Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Nuclear Materials 337–339 (2005) 659–663
journal of nuclear materials
www.elsevier.com/locate/jnucmat

Characterisation of flakes generated in JET after DD and DT plasma operations

N. Bekris [a,*], J.P. Coad [b], R.-D. Penzhorn [a], S. Knipe [b],
L. Doerr [a], R. Rolli [c], W. Nägele [c]

[a] *EURATOM Association, Forschungszentrum Karlsruhe, Tritium Laboratory, Bau 451, Postfach 3640, Karlsruhe 76021, Germany*
[b] *EURATOM/UKAEA Fusion Association, Culham Science Centre, Abingdon, Oxon OX14 3DB, UK*
[c] *EURATOM Association, Forschungszentrum Karlsruhe, Hot-Cells, Postfach 3640, 76021, Germany*

Abstract

Approximately 1 g of the 150 g collected at the JET was send to the Tritium Laboratory Karlsruhe (TLK) for physico-chemical characterisation. The flakes were extensively analysed using several experimental tools, such as calorimetry, X-ray-diffraction, thermal desorption, helium pycnometry, scanning electron microscopy, etc. The specific surface area measurements according to the Brunauer–Emmett–Teller (BET) method, showed a value of about $(4.7 \pm 0.3)\ \mathrm{m^2\ g^{-1}}$ while their average tritium activity was estimated to be $(1.17 \pm 0.1)\ \mathrm{TBq\ g^{-1}}$ (i.e. 3–3.3 mg of tritium per gram of flakes) and their average real density $(1.69 \pm 0.02)\ \mathrm{g\ cm^{-3}}$. Based on these results we estimate that at the end of the remote tile exchange (RTE) at JET the 3.0 g of tritium which did not return to the AGHS after the DTE1 remained in the vessel mainly in form of flakes, i.e. approximately (950 ± 80) g of flakes are still inside the machine.

Keywords: Carbon films; Codeposition/tritium; Erosion/deposition; Flakes; JET divertor tiles

---

1. Introduction

When hydrogen isotopes from the plasma interact with graphite or CFCs lining the fusion reactor wall, three distinct processes take place by which the hydrogen is retained in the hydro-carbonated material:

- (i) surface saturation of the implantation region of the plasma-facing first wall components,
- (ii) diffusion into the bulk of first wall materials via the internal porosity, and/or transgranular diffusion,
- (iii) re-deposition of sputtered carbon with incorporation of tritium into the co-deposited films.

All these mechanisms are contributing to increase the tritium inventories locked inside the torus to an extremely high level (11.5 g in JET cf. Table 1). Such a tritium sequestration on plasma facing components (PFCs) constitutes an issue for future burning-plasma machines not only because it immobilises fuel material but also for safety reasons. Among the above mentioned processes involved in the fixation of tritium on PFCs, the highest contribution arises from the co-deposition of sputtered carbon together with plasma material (tritium).

---

[*] Corresponding author. Tel.: +49 7247 82 2932; fax: +49 7247 82 2868.
E-mail address: nicolas.bekris@hvt.fzk.de (N. Bekris).

0022-3115/$ - see front matter
doi:10.1016/j.jnucmat.2004.09.072

Table 1
Closing the tritium balance at JET (MKIIA)[a]

35 g tritium were introduced to the JET torus from May to November 1997 during DTE1
11.5 g retained after the last tritium-fuelled pulses of DTE 1
6.2 g still outside the AGHS after clean-up with deuterium plasmas
2.5 g recovered during venting before RTE
0.5 g recovered in 150 g flakes
~0.1 g was estimated to be trapped by the 480 divertor tiles
0.1 g was estimated to be trapped by the rest of the inner and outer walls
3.2 g recovered during RTE
3.0 g remains in the vessel most probably as flakes (at the end of RTE)
Average tritium activity (1.2 ± 0.1) TBq g^{-1} or 3.3 mg tritium per g of flakes, i.e. (950 ± 80) g of flakes must be present in the vessel
Inspection of the sub-divertor volume using an endoscope has confirmed that there are large quantities of flakes present in this region

Estimation based on hundreds analysis of a complete set of 10 divertor tiles.

