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Assessment of the heating technique as a possible ex situ detritiation method for carbon wall materials from fusion machines

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Abstract

Detritiation by heat treatment of graphite or carbon fibre composite (CFC) tiles retrieved from the Tokamak Fusion Test Reactor (TFTR) was assessed using the standard and well proved technique of full combustion combined with liquid scintillation analysis. Complete carbon tiles were heated in a oven to 500 °C in air for one hour at Princeton Plasma Physics Laboratory (PPPL) and sent to Tritium Laboratory Karlsruhe (TLK) for surface and depth profile analysis. Coring/full combustion technique performed on the treated and untreated tiles, both graphite and CFC, has shown that only the tritium held close to the surface (few tens μm) is efficiently released by baking in air while the bulk tritium is almost unaffected. Therefore, baking the tile under air, even at 500 °C, does not detritiate the bulk.

1. Introduction

The erosion of the carbon first wall material (FWM) of fusion machines by D–T plasmas leads to a co-deposition of hydrogenated carbon films mainly in the colder part of the machine. This immobilises substantial amount of tritium in thin layers that are inaccessible to further erosion. The formation of such co-deposited tritiated layers constitutes a major issue for ITER as it will tend to increase the tritium inventory trapped inside the machine.

Moreover, tritium depth profiles obtained recently for JET divertor tiles by the coring/full combustion technique revealed that a surprisingly large fraction of the total tritium trapped by a tile >61% had diffused deep into the bulk of the tile, most probably between the CFC fibres [1]. Nevertheless, the full combustion measurements on a complete set of poloidal divertor tiles from JET (MKIIA) have shown that, in comparison to the 6.2 g tritium which did not return to the Active Gas Handling System (AGHS) a total amount of about 0.1 g tritium was estimated to be trapped by the 480 divertor tiles and another 0.1 g by the rest of the walls. As during a long run D–T campaign (such as it is foreseen in ITER) tritium will be accumulated in the bulk of these materials (carbon vertical targets on the divertor region) and as the accumulation of tritium inventory in FWM of fusion machines constitutes an important safety issue, the removal in situ or ex situ of the tritium trapped in the in-vessel components is mandatory for their safe disposal.

A variety of techniques have been tested for the in situ removal of tritium from plasma facing

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components, i.e. glow discharge, air ventilation, thermal release under vacuum and more recently the use of Nd:YAG lasers [2,3]. Nevertheless, the experimental techniques investigated until now have been limited not only by the conditions permissible inside the torus but also because they treat only the plasma exposed surface of the tile, though air ventilation also reaches the gaps and areas which are not in line of sight of the plasma. They have, however, a major drawback in that they are time consuming.

When dealing with the tiles removed from the reactor more severe heat treatment are acceptable, because no precautions concerning the possible collateral damages on structural parts of the machine need to be taken. Therefore, the higher temperatures that can be reached could be sufficient to initiate the tritium release from the bulk of the tiles as well. During collaboration between PPPL and TLK the detritiation of complete tiles by heating was investigated. In a series of experiments complete CFC and graphite tiles retrieved from TFTR were heated at PPPL under air at temperatures up to 500 °C for one hour. The efficiency of this technique was assessed at TLK by the coring/full combustion technique combined with the liquid scintillation tritium analysis [4]. As the deuterium and oxygen content of similar tiles was already known [5,6] in this report the results related to the tritium content of the CFC tiles as well for graphite tiles is presented.

2. Experimental

Graphite and CFC tiles used at TFTR were manufactured by Fiber Materials Inc. (USA) from fibre reinforced graphite by chemical vapour deposition (CVD) and have a multi-directional (4D) fibres weave.

The available tiles for the present tritium analysis at TLK were:

(I) Two 4D CFC tiles (KC11 and KC18). Tile KC11 had been baked.
(II) Two graphite tiles (KC19 and KC20). Tile KC20 had been baked.

