacuum or in argon at temperatures ranging from 600°C to 1200°C for durations varying from 30 minutes to 192 hours.

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For each sample and at any temperature, the release follows two stages: a rapid step where the release occurs within a few hours (ranging from 30 minutes to around 12 hours) is followed by a much slower release step (up to around 192 hours) during which the release of deuterium saturates. The initial stage is characterized by an activation energy of 1.2 eV and might correspond to detrapping of deuterium located at crystallites edges and its diffusion at the crystallite surfaces as well as its permeation through the open pores. Compared to this "loosely" bound deuterium, the total release of deuterium located inside the crystallites and chemisorbed to carbon atoms through sp2 or sp3 bounds requires temperatures above 1100°C.

Thus, this study shows that at UNGG reactor temperatures that do not exceed around 500°C, there is no significant deuterium release in inert atmosphere or vacuum. However, complementary experiments are presently conducted in order to check the role of gas containing traces of hydrogen bearing molecules (i.e. UNGG gas) with respect to isotopic exchange. As a matter of fact, the presence of these molecules might enhance the deuterium release.

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