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L. Avotina et al.

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Spectrometric analysis of inner divertor materials of JET carbon and ITER-like walls

Liga Avotina^a, Davis Conka^a, Aigars Vitins^{a,b}, Elina Pajuste^a, Larisa Baumanė^{a,c}, Andris Sutka^d, Natalija Skute^e, , Gunta Kizane^a and JET Contributors^{f*}

^aUniversity of Latvia, Riga, Latvia

^bUniversity of Latvia, Institute of Solid State Physics, Riga, Latvia

^cLatvian Institute of Organic Synthesis, Riga, Latvia

^dRiga Technical University, Riga, Latvia

^eDaugavpils University, Daugavpils, Latvia

^fEUROfusion Consortium, JET, Culham Science Centre, Abingdon, OX14 3DB, UK

* See the author list of X. Litaudon et al., Nucl. Fusion 57 (2017) 102001

One of main reasons of the Joint European torus (JET) transformation from the carbon (JET-C) to ITER-like (JET-ILW) wall was high tritium retention of carbon. In order to compare the tritium retention in plasma facing materials in two campaigns, JET C-wall, 2008-2009 and JET-ILW, 2011-2012, corresponding samples were cut out of analogous positions of the plasma-facing side of vertical tiles No. 3.

Temperature-programmed tritium desorption spectrometry in He + 0.1% H₂ gas flow showed that JET-C sample without a tungsten coating had by a factor of >20 higher surface concentration of tritium than JET-ILW tungsten-coated sample: 4.9×10^{13} and $1.7\text{-}2.2 \times 10^{12}$ T atoms/cm², respectively.

Installation of metallic plasma facing wall in the JET was a unique possibility to collect from the vacuum vessel the first wall erosion products (EP) – dust and flakes. Selected EP were investigated by means of energy dispersion X-ray (EDX), electron spin resonance (ESR), infrared and Raman spectrometry. EDX analysis shows presence of metallic impurities and carbon as a main component. Investigations with ESR spectrometry allows to estimate presence of two main paramagnetic centres - $g=2.002$ and $g=2.12$. Infrared spectra show presence of inorganic oxides. The obtained results supplement the information about composition of the EP and tritium release from fusion devices materials.

Keywords: *JET, divertor, tritium, temperature programmed tritium desorption, spectrometry.*

1. Introduction

Reason to transform the JET from the carbon (JET-C) to ITER-like (JET-ILW) wall was high tritium retention in carbon plasma facing materials [1]. One of the objectives of the present study was to compare the tritium retention and release in analogous positions of the lower parts of vertical tiles No. 3 of both campaigns: 2IWG3A without a tungsten coating (JET-C) and tungsten-coated 14ING3B (JET-ILW). Installation of metallic plasma facing wall (ITER-like wall – ILW) [2] and replacing the previous carbon wall (JET-C) in the Joint European torus (JET) was a unique possibility to collect from the tokamak vacuum vessel the first wall erosion products (EP) – dust and flakes. Analyses of EP from JET [3, 4] and films formed due erosion in T-10 [5] tokamak provide insights into composition and properties of the EP. Carbon based materials are considered as plasma facing materials in stellarators.

A comparison between tritium release and chemical composition of plasma exposed materials will add the knowledge about materials behaviour in fusion devices.

2. Experimental

2.1 Temperature programmed tritium desorption spectrometry

In order to compare ways of tritium retention under JET-C and JET-ILW conditions, inner divertor vertical tiles have been removed for analysis after JET operation period 2008-2009, 6937 plasma pulses [6] with carbon as a plasma facing material and after ILW operations in 2011-2012, ~3500 plasma pulses [7]. As pure deuterium (D) plasmas were used in JET in the years 2007-2012 [8], tritium (T) measured in this study was generated by DD fusion reactions and that remaining in the vacuum vessel from previous DT campaigns. Thus tritium was a minor component of the total hydrogen fuel inventory in the vessel.

Cylinders were core-drilled out of analogous position 3/2 in the lower parts of vertical tiles No. 3 [9, 10] of both campaigns: 2IWG3A without a tungsten coating (JET-C) and tungsten-coated 14ING3B (JET-ILW). In order to analyse tritium release on annealing, ~1 mm thick slices were cut out of the plasma facing side. Thermal treatment was performed in He + 0.1% H₂ gas flow 14-15 L/h with a heating rate of 5 K/min [11].