The four tiles were retrieved from the Bay K of the inner limiter of TFTR after exposure to D–D and D–T plasmas [7]. The 4D CFC tiles are woven with yarns oriented in four directions giving to the microstructure a tetrahedral shape.

Several cylindrical specimens were retrieved from each tile using the coring technique described in Ref. [8]. The cylinders obtained had a diameter of ≈0.78 cm and a height corresponding to the thickness of the tile. Every cylinder was cut into disks with a thickness of 0.1 cm. The 4D configuration appeared to be harder than the 2D (as used for the CFC tiles used at JET). More than one hour was needed to core a cylinder from a 4D tile in comparison to about 20 min needed for the same operation for a 2D CFC tile. Quantitative determinations of the tritium depth were obtained using the well established and very accurate full combustion technique in a Vance-type apparatus followed by liquid scintillation detection of tritium [9].

3. Results and discussions

3.1. Detritiation by oxidation in air

A variety of techniques were tested at laboratory scale [10,11]. Tritium release from co-deposited layers of graphite samples is known to be very rapid when temperatures rise above 350 °C [12]. Nevertheless, a substantial amount of tritium is still present in the sample after the thermal treatment. In a new series of experiments, complete CFC and graphite tiles retrieved from TFTR were heated under air at higher temperatures not only to improve the detritiation factor but also to assess the technique with full scale components.

The tiles were heated up to 500 °C for one hour at PPPL. The heating process was performed under air atmosphere as in preliminary test it was showed that during baking at 240 °C a rapid increase of tritium release was observed when the purging gas was changed from pure Ar to Ar–1%O_2 during baking at 240 °C. Oxygen significantly enhanced tritium release [13]. After the bake out of one graphite (KC20) and one CFC tile (KC11), the tritium released was 3.0×10^{10} and 2.4×10^{10} Bq respectively. The tritium surface activity was measured for each baked tile at five different locations on the tiles prior and after the bake using an open wall ion chamber as detector and repeating each measure three times. The tiles' physical parameters and the released activity observed during treatment are reported in Table 1.

In a previous experiment, where the gases flowing out of the tile chamber during the bake were sampled and analysed, it was discovered that CO and not CO_2 was the major gaseous product released during the thermal treatment.

After the heat treatment the tiles were packed and sent to TLK where the efficiency of the detritiation technique was assessed by coring full/combustion measurements. From each tile at least five cylinders were cored from the surface and sometimes from the sides of the tiles for full combustion and accelerator mass spectrometry (AMS).

As already observed for JET tiles [14], a substantial tritium fraction was also found in the bulk of the TFTR tiles. Although co-deposition of films and flakes is taking place at different locations in both machines (for JET it was observed on the bottom of the divertor on colder

Table 1
Tritium released activity during the bake out of KC11 (CFC) and KC20 (graphite)

Tile	Tile's area (cm^2)	Mass (g)	Middle of the tile ($\mu Ci\,cm^{-2}$)	Rest of the tile ($\mu Ci\,cm^{-2}$)	Average activity ($\mu Ci\,cm^{-2}$)	Mass loss (g)	Released activity	
							(Ci)	(GBq)
KC11 (b.b.)	104.33	780.08	77.1	255.1	219.5			
KC11 (a.b.)		779.81	19.5	12.7	14.1	0.27	0.648	24.0
KC20 (b.b.)	165.33	939.74	66.6	88.9	84.5			
KC20 (a.b.)		939.18	03.4	03.2	03.3	0.56	0.808	29.9

b.b. = before bake out.
a.b. = after bake out.