[a] JET Report on FT task JW 1-1.1 (N. Bekris et al.) available here: http://users.jet.efda.org/documents/selectedpapers/bekris.pdf.

Therefore, the characterisation of these co-deposits and the identification of the chemical bonds involved in the sequestration of such large tritium amounts by carbon is essential.

In the Joint European Torus (JET) a very large fraction of tritium was retained in co-deposits in the vicinity of the water cooled louvres adjacent to the inner divertor, but not in line-of-sight of the plasma. These co-deposits sometimes become so thick that they spall off to form flakes, many of which fall into the sub-divertor zones of the machine.

A high specific surface area (SSA) for flakes could also have a tremendous impact in terms of reactivity with hydrogen isotopes (mainly tritium). Indeed, the total effective surface area of small particles, i.e. dust and flakes, in a fusion device is an important factor when considering safety scenarios. When such a reactive compound containing high amounts of tritium and having a high specific surface area is exposed to steam or moist air, as could be expected in a loss of coolant accident (LOCA), oxidation of these materials may occur with a simultaneous production of explosive concentrations of hydrogen or worse, tritium.

With a view to resolving the existing discrepancy between the various measurements on the specific surface of flakes, a thorough physico-chemical investigation was undertaken to determine not only the specific surface of some flakes collected at JET but also the composition, density and the specific tritium concentration of such flakes.

2. Co-deposited layers and flakes at JET

Thick carbon deposits containing high levels of hydrogen isotopes have been observed in JET as well as in TFTR after exposure of first wall materials to deuterium–tritium (DT) discharges [1–3]. In the vacuum vessel of JET the deposition was found to be asymmetric, i.e. while heavy deposition occurs at the inner divertor region there is comparatively little on the opposite side. Examination of a complete poloidal set of 10 MKIIA divertor tiles revealed that the highest deposition was on the plasma shaded lower edge of inner tiles 3 of the divertor [1,2] (Fig. 1). Indeed, the edge region of that tile showed two distinct regions, one closer to the plasma-exposed surface of the tiles having comparatively low tritium concentrations (0.2 GBq cm^{-2}) and another region, further away from the surface, of thick deposit with a clear tendency of spall off and exhibiting a tritium concentration of 3.3 GBq cm^{-2} (see Fig. 1).

Inner base tiles 4 were also characterised by strong deposition which sometimes was falling off or hanging from the shadowed side of these tiles in form of flakes (Fig. 2). In fact, when the tiles were retrieved from the machine during the RTE the deposits observed on tile 4 and at the end of tile 3 were well-adhered, but almost

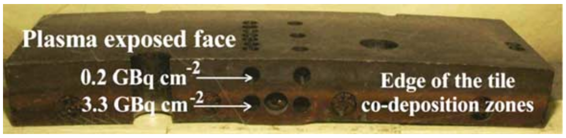

Fig. 1. Plasma exposed side and edge of tile 1IN3, retrieved from JET after the DTEl campaign. Two strong co-deposited zones are visible on the bottom side of the edge of the tile.

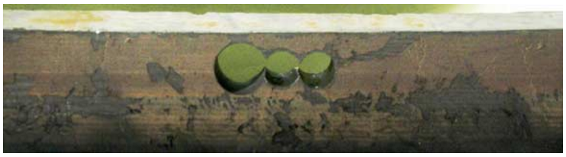

Fig. 2. Plasma exposed side of tile 1BN4 retrieved from JET after the DTEl campaign. A strong co-deposited zone is visible on the bottom of the tile where it is shadowed from the plasma by tile 3.

complete spalling-off has occurred in air storage since that time.

The amount of hydrogen trapped by these co-deposits depends not only on the specific material used as first wall (graphite, CFC type, etc...), but also on the temperature, surface area, exposure time, type and plasma operation conditions of the tokamak.