In order to determine tritium content, the full combustion (FC) technique followed by liquid

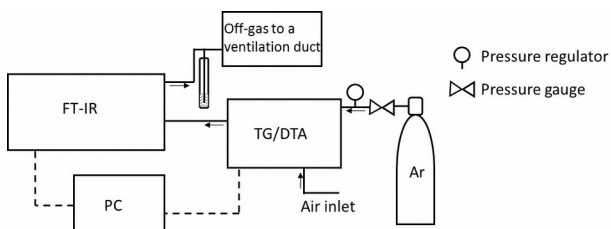
scintillation method (LSM) was applied, the process was performed as described in [12].

2.2 Spectrometric investigations

First wall erosion products (EP) – dust and flakes, were collected from inner divertor area in the year 2010 before installation of the JET ILW. EP were investigated by means of energy dispersion X-ray (EDX), electron spin resonance, infrared and Raman spectrometry. Scanning electron microscope *Hitachi S-4800* and EDX detector *Quantax Esprit 1.9* were used in this study. The ESR spectra were recorded by a Bruker BioSpin X-band ESR spectrometer at room temperature (microwave frequency: 9.8 GHz, microwave power: 0.2 mW, field sweep: 20 and 100 mT, modulation amplitude: 0.5 mT). Raman spectra were recorded with Renishaw InVia spectrometer Ar+ ion laser 514 nm, scan diameter 2 μm , laser power <5 mW. Chemical bonds were studied with a Fourier transform infrared spectrometer equipped with an attenuated total reflection (FTIR-ATR) accessory. Parameters for the spectra recording: 400–4000 cm^{-1} , $\pm 2 \text{ cm}^{-1}$, vacuum 2.95 hPa. FTIR spectra in a gas phase were recorded in a heated diluted gas flow. For a first time divertor materials are studied with a coupled system, where the FTIR gas phase cell is coupled with thermogravimeter-differential thermal analysis device TG/DTA Exstar 6300. The crucible was placed on a horizontal balance beam system, where an empty second crucible is used as a reference, in a furnace, that is heated with a programmed rate of temperature increase. Heating performed in gas flow, where atmospheric air was diluted with approximately 50% Ar, to decrease oxidation intensity. Heating regime: 90 K/min, 300–1270 K, hold time 5 min at the maximum temperature of 1270 K, inertial cooling afterwards. gaseous products from EP oxidation were guided through gas cell and FTIR spectra were recorded. In order to collect tritium containing compounds, the gas flow was directed through a Drechsel type gas washing bottle filled with deionised water. A scheme of thermal analysis system is in Fig. 1.

Fig. 1. Scheme of a thermal analysis system coupled with an infrared spectrometer..

3. Results and discussion



3.1 Temperature programmed tritium desorption spectrometry

Results of temperature programmed tritium desorption spectrometry from ILW and C-wall plasma facing surface samples are shown in Figs. 2 and 3 respectively.

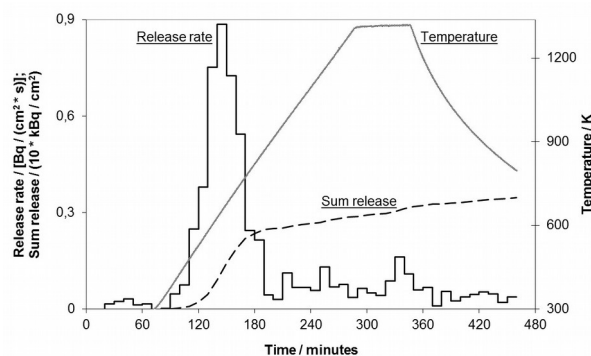


Fig. 2. Tritium desorption from a sample (mass 0.04385 g, plasma-facing surface area 32.2 mm^2) cut out of the tungsten-coated plasma facing surface of tile 14ING3B (2011-2012) from the JET vacuum vessel. Initial background of the tritium detector: 0.965 cps. The maximum temperature of the thermal desorption: 1319 K. The final value of the tritium sum release: 3.5 kBq/cm^2 (2.0×10^{12} T atoms/ cm^2).

Comparison with a blank experiment suggests that the tritium release from a sample cut out of tungsten-coated ILW inner divertor vertical tile No. 3 occurred in the temperature range of 420–870 K with a maximum release rate at 670 K (Fig. 2). The small tritium release in the time range of 190–460 min in Fig. 2 can be attributed to a slightly increased final background of 1.00–1.16 cps with an average value of 1.040 cps similarly to the blank experiment. By the end of the maximum at 670 K, 2.5 kBq/cm^2 (1.4×10^{12} T atoms/ cm^2) of tritium were released, and the final value of the tritium sum release was 3.5 kBq/cm^2 (2.0×10^{12} T atoms/ cm^2), (Fig. 2). Prior the analysis the plasma facing surface was measured and the tritium sum release was recalculated as the tritium surface concentration. Surface concentration to the JET shutdown in July 2012 [7] gives 2.9 and 4.0 kBq/cm^2 (1.6 and 2.2×10^{12} T atoms/ cm^2) respectively.