and areas inaccessible by the plasma, while for TFTR co-deposition was found on the whole interior wall) the tritium migration throughout the bulk of the tile material seems to take place in a same manner. Tritium migration seems to take place via the interconnected porosity, and/or transgranular diffusion. Graphite and carbon composites are very porous materials (open porosity ranging between 15% and 20%) and these pores affect the tritium uptake. Moreover, at elevated temperatures, molecular tritiated species such as HT or DT can easily penetrate very deeply into the tile material via the pores where nearby a 'reactive centre' it could lead to a molecular homolytic dissociation (see reactions below). The latter provides very reactive atoms which will react with the first available species present in the 'surrounding'. Of course, when such an atomic species having an odd number of electrons (H^0, D^0, T^0) reacts with a molecule (which has an even number of electrons), the total number of electrons in the product must be odd. Therefore, the product in such a case must be the production of another radical which nevertheless, is firmly located in the bulk of the tile.

$$\mathrm{H{-}Q} \rightarrow \mathrm{H^{\bullet}} + \mathrm{Q^{\bullet}} \text{ (homolytic dissociation)}$$

$$\mathrm{Q^{\bullet}} + {>}\mathrm{C} = \mathrm{C}{<} \rightarrow {>}\mathrm{CH^{\bullet}{-}C}{<} \text{ (generation of new radical)}$$

where Q stands for any hydrogen isotope, H, D or T.

The last step is a kind of propagation of the radical formation process as the newly formed radical can now react with another molecule and produce another radical or it can react with any isotope of hydrogen in the atomic state. After trapping the later the propagation process is terminated.

$${>}\mathrm{CH^{\bullet}{-}C}{<} + \mathrm{Q^{\bullet}} \rightarrow +{>}\mathrm{CH{-}CQ}{<} \text{ (termination reaction)}$$

The presence of metallic impurities or oxygen in the lattice or even point defects can also react with radicals acting as radical traps and will therefore also terminate the propagation reactions. Indeed, the oxygen content found in CFC tiles and retrieved from TFTR where they were exposed to the plasma, was rather high. Measurements performed on the KC17 CFC tile in Los Alamos by Paffett et al. [15] showed that for the plasma exposed samples the oxygen atomic concentration ranged from 20% up to 50% indicating that an extensive part of the carbon tile was oxidised (via the CO organometallic ligand) while the oxygen concentration drops between 2% and 6% in the bulk material. The presence of oxygen in the bulk of the tile is most probably due from the long exposure to air after retrieval from the vessel.

3.2. Tritium profile of TFTR 4D CFC tile KC11 (baked) and KC18 (unbaked)

The cylinders were cored from the plasma exposed side of the tile for both tiles. The results of the full combustion are shown in Table 2 together with the corresponding results for the baked and unbaked graphite tiles. Comments on the position of the cylinders in terms of location on erosion or co-deposition areas were reported earlier [1]. In Fig. 1, tritium depth profiles for the CFC tile KC18 are compared. For a better comparison with results published previously, the activities are expressed in tritons per unit area of the plasma exposed surface. Naturally, bulk activities are better expressed in tritons per unit volume and are exactly 10 times higher than the values illustrated in the figures as the thickness of each sample is 0.1 cm. For the following comparison between different tiles before and after heat treatment we have always to keep in mind that there is a variation of the surface T concentration from tile to tile and even across one tile.

Comparing all cylinders retrieved from the unbaked tile KC18 we notice that they exhibit almost the same surface activity i.e. $(7.67 \pm 1.9) \times 10^{16}$ T cm^{-2} and an average bulk activity of $(1.27 \pm 1.9) \times 10^{14}$ T cm^{-3}. The surface tritium is related to co-deposited films while the bulk tritium has to be attributed to the diffusion between the interconnected pores of the carbon tile. Indeed, graphites and carbon fibre composites (CFC's) are porous materials. These pores affect the tritium uptake in carbonaceous materials in two different ways. At elevated temperatures, tritium molecules easily enter the

Table 2
Tritium fractions comparison for the TFTR, baked tiles KC11 (CFC) and KC20 (graphite) and the unbaked tiles KC18 (CFC) and KC19 (graphite) tile

