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Thermal release rate of tritium trapped in bulk and plasma exposed surfaces of carbon specimens obtained from JET divertor

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Abstract

Tritium co-deposition with carbon in the colder remote areas of the JET vessel immobilises a substantial amount of the fuel and increases the tritium inventory of the machine. A well defined physical or chemical description of these co-deposits is still not available. Therefore they are reported in the literature as a carbonaceous amorphous C:H layer, and unfortunately sometimes as a 'diamond-like film' referring to their sp^3 hybridisation. From the present study it appears that the gas–solid reactions taking place during the thermal treatment of carbon samples involves various tritiated hydrocarbon species having one or two carbon atoms in their structure like methyl ($-CH_3$) or ethyl ($-CH_2CH_3$), having practically all bonds saturated with heavier hydrogen isotopes. The thermal response of the samples was also investigated by laser irradiation. During the laser scans the co-deposited layers reach high temperatures, sometimes exceeding 2300 °C, releasing all co-deposited tritium to the gas phase.

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1. Introduction

Tritium co-deposition with carbon in the colder remote areas of the JET vessel immobilises a substantial amount of the fuel and increases the tritium inventory of the machine. A well defined physical or chemical description of these co-deposits is still not available, therefore, they are reported in the literature as a carbonaceous amorphous C:H layer, and unfortunately sometimes as a 'diamond-like film' referring to their sp^3 hybridisation.

In a former experimental investigation an elemental analysis of such co-deposited layers found on the JET divertor tiles, gave a D/C ratio of ~0.75 [1]. Such a high ratio could only be explained if the layers are composed of short chains of aliphatic carbons almost completely saturated with heavy hydrogen isotopes, i.e. carbon chains having sp^3 hybridisation and also having practically all bonds saturated with heavier hydrogen isotopes, such as $C_2Q_xH_y$ ($x + y = 6$; $Q = D, T$). In such compounds hydrogen is strongly bounded to the carbon. During thermal treatment, alkyl fragments (such as $-CH_3$) are believed to be important intermediates

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of such co-deposited layers and play an important role in the subsequent reactions. On the other hand, the presence of oxygen also has a great influence on the thermally induced reactions.

As the phenomena taking place at the interface between the co-deposit layer and the gas phase play an important role as far as the tritium release is concerned, these gas–solid interactions need to be explored with the intention of discovering which species are involved during such thermal treatment. For that purpose, several carbon specimens retrieved from the JET divertor tiles were heated and the released gases analysed by spectrometry.

2. Experimental details

Thermal release studies of tritium from specimens from the plasma exposed side of tiles used in JET have already shown that moist air temperatures above 400 °C are required for the liberation of most of the tritium [2]. A new set of thermal experiment have been conducted under a helium atmosphere, heating the samples to as high a temperature as possible to liberate the maximum amount of tritium.

The experimental set-up basically comprises a controlled purge gas supply, a high temperature stainless steel chamber containing the sample, a reduction bed containing granulated zinc at approximately 390 °C and a calibrated proportional counter for the detection of tritium. The sample chamber is externally heated by a controllable tubular furnace. The zinc bed converts tritiated water to molecular gaseous tritium (HT, DT, and traces of T_2). Except for the purge gas supply and control, the whole system is contained in a glove box. A quadrupole mass spectrometer outside the glove box was also used for the analysis of the released gaseous species.

The purge gas used was helium containing 0.1 vol.% hydrogen. In this series of experiments the addition of hydrogen follows the conclusions of a previous investigation which demonstrated that while the tritium release is not affected by the pressure or the flow rate of the inert gas, the addition of hydrogen reduces the tritium release maxima by up to 100 °C [3]. Typical flow rate was $10\ \mathrm{cm}^3\ \mathrm{min}^{-1}$. In normal operation, the sample temperature is initially increased linearly with time up to a maximum temperature of 1000 °C.

The purge gas flow rates, the sample temperatures and the tritium activity in the purge gas, are continuously measured and recorded. The total released activity is calculated by integrating the release rate over time.