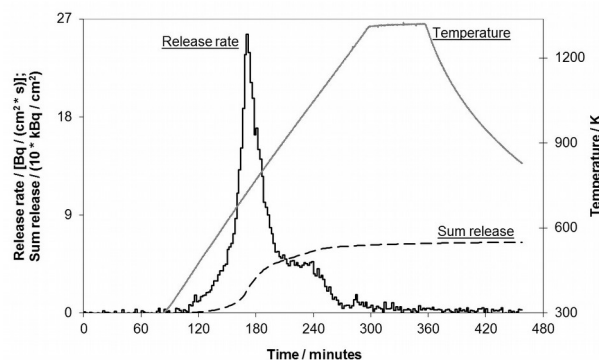


Fig. 3. Tritium desorption from a sample (mass 0.02433 g, plasma-facing surface area 14.3 mm^2) cut out of the plasma facing surface of tile 2IWG3A (2008-2009) without a tungsten coating from the JET vacuum vessel. Initial background of the tritium detector: 0.970 cps. The maximum temperature of the thermal desorption: 1325 K. The final value of the tritium sum release: 65 kBq/cm^2 (3.7×10^{13} T atoms/ cm^2).

As it is shown in Fig. 3, a sample cut out of an analogous position of JET-C plasma-facing wall without a tungsten coating had by a factor of >10 higher tritium release than the ILW tungsten-coated sample. The tritium release from

the JET-C sample occurred in the temperature range of 420-1180 K (Fig. 3). The curve of the tritium release rate of the JET-C sample has a distinct maximum in a range of 420-870 K with a maximum release rate at 730 K and a 'shoulder' at 870-1180 K. The maximum and the 'shoulder' contributed 71% and 23% respectively in the final value of 65 kBq/cm² (3.7×10^{13} T atoms/cm²) of the tritium sum release. Recalculation of the value of 65 kBq/cm² (3.7×10^{13} T atoms/cm²) of the tritium surface concentration to the JET shutdown on 23rd October 2009 [13] gives 88 kBq/cm² (4.9×10^{13} T atoms/cm²). The result obtained that JET-C sample 2b-1 of 2IWG3A without a tungsten coating at the shutdown in October 2009 had by a factor of >20 higher surface concentration of tritium than JET-ILW tungsten-coated sample 2b-1 of 14ING3B at the shutdown in 2012. While tritium content in EP is two orders of magnitude higher than in JET-ILW tungsten coated samples. 88 and 3-4 kBq/cm² (4.9×10^{13} and $1.7-2.2 \times 10^{12}$ T atoms/cm²) respectively, is in line with the observation reported in [1] that the long-term fuel retention in JET-ILW is by a factor of 10-20 lower than that in JET-C.

Tritium desorption from the JET-ILW divertor sample started at about the same temperature as from the JET C-wall sample, but the maximum release rate for the C-wall sample was at a higher temperature of 730 K than that of 670 K for the ILW sample, and a large fraction of tritium from the C-wall sample was released at higher temperatures than that from the ILW sample. For the JET C-wall materials the tritium release temperature is higher, the maximal release rate is at 460 C.

3.2 Spectrometric analysis

Erosion products from the JET-C wall were analysed by means of X-ray energy dispersion (EDX), infrared, Raman and electron spin resonance spectrometry. EDX results show presence of metallic (Be, W, Ni, Fe) and non-metallic impurities (O, N), and carbon as the main component. Selected Raman spectra of EP are in Fig.4. In Raman spectra of EP two main signals occur – at 1350 and 1580 cm⁻¹. Presence of both signals in the Raman spectrum show, that carbon in the EP is in form of nanocrystalline graphite [14].

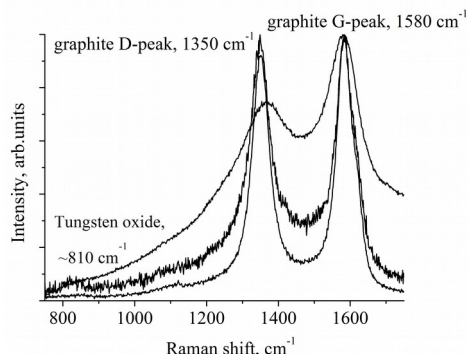


Fig. 4. Examples of Raman spectra of erosion products from the JET C-wall inner divertor.