Tile /cylinder[a]	Volume of the cylinder (cm^3)	Plasma exposed disk[b] (A_l) (T/cm^2)	Total activity (A_t) (T/cyl)	Average bulk activity (T/cm^3)	Bulk fraction activity[c] (%)
CFC tiles					
Unbaked KC18 cyl_1	1.79	5.48×10^{16}	2.65×10^{16}	5.06×10^{13}	1.1
Unbaked KC18 cyl_2	0.68	8.59×10^{16}	4.13×10^{16}	24.4×10^{13}	0.7
Unbaked KC18 cyl_3	1.73	8.95×10^{16}	4.31×10^{16}	8.52×10^{13}	0.7
Average	–	$(7.67\pm1.9)\times10^{16}$	–	$(1.27\pm1.9)\times10^{14}$	–
Baked KC11 cyl_1	1.73	7.36×10^{14}	5.87×10^{14}	1.45×10^{14}	39.3
Baked KC11 cyl_2	1.38	12.6×10^{14}	6.89×10^{14}	0.32×10^{14}	12.8
Baked KC11 cyl_3	1.61	0.40×10^{14}	1.51×10^{14}	0.78×10^{14}	87.2
Average	–	$(6.79\pm6.1)\times10^{14}$	–	$(0.85\pm1.7)\times10^{14}$	–
Graphite tiles					
Unbaked KC19 cyl_1	1.41	3.91×10^{16}	1.88×10^{16}	6.80×10^{13}	0.5
Unbaked KC19 cyl_2	1.19	5.90×10^{16}	2.83×10^{16}	3.93×10^{13}	0.3
Unbaked KC19 cyl_3	1.25	3.14×10^{16}	1.51×10^{16}	4.05×10^{13}	0.7
Unbaked KC19 cyl_4	1.74	9.17×10^{16}	4.41×10^{16}	4.45×10^{13}	0.7
Unbaked KC19 cyl_5	1.79	3.45×10^{16}	1.66×10^{16}	3.37×10^{13}	0.6
Average	–	$(4.75\pm2.9)\times10^{16}$	–	$(4.52\pm7.7)\times10^{13}$	–
Baked KC20 cyl_1	1.28	11.9×10^{14}	9.29×10^{14}	1.02×10^{14}	39.0
Baked KC20 cyl_2	0.53	1.20×10^{14}	1.26×10^{14}	0.77×10^{14}	54.5
Baked KC20 cyl_3	0.52	1.14×10^{14}	0.97×10^{14}	0.81×10^{14}	07.0
Average	–	$(4.75\pm6.2)\times10^{14}$	–	$(0.87\pm0.7)\times10^{14}$	–

[a] The cylinders had a diameter of 0.78 cm and a length equal to the tile's thickness.

[b] Disks had a diameter 78.0 or 78.5 mm and a thickness of 1 mm.

[c] The bulk fraction activity is calculated using the formula $\{(A_l * \text{disk's surf})/A_t * 100\}$.

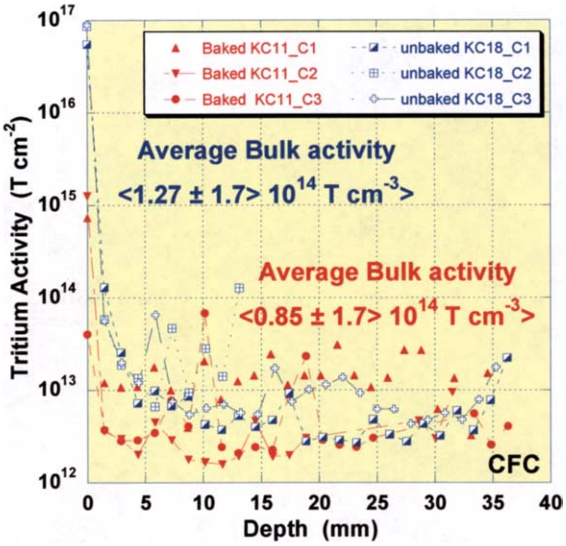

Fig. 1. Tritium depth profile comparison for the CFC tiles KC18 (unbaked) and KC11 (baked) retrieved from the K bay of TFTR.

pores where molecular dissociation provides atoms for transgranular diffusion and trapping (see below). At lower temperatures, tritium ions and neutrals from the plasma adhere to the external carbon surface. Some of these atoms are channeled into the pores where they diffuse into the carbon materials along the pore surfaces.