In JET the flakes collected under the divertor structure are saturated with hydrogen isotopes, i.e. their hydrogen/carbon ratio can be as high as 0.75 and the weight of a single flake may be of the order of 5 mg. The flakes exhibit a layered structure and they are archeologically deposited with the most recent layer being at the surface while the oldest one is deeper into the surface in contact with the substrate (PFC material). Optical spectroscopy revealed such a layer type structure while scanning electron microscopy (SEM) of the carbon flakes showed that flakes having dimensions of 0.5 mm are not exceptions [4]. Both techniques revealed as well the occasional presence of metallic particles. After the first deuterium–tritium experimental campaign (DTE1) in JET, the machine was submitted to an extensive cleaning campaign essentially using deuterium discharges [5]. Hence it can be expected that some layers of the flake section closer to the outer surface contain much more deuterium than tritium while others deeper within the flake structure will contain deuterium and tritium amounts which represents the DT plasma composition during normal operation of the machine.

In a preliminary analysis of such type of flakes, a surprisingly high value of 675 $m^2 g^{-1}$ was reported for their specific surface area (SSA) [6,7]. This value is excessively high and is in contradiction with previous measurements performed on dust material retrieved from other machines.

Indeed, using the Brunauer, Emmett, Teller (BET) method, dust produced from a JET tile is shown to have a SSA ranging between 11 and 36.4 $m^2 g^{-1}$ [8]. While for dust material retrieved from JET after DTE1 a BET specific surface area of 4 ± 2 $m^2 g^{-1}$ has been reported [9]. The latter is in line with the measurements performed at the TLK on pre-DTE JET flakes. Indeed, a sample having a mass of 155.9 mg, and an average tritium activity of 10^6 Bq g^{-1} exhibited a BET SSA of 7.2 $m^2 g^{-1}$. It thus appears that the value reported in references [6,7] is exceedingly high. It was therefore considered necessary to verify these measurements by additional experiments. This work was undertaken at TLK with flakes retrieved from the JET vessel during the RTE campaign, i.e. after the DTE1.

3. BET measurements on post-DTE flakes

During the DTE1 campaign at JET, the torus was fuelled with a total of 35 g of tritium. During the tritium fuelling period the amount recovered from the vessel and measured by the active gas handling system (AGHS) showed that the tritium inventory retained in the vessel was ~40% of the input.

Approximately 150 g of flakes collected in two cyclone pots (56.8 g and 97.5 g) were retrieved from JET during 1998 after the DTE1 campaign during a difficult remote operation using a modified vacuum cleaner provided with a cyclone dust separator. The average tritium content of these flakes was determined calorimetrically at JET to be 1.06 TBq g^{-1} [10]. During another separate determination, the tritium content of three flake samples was obtained by heating specimens under air at 800 °C and collecting the liberated tritiated water in bubblers containing water. Based on these three measurements the average tritium content of the JET flakes was estimated to be (1.17 ± 0.11) TBq g^{-1}, in good agreement with the calorimetric data.

Approximately 1 g of these flakes was also send to the TLK. It was determined that during a period 35 months a total amount of 4.96×10^{11} Bq (13.4 Ci) of tritium was released by off-gassing. The tritium content of the flakes was then measured by calorimetry at the TLK and it established that 0.93 g of flakes still contain 6.03×10^{11} Bq of tritium (16.3 Ci). These figures give a total tritium inventory of 1.18×10^{12} Bq of tritium per gram of flakes (31.9 Ci), or 3.3 mg of tritium per gram of flakes, and an average off-gassing rate of 2.1×10^7 Bq $h^{-1} g^{-1}$ of flakes. This off-gassing rate is much lower than the one measured at JET after the flake collection. Indeed, during the initial stage of the measurement a tremendous out-gassing rate ranging between 1.5×10^9 and 2.6×10^9 Bq $h^{-1} g^{-1}$ was noticed which was associated to a rapidly decaying heat source. This was attributed to the oxidation of hydrogen, which only ended after all oxygen present in the vessel was consumed [10].

The BET measurements were performed in three steps. During the first step only a small part of the flakes was measured. Then a second series of measurements was operated on a larger amount of flakes and finally the entire amount of the flakes was measured.

It is worth mentioning that the last experiment was repeated several times during several days and also after we having purged the dried flakes over night (16 h) with pure nitrogen 4.0 using a flow rate of 25 l min^{-1}. Moreover, before purging one night with nitrogen the water adsorbed in the surface of the flakes was removed using a heating gun. During the whole series of experiments the BET specific surface area remained remarkably constant giving an average value of (4.7 ± 0.3) $m^2 g^{-1}$.