In some spectra of EP an increased luminescence background occur, that could be due the presence

hydrogenated, amorphous carbon [15]. A signal around 805-810 cm⁻¹ observed in several spectra approves the presence of tungsten oxide [16, 17]. The FTIR spectra of EP and plasma non-exposed carbon fibre composite (CFC) are in Fig. 5. In the range 1000-4000 cm⁻¹, similar vibrations occur. The spectral distortions in the range 1900-2300 cm⁻¹ are related to similar refraction indices of diamond crystal and the CFC, such distortions are characteristic in case of carbon allotropes [18]. Main differences occur in the range 400-900 cm⁻¹.

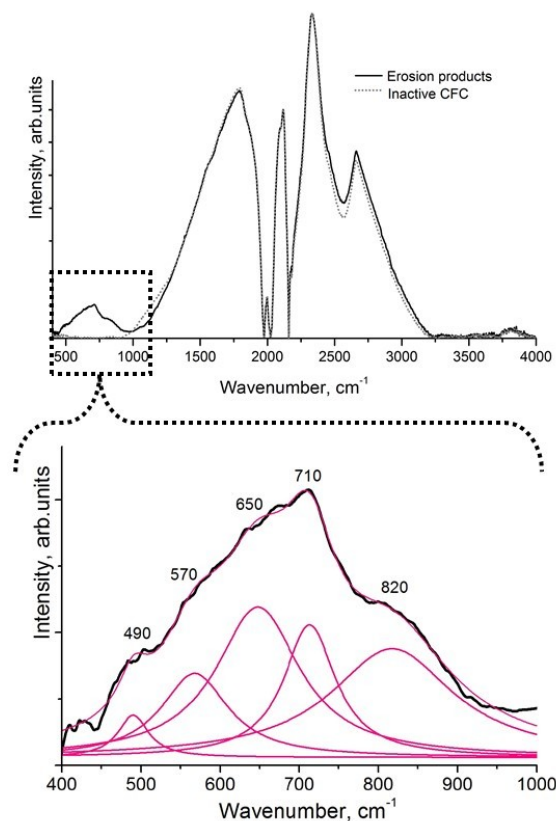


Fig. 5. FTIR spectra of EP and plasma non-exposed carbon fibre composite (CFC).

Signals in this range could be due to the metal-oxygen bonds, such as Fe-O [19] and W-O [20, 21]. To oxidize carbon to volatile compounds, EP were heated in the presence of oxygen.

The released gaseous products were analysed with FTIR. The scheme of the system used is in Fig. 1. Heating in air presence was performed to follow the oxidation process of the carbon containing components of EP. During heating mass of the sample decreases. The mass decrease rate (black line in the Fig.7, left side) starts to increase above 100 °C, that could be due desorption of moisture. The chemical bonds of released gaseous products are registered with FTIR – the peaks in FTIR spectra at 670 and 2300 cm⁻¹ (Fig.6 right side) are due to release of CO₂, minor peaks around 1400 and above 3000 cm⁻¹ are from -OH bonds [22]. Intensities of OD bonds are below the detection limit. The overall mass loss during the heating is 70%. Therefore, oxidisable carbon-based compounds can be estimated to be approximately 70 wt% of the sample,

though the mass gain by oxygen uptake of the sample, by forming metallic oxides, can affect the overall mass change.

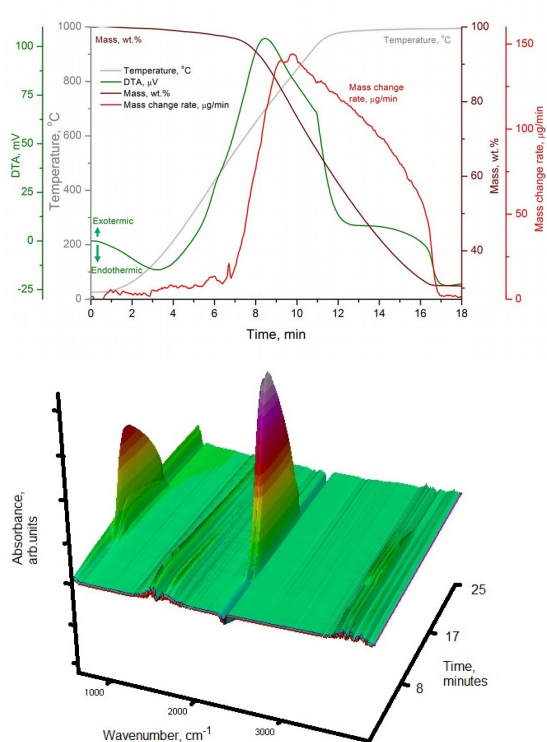


Fig. 6. Thermal oxidation of JET C-wall divertor erosion products, 2.58 mg – mass decrease (upper image), FTIR spectra of released gaseous products (down).