Applying mass spectrometry to the thermal desorption process allows accurate measurement to very low partial pressure down to 10^{-11} Torr. This allows the monitoring of a large spectrum of gas compositions released during the thermal treatment of the sample. Unfortunately, it was not possible to bypass the Zn-bed, and therefore it is not possible to measure the amount of water released by the sample because it was reduced by the Zn-bed to molecular hydrogen (H_2, or HT).

3. Thermal tritium release from surface samples from the outer divertor tile 1BN7

In order to determine the gaseous species released during the thermal treatment of the sample, three discs retrieved from the JET divertor tile 1BN7 (Cyl 16, 17 and 18) were heated up to 1000 °C under He containing 0.1% hydrogen. The heating ramp rate was $5\ \mathrm{K\ min}^{-1}$ and the He flow rate $10\ \mathrm{cm}^3\ \mathrm{min}^{-1}$. The location of the cylinders on the surface of the tile is illustrated in Fig. 1, while their tritium depth profile was reported elsewhere [4].

Among the possible species recorded by the 12 available channels of the gas analyser, only masses 2, 3, 4, 16, 17, 18 and 20 contributed to the total measured pressure of 2.1×10^{-7} Torr. As the Zn-bed reduces the water released by the sample to molecular hydrogen, the compounds corresponding to masses 16, 17, 18 and 20 have to be attributed only to methane and its isotopic combinations. Since masses 2 and 4 are mainly associated with the purge gas (H_2/He), only masses 16, 17 and 18 related to methanated species such as CH_4, CH_3D and CH_3T, respectively, are contributing to the total pressure. Whereas the masses 17 and 18 are generated after the substitution of one hydrogen atom by a deuterium or tritium atom producing respectively the CH_3D and CH_3T isotopic species, the replacement of more than one hydrogen (multi-substitution) is a less probable mechanism as it requires a multi-step reaction process, taking place on the same molecule, which is statistically less favourable and even if possible the statistical concentration of such species is limited and can hardly be distinguished from the background. Nevertheless, a very small amount of the mass 20 corresponding to a multi-substituted methane such as CH_2T_2, CHD_2T, or even CD_4 (all hydrogen atoms are substituted by deuterium) was detected. Of course, the more

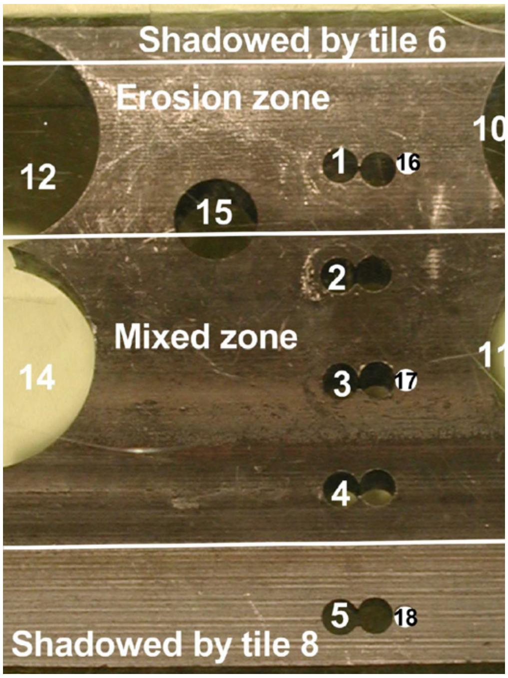

Fig. 1. The various zones observed for 1BN7 outer divertor tile of JET. The positions of the samples treated by thermal desorption (16, 17 and 18) are also illustrated.

hydrogen substituted the less probable is the formation of such species. However, the total concentration of all these compounds contribute to the detected mass 20 (Fig. 2).

Fig. 2 shows a typical thermo-desorption spectrum for Cyl 16. Thermo-desorption spectra for cylinders 17 and 18 exhibit similar behaviour.