This value is in line with previous measurements mentioned above and reported for dust particles retrieved after DTE by Peacock [9] reporting a specific BET surface area of (4 ± 2) $m^2 g^{-1}$ and confirmed by measurements made at TLK also on JET flakes specimen from the pre-DTE campaign. Similar BET measurements performed on dust material from ASDEX-Upgrade and reported by Sharp [11] ranged between 0.70 and 3.70 $m^2 g^{-1}$ while dust retrieved from TFTR showed a larger variation range for BET SSA ranging between 6.9 $m^2 g^{-1}$ and 26.9 $m^2 g^{-1}$ [12].

It is also worth mentioning that applying an external magnetic field on the flakes (using a magnet) allows a visible separation of a small fraction of paramagnetic metallic particles. The presence of such particles has to be related to the erosion of the metallic parts of the first wall and as it was already shown by the beta-induced X-ray spectroscopy (BIXS) various metallic species such as Fe, Ni, Co, and Cr are present on the surface of all MKIIA inner divertor tiles retrieved after DTE1 [13]. Of the tiles from the outer divertor of the same series, only tile 7 shows a similar behaviour. This proves the existence of a transport mechanism inside the vessel bringing sputtered material, or/and impurities such as metallic particles, from the outer part of the divertor to its inner part.

The density measurement on the complete batch of flake material was performed using the helium pycnometry method. No less than 20 measurements gave an average value for the flakes' density of (1.69 ± 0.02) g cm^{-3}.

4. Closing the tritium balance at JET

At the start of RTE there were 6.2 g of tritium missing. During RTE, 2.5 g were released into the air on venting and continuous release into the gas phase and recovered by the AGHS. This leaves 3.7 g, of which 0.5 g is in the collected flakes and approximately 0.2 g is in the divertor and wall tiles. Therefore, at the end of RTE, approximately 3.0 g was not accounted for. This must remain in the vessel as flakes. If they have the same content of tritium as the above analysed flakes (3.3 mg of tritium per gram offtakes) then a further (950 ± 80) g of flakes must be still present in the vessel (see Table 1). This amount offtakes refines an earlier estimation stating that about 1 kg flakes were still present in the vessel after the DTE1 campaign [14].

Recently it was possible to validate this supposition as, by using an endoscope inspection of the sub divertor volume, large quantities of flakes were found in this area. We can hopefully close the tritium balance at JET assuming that this material has the same specific tritium activity as the recovered and analysed flakes.

5. Mechanism of the flakes' formation

A possible mechanism to explain such high tritium incorporation into the flakes is the following. The main wall is the primary erosion area of the fusion vessel. Even if isolated particles are leaving the Scrape of Layer (SOL) and interact with the first wall, the major part of the interaction is the result of plasma with the wall eroding the surface. Therefore, when the plasma hits the surface it removes a thin carbon sheet (skin of carbon containing many carbon atoms with almost no hydrogen). If this 'carbon-skin' is sufficiently large it could roll or curl up to form spheres incorporating more plasma material (H,D,T) and thus produce fullerenes which are then deposited in the areas surrounding their production. If the eroded carbon skin is not big enough, instead of fullerenes the production of nano-tubes (or macro-tubes) may be possible. Fullerenes and nano structures have already been observed in Tore Supra [15]. Fullerenes or macro-tubes should contain limited amounts of hydrogen like material collected in the hot areas of JET which has a D/C ratio approximately equal to 0.4 and is reported as 'hard' co-deposited film [16]. Such films after their deposition are continuously bombarded (re-eroded) and the long chains of hydrocarbons are therefore broken down to smaller chains. During this step (re-erosion) they continue to incorporate more hydrogen isotopes, becoming lighter (more volatile) and therefore have a longer 'free-path' range, and are then re- deposited further away from the place where they were produced. After several erosion-deposition cycles the flake material end up in the bottom of the divertor in the colder part of the machine where they 'condense' in places which are not in the line of sight of the plasma, i.e. they are protected from further erosion. The flakes collected in these parts of the machine were found to have a D/T ratio ~0.75 and reported as 'soft' co-deposited films [16].