Electron spin resonance (ESR) spectrometry gives additional information about the free radicals in the erosion products. The ESR spectra of plasma non-exposed carbon fibre composite material and JET erosion products are given in Fig.7a, c.

Two main signals can be distinguished. A signal with a g -factor 2.002 can be related to paramagnetic centres in the aromatic units and delocalized π electrons from multi-ring aromatic structures [23, 24]. ESR spectra for several long-chain hydrocarbons as well as fullerene C_{60} were measured (Fig.7b) for estimating their presence in erosion products. Presence of nanotubes and nanoglobules in the dust and flakes from tokamak devices has been reported [25, 26]. A signal with $g=2.002$, occurring in the spectra of erosion products could be a superposition of graphite-like units, multi-ring aromatic structures, fullerene-like compounds as well as hydrocarbons. A second signal with a g -factor 2.12 is not related with the carbon structures. Several oxides, ferrites and mixtures were investigated and as the closest form of chemical compound, that could give contribution in the presence of the signal could be due presence of nickel ferrites, however the presence of other ferrites and oxides in not excluded. The signal with a g -factor 2.12 could be a superposition of signals from several free radicals.

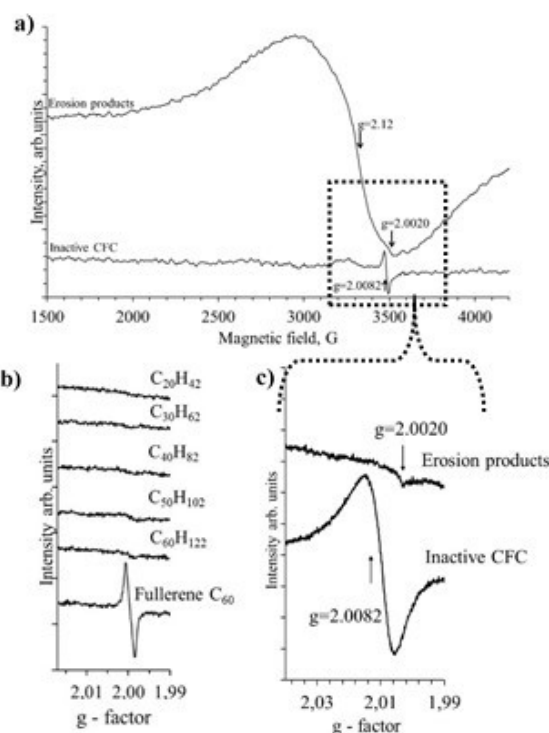


Fig. 7. Electron spin resonance spectra of a) and b) JET C-wall erosion products in comparison with plasma non-exposed (inactive) carbon fibre composite, c) long chain hydrocarbons and fullerene C_{60} .

Conclusions

This work demonstrates the analysis of tritium, showing that in He + 0.1% H_2 gas flow 14- tritium 15 L/h at a heating rate of 5 K/min in JET-C sample 2b-1 of 2IWG3A without a tungsten coating at the shutdown on 23rd October 2009 was by a factor of >20 higher surface concentration of tritium than JET-ILW tungsten-coated sample 2b-1 of 14ING3B at the shutdown in July 2012: 88 and 3-4 kBq/cm² (4.9×10^{13} and $1.7-2.2 \times 10^{12}$ T atoms/cm²) respectively. This result confirms the reduction by a factor of 10-20 of the long-term fuel retention in JET-ILW with respect to JET-C. The tritium release of samples 2b-1 of 2IWG3A and 14ING3B occurred in the temperature ranges of 420-1180 K and 420-870 K respectively. Presence of metallic impurities (Fe, Ni, W, Be etc.) and carbon as main component in the C-wall erosion products is estimated. With electron spin resonance spectrometry two types of paramagnetic centres – g -factor 2.002 and 2.12, are characterized. Raman and infrared spectrometry show that information on graphite containing structures and inorganic oxides may be obtained, the results supplement the information about composition of the EP from fusion devices.

Acknowledgments

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