After the bake out of the similar CFC tile KC11 the surface tritium activity decreases by about 2 orders of magnitude to $(6.79\pm6.1)\times10^{14}$ T cm^{-2} while the bulk tritium activity is hardly affected by such a thermal treatment $(0.85\pm1.7)\times10^{14}$ T cm^{-3}.

Another remarkable point is that the bulk activity of all cylinders sharply decreases after the first sample (1 mm below the plasma exposed surface) and seems to reach an almost constant value at about 8.1 10^{13} T cm^{-2}. For both tiles, the bulk concentrations of tritium appear to be fairly homogeneous, irrespective of large variations in tritium concentrations on the plasma exposed surface (see Table 2 and Fig. 1). Therefore, as the bulk tritium concentration cannot be reduced in situ by heating the tile at 500 °C and as heating the whole tiles at higher temperatures is not possible (not to mention the collateral damage that will affect the metallic surfaces in the vacuum vessel), the only successful tritium removal can only be performed after the removal of the carbon tiles themselves from the vacuum vessel. However treating the plasma exposed surface of the tiles (co-deposits) in situ, will reduce significantly the tritium content of the tiles and detritiation techniques exploiting this have already been successfully tested in laboratory scale. Indeed, transient heating by laser scans of 2D and 4D CFC's have produced similar temperature excursions when a similar type of the tile surface was treated (co-deposited, or eroded zone) [16].

3.3. Tritium profile of TFTR graphite tile KC20 (baked) and KC19 (unbaked)

What was observed for the CFC tiles is also valid for the graphite ones. The surface tritium concentration is 2 orders of magnitude lower after the bake out while the bulk tritium concentration remains almost unchanged (see Table 2). The fraction of tritium in the bulk the (excluding the plasma facing disk) after the bake out, ranges from 7% to about 54% of the total in the core sample and depends on the position where the analysed cylinder was removed from the tile (erosion or co-deposited area) and on its length.

When comparing graphite and CFC tiles the main difference is the tritium amount trapped in the bulk of the graphite tiles. Tritium trapped in the bulk of graphite is more homogeneously distributed than in the bulk of CFC. Moreover, the tritium concentration in graphite seems to be slightly lower than the corresponding in CFC. Nevertheless, this difference is not large enough to be attributed to the different structure of these two materials. In addition, migration via the open porosity of the material or transgranular diffusion is the main mechanism which drives hydrogen isotopes into the bulk of both types of tiles. We may then conclude that the structure of the tile (graphite or CFC) hardly affects the migration of tritium in the bulk of the tile (Fig. 2).

3.4. Depth profiles obtained by AMS

The experimental set-up and the method to obtain a uniform erosion of the sample inside a commercial sputtering ion source are described in previous papers [17].

As illustrated in Fig. 3, measured tritium profiles for various samples retrieved from KC11 are very similar to the deuterium profiles. As the D and T atoms have different energies (deuterium particles have a thermal energy less than 1 keV, while the tritium particles are generated by a DD nuclear reaction generating tritons with an average energy of 1 MeV), these profiles suggest that D and T belong to the same co-deposited layer. The mean range of 1 MeV tritium in graphite at normal incidence is about 8 μm, while the mean range of 100 eV deuterium is less than 0.01 μm. The range of deuterium and tritium in Fig. 3 is higher than it can be expected from their initial energy. This may be explained by the diffusion beyond the range of implantation mainly due to the high porosity of these carbon tiles and favoured by the elevated temperatures and the surface roughness of these materials. Measured tritium profiles in thermally treated samples [18] have demonstrated a decrease of the maximum concentration and a slight broadening of the range distribution due to diffusion already at temperatures of about 300 °C. The influence of co-deposition in Fig. 3 can be neglected, because after