A typical reaction could be the deuteration of methane. Such a mono-substitution mechanism is also supported by the thermogram presented on Fig. 2, where the correlation between the behaviour of species corresponding to masses 3 (HD) and 17 (CH_3D) is illustrated. It is worth mentioning that in this thermogram the sum of the partial pressures of the two compounds corresponding to masses 3 and 17 remains constant during the whole thermal process indicating the presence of a common reaction mechanism.

Comparing the thermo-desorption spectra (Fig. 3) of the three samples (C16, C17 and C18) retrieved from the outer divertor tile 1BN7, we may make the following remarks.

First, there are two orders of magnitude difference between the tritium activities measured in sample C16 and the samples C17 and C18. Indeed, contrary to what was expected, C18 shows higher tritium content than C16. This is quite surprising as C18 is located in a shadowed area of the 1BN7 tile where co-deposition was not observed (see Fig. 1).

Second, the release profile of the tritium trapped in C18 is quite different than the profile exhibited by the C16 and C17 samples, located respectively in eroded and mixed areas of the tile. This can be related to a different kind of tritiated species trapped by C18 compared to C16 and C17. Indeed, we may discern a slight evolution of the peak maxima corresponding to the tritium released activity. While for 1BN7 C16 and C17 there is only a broad 'single' peak at approximately 870 °C and 800 °C, respec-

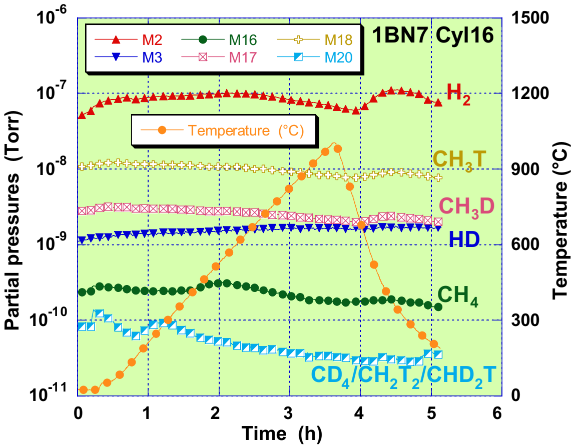

Fig. 2. Compounds detected by mass spectrometry after heating the 1BN7-Cyl-16 (A_1) sample under He containing 0.1% H_2.

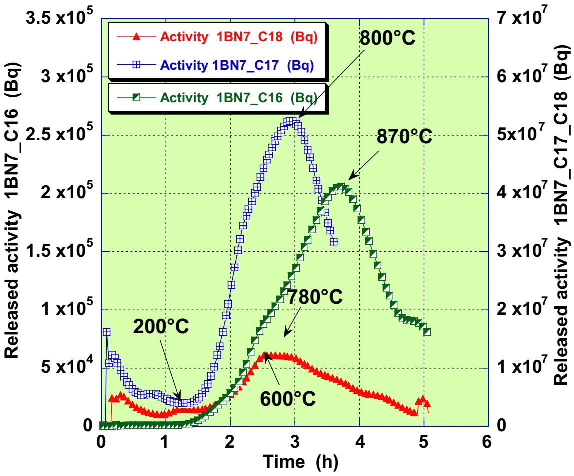

Fig. 3. Tritium released activities for plasma exposed samples 16, 17 and 18, retrieved from 1BN7 JET divertor tile.

tively, for the sample 1BN7 C18 the corresponding peak is very broad starting at 600 °C and extended to ~780 °C. If there is a mislabelling between samples, then the interpretation of Fig. 3 could be fully understandable and in line with the results obtained earlier by full combustion [5].

After heat treatment to 1000 °C the subsequent combustion of these samples does not release any more tritium. Two types of tritium were identified, one for the low temperature tritium release (~400 °C) and corresponding to the breaking of T—C bonds when the carbon has sp^3 hybridisation and the second type (above 800 °C) to the breaking of T—C bonds but with the carbon having either sp^2 or sp hybridisation. A more detailed analysis will be published elsewhere [6].

Presently it is not possible to identify the chemical reactions taking place during the thermal treatment, as it is impossible to bypass the Zn-bed which reduces all water to molecular hydrogen. To overcome this, a modification of the experimental set-up is planned for the next series of experiments.