6. Conclusions

Flakes are radioactive material containing substantial amounts of tritium and may be chemically very reactive and may yield explosive concentrations of hydrogen when exposed to steam or moist air as it is postulated in case of a loss of coolant accident (LOCA) if their specific surface is large. The chemical reactivity of flakes depends on the composition as well as the effective surface area. Until recently it was supposed that the large surface area of the flakes is the main parameter responsible for the absorption of large tritium quantities, thus increasing the overall tritium in-vessel inventory.

Nevertheless, the present results shown that the SSA of the flakes is relatively small 4.7 ± 0.3 $m^2 g^{-1}$ and therefore, their specific surface cannot explain the high tritium concentration observed for these flakes. Their high tritium content has to be related to the early formation of the co-deposited material. As the specific surface area measured for these flakes is only 4.7 ± 0.3 $m^2 g^{-1}$ that does not imply that this material would be very reactive in presence of water as it is postulated to be the case of a vacuum accident and consequently will not release its total tritium content in case of such an event.

However, if the specific surface of the flakes it is not an issue for future fusion machines using graphite or CFC's as first wall material, one pressing problem still remains unresolved, i.e. how to remove these co-deposited layers and flakes, or the hydrogen isotopes that they contain, once the co-deposited layer it is formed. At present there is not a satisfactory method available for the *in-situ* detritiation of such co-deposits and there is only a limited amount of research going in that direction.

References

[1] A.T. Peacock, P.A. Andrew, J.P. Coad, R. Cusack, F.H. Hurd, S. Mills, R.-D. Penzhorn, M. Pick. in: Proc. 20th Symp. on Fusion Technol. (SOFT), Marseille, France 7–11 September, 1998, Vol. 1, p. 233.

[2] R.-D. Penzhorn, N. Bekris, U. Berndt, J.P. Coad, H. Ziegler, W. Nägele, J. Nucl. Mater. 288 (2001) 170.

[3] C. Skinner, C.A. Gentile, K.M. Young, J.P. Coad, J.T. Hogan, R.-D. Penzhorn, N. Bekris, Europhys. Conf. Abstr. 25A (2001) 1621.

[4] N. Bekris, R.-D. Penzhorn, J.P. Coad, L. Doerr, S. Knipe, M. Sirch, R. Rolli, H. Ziegler, FZK report-6858, April 2003.

[5] P. Andrew et al., Tritium retention and clean-up in JET, Fus. Eng. Des. 47 (1999) 233.

[6] A.C. Francis, J. Foster. Analytical results and data for JET in-vessel flakes after DTE1, JET Report, October 1999.

[7] A.C. Francis, Analytical results and data for JET in-vessel dust after the DTE1, JET Report, April 1999.

[8] D. Boyer, Ph. Cetier, L. Dupin, Y. Belot, C.H. Wu, Tritium sorption in carbon dust, Fus. Technol. (1996) 1751.

[9] A. Peacock, P. Andrew, P. Cetier, J.P. Coad, G. Federici, P.M. Hurd, M.A. Pick, C.H. Wu, J. Nucl. Mater. 266–269 (1999) 423.

[10] S.J. Knipe, A.C. Bell, P.D. Brennan, J.P. Coad, C.J. Manning, A.N. Perevezentsev, Fus. Eng. Des. 58&59 (2001) 383.

[11] J. Phillip Sharpe, V. Rohde, J. Nucl. Mater. 313–316 (2003) 455.

[12] G.R. Smolik, R.A. Anderl, R.J. Pawelko, W.J. Carmack, P.B. Hembree, M.A. Gates, in: Proceedings of the 17th IEEE/NPSS Symposium on Fusion Engineering, San Diego, CA, 6–7 October 1997, Vol. 1, p. 183.

[13] M. Matsuyama, N. Bekris, M. Glugla, N. Noda, V. Philipps, K. Watanabe, J. Nucl. Mater. 313–316 (2003) 494.

[14] J.P. Coad, N. Bekris, J.D. Elder, S.K. Erents, D.E. Hole, K.D. Lawson, G.F. Matthews, R.-D. Penzhorn, P.C. Stangeby, J. Nucl. Mater. 290–293 (2001) 224.

[15] Ph. Chappuis et al., J. Nucl. Mater. 290–293 (2001) 245.

[16] W. Jacob, B. Landkammer, C.H. Wu, J. Nucl. Mater. 266–269 (1999) 552.