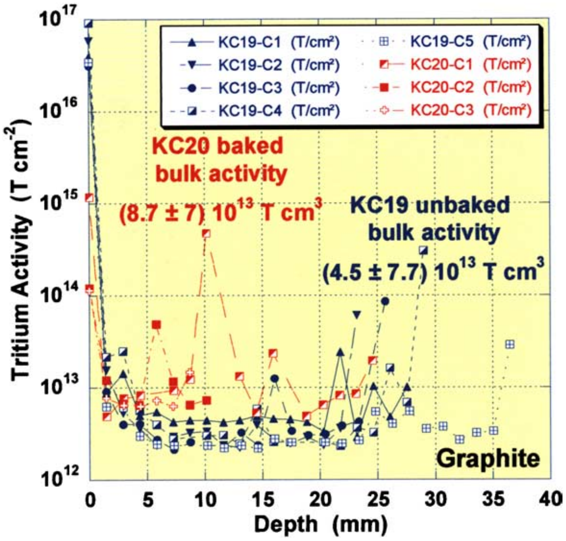

Fig. 2. Tritium depth profile comparison for the graphite tiles KC19 (unbaked) and KC20 (baked) retrieved from the K bay of TFTR.

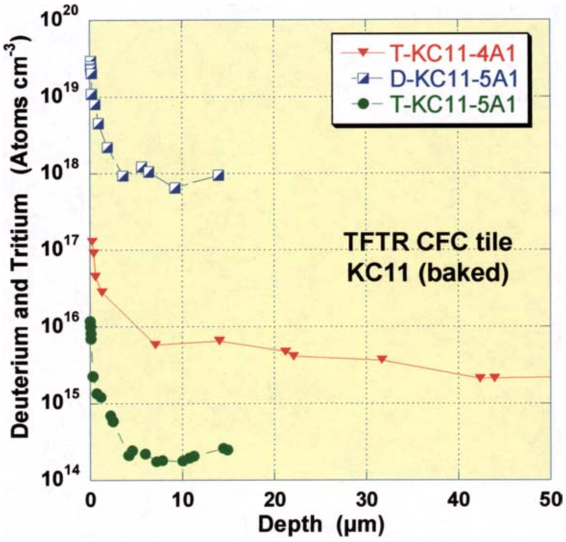

Fig. 3. Deuterium and tritium depth profiles obtained by AMS for the plasma exposed side of the CFC tile KC11 (baked) retrieved from TFTR.

thermal treatment no shift of the deuterium peak into the sample is observed. Finally, it also worth mentioning that lithium was used for wall conditioning in TFTR and it was detected in the bulk of the samples by AMS together with boron.

4. Conclusions

Tritium depth profiles of tiles retrieved from TFTR have been obtained by the coring/full combustion technique. For approximately identical surface activity, the tritium distribution into the bulk is quite similar in concentration and profile. The most probable mechanism for tritium migration to the bulk involves tritium diffusion via the open porosity of the carbon material.

Additionally, the coring/full combustion technique has shown that only the surface tritium implanted and/or co-deposited (few tens of μm) is efficiently released by baking the tile under air even at 500 °C while the bulk tritium concentration is almost unaffected. Therefore, other techniques, such as laser heating [19], are more efficient for surface detritiation and more advantageous as they do not require tile removal and manipulation.

In conclusion, if the multi-directional CFC and graphite tiles allow a similar amount of tritium to be trapped by the bulk of the tiles the tritium traps presents in both materials must be of the same physico-chemical nature (defects, impurities…). But what is the chemical form of such traps is not yet known.

Knowing in which form tritium is trapped in the bulk of the sample will be very useful as preventing the presence of such an impurity will reduce substantially the tritium amount trapped by the bulk of the material. Investigations in that direction are still on going in TLK.

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