4. Thermal response of inner and outer JET divertor tiles to laser treatment

Thermal desorption experiments are based on the assumption that all or most of the gas leaving the surface of the sample will appear in the gas phase and will not diffuse into the bulk of the sample. We may assume that this is the case here as the co-deposited layers are very poorly bonded to the substrate (tile). This assumption is also consistent with the big difference in thermal conductivity between the co-deposit layer and the substrate, probably related to the difference in chemical composition of these two materials. The co-deposited layer is characterised mainly by C—H bonds whereas the substrate is mainly organised by C—C bonds. Such a difference in structure leads to a poor interconnection between the two compounds.

A series of laser experiments at the Princeton Plasma Physics Laboratory (PPPL) on material similar to the previous JET samples support this conclusion.

The experimental set-up was fully reported in [7]. A 325 W continuous wave Nd laser beam was used, focused inside a chamber on a tile sample. The laser spot can be scanned over an area of 75 × 75 mm with a velocity of up to $2\ \mathrm{m\,s^{-1}}$.

A total of seven samples from JET were irradiated by the laser. These were 2 cm diameter cylinders cut from carbon fibre composite divertor tiles (type MKIIA) and a graphite poloidal limiter tile. The samples were from the plasma facing side of the inner divertor vertical tile (IN3-cylinder 16), the bottom edge of this tile at the entrance to the louvres (IN3-15, an area known for its very high tritium concentration); the inner base divertor tile 1BN4, cylinders 8, 9 and 10; the outboard base divertor tile 1BN7 cylinder 15 and the poloidal limiter tile 4B cylinder 6 (PL4B7top-6). The plasma facing surface was typically divided into four zones that were irradiated separately at different laser power and scan speeds. The most conspicuous feature of response of the JET samples to laser irradiation was the much higher surface temperature increase for co-deposits compared to the bare tile material, as was the case for the TFTR samples. Indeed, often the peak temperature of JET samples exceeded 2300 °C, the upper limit of the pyrometer. The lowest measurable temperature for the pyrometer is 500 °C.

Fig. 4 compares the thermal response for three JET samples. The JET sample 1BN4-8-4L (1) reaches a peak temperature of 1434 °C and remains above 500 °C for 5.3 ms. This sample is from an erosion area on the base divertor tile 4 on JET, while sample PL4B7-Top (2), is from a deposition area on the JET poloidal limiter. For the latter,

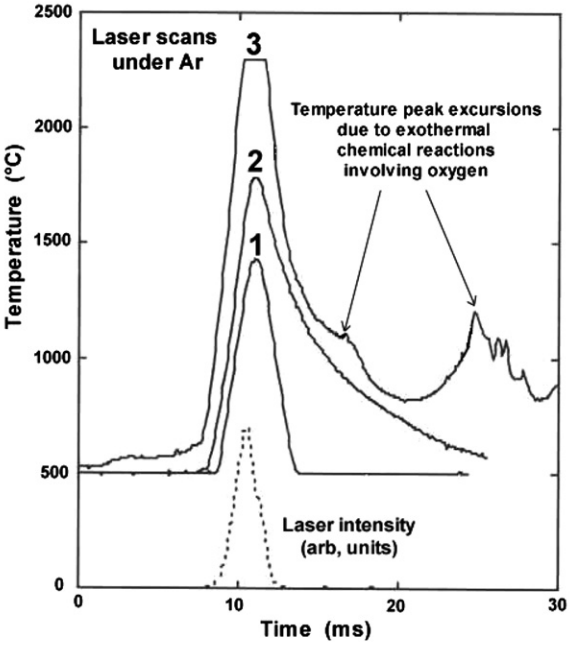

Fig. 4. Thermal response of three plasma exposed discs during laser heating: (1) 1BN4-8-4L, (2) PL4B7 top and (3) IN3-15-2L.

the temperature response peak reaches 1790 °C and shows a longer cool down time or 'tail' in the time history due to lower conductivity or poor thermal contact between the deposit and underlying tile.

JET sample IN3-15-2L (3) had a particularly striking temperature response. This sample is from the lower edge of divertor tile 3 (adjacent to the louvers) where the co-deposit was found to have the heaviest tritium concentration of any analysed JET or even TFTR tile.

Remarkably, the temperature increases to above 2300 °C and then rises again after the laser pulse has passed (before the next pass of the laser spot). This 'ragged' character in the temperature time history was evident on several samples with thick co-deposits, even though the ambient atmosphere is argon. These temperature excursion peaks were attributed to exothermal chemical reactions involving the oxygen present in the tiles. Indeed, X-ray photoelectron spectroscopy (XPS) analysis performed on many TFTR tiles has shown [8] that oxygen content in the plasma facing surfaces can reach 50 at.% while oxygen content for bulk samples ranges from 2 to 6 at.%.

The striking difference characterising these samples is the presence or absence of a co-deposited layer, which could also explain the difference in the maximum peak temperature observed for these three samples. Indeed, for a bare tile the heat deposited by the laser beam is easily conducted away through the CFC layers (sample 1 BN4-8-4L) and the peak temperature does not exceed 1500 °C. In the presence of a thin co-deposit, the energy is less easily removed, either because the C:H polymer film is a good isolator or the thermal contact with the substrate is poor, or both. One possibility does not necessary exclude the other, and consequently the temperature rises to ~1800 °C.

Finally, in the case of a heavy co-deposition (there is a thick film in case of 1IN3-15-2L) almost all the energy deposited by the laser beam 'remains' in a very restricted volume and the temperature exceeds 2300 °C for a 'long time'.

The second peak (~1200 °C) observed about 15 ms after the first (for 1IN3-15-2L), corresponds to a sudden increase of energy from a process such as an exothermic chemical reaction. A second laser pass on a treated surface does not exhibit the same 'ragged' peak because during the first shot the reaction has consumed the reactants (H_2 or O_2).

Finally the small peak observed for IN3-15-2L slightly above 500 °C, before the peak maximum, can be explained by the poor thermal contact existing between the co-deposited layer and the substrate. Indeed, the co-deposited layer is not well thermally connected to the substrate and the surface temperature then is very sensitive to any laser flux from the fringes of the laser spot.

After 4 laser scans at full power (37.8 A), 45% of the total amount of tritium contained into the JET 1IN3-Cyl 16 was released. A fifth scan did not release more tritium. However, after baking the sample at about 500 °C another 55% tritium was released. The latter amount of released tritium is not the part diffused into the bulk after the 5 laser scans, but is the tritium incorporated in the bulk of the sample during the Deuterium–Tritium (DT) operation of JET. Indeed, in previous investigation combustion measures have already shown that this tile (1IN3) contains up to 67% of the total tritium in the bulk [4].

The latter experiment supports the assumption that after thermal treatment tritium mainly leaves the co-deposited layer of the sample for the gas phase and does not migrate into the material.

5. Conclusions

The present study shows that the gas–solid reactions taking place during the thermal treatment of a carbon sample is quite complicated, involving various tritiated species and other gaseous species such as small chain hydrocarbons.

At present, it is not possible to identify the chemical processes taking place. But as the laser experiment shows, oxygen is also taking part in the total reaction scheme making the chemistry very complicated as many reactants can participate in the total process (carbon/hydrogen/oxygen).

Moreover, the very poor bonding between the co-deposited layer and the substrate (tile) does not allow tritium migration from the co-deposited layer into the bulk of the carbon tile.

The thermal response of the samples can be adequately explained in terms of co-deposition. In the absence of any co-deposition the good thermal conductivity of the bare tile conducts the heat deposited by the laser pulses into the bulk and the maximum peak temperature did not exceed 1500 °C. When a co-deposit is present either the poor thermal conductivity of the layer or its poor thermal contact with the substrate does not allow efficient conduction of the heat deposited by the laser beam and consequently the maximum peak temperature can attain higher values depending the thickness of the co-deposited layer; the thicker the layer, the higher the temperature.

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