ELSEVIER

Journal of Nuclear Materials 258–263 (1998) 764–769

journal of nuclear materials

# Oxidation induced release of deuterium from carbon based plasma facing materials

S. Alberici [a,*], J.P. Coad [c], H.-K. Hinssen [a], R. Moormann [a], P. Wienhold [b], C.H. Wu [d]

[a] *Forschungszentrum Jülich GmbH, ISR-1, D-52425 Jülich, Germany*
[b] *Forschungszentrum Jülich GmbH, IPP-A, D-52425 Jülich, Germany*
[c] *JET, Abingdon, OX14 3EA, UK*
[d] *NET, D-85748 Garching bei München, Germany*

**Abstract**

Following a description of the state of knowledge concerning cleaning of the vacuum vessel of fusion reactors from Tritium by controlled oxidation of codeposited layers of carbon and hydrogen isotopes the experimental facility Deuterium Release Experiment (DEREX) is explained. In this facility a codeposited a-C:D layer from TEXTOR (1 μm thickness, $D/C = 0.03$) has been oxidised in oxygen (300–600 Pa) at 523–673 K. The results indicate, that substantial release rates, leading to complete D-release within some days, are obtained at $T \geqslant 623$ K. Surprisingly, an over proportional dependence of release rate on oxygen partial pressure was observed; this result seems worth to be examined in more detail in order to optimise the cleaning method.

## 1. Introduction

During fusion reactor operation first wall materials (carbon, beryllium) can be eroded by various mechanisms and redeposited on certain surfaces. This redeposition is accompanied by simultaneous deposition of hydrogen isotopes (codeposition) [1–4]. Codeposition of tritium is a significant safety problem, because large amounts of this radiotoxic material can be stored on first wall surfaces: In the event of accidents like air or steam ingress this tritium will easily be released. Accordingly, it is an important task to find procedures which allow the aforementioned accumulation of tritium to be avoided [3]. This paper deals with the removal of codeposited carbon/hydrogen layers by controlled oxidation in oxygen, leading to volatile products (which can be removed from the vacuum vessel by pumping). Technical application of such a procedure requires temperature and oxygen pressure as low as possible.

Much work has been done on the structure of amorphous carbon/hydrogen (a-C:H) layers because of their general technical importance [2,3,5,6]. Particularly it is known, that mainly $sp^3$ but also $sp^2$ and $sp^1$ C–H bonding occur. In polymer-like a-C:H, which is weak and has a high H:C ratio of $\geqslant 1$, $sp^3/sp^2$ is usually $>2$, whereas in hard diamond-like a-C:H layers (DLC, H:C ratio up to 0.5) $sp^3/sp^2$ is in the range of 1. In addition, chemisorbed hydrogen is found near to surfaces.

An overview on chemical erosion of carbon is given in [7]. Experiments on release of hydrogen from fusion relevant a-C:H layers by chemical reactions have been performed since 1989: In [8] it was shown that glow discharges in $O_2$, leading to excited atoms, result even at room temperature in substantial reaction with carbon and volatilisation of its hydrogen content. Other gases like He and $N_2$ were shown to be less active. In the fusion device TFTR the release rate by $O_2$-glow discharge was found to be an order of magnitude smaller than in laboratory experiments [9]. Also thermal reactions of oxygen with a-C:H layers at temperatures up to 773 K have been examined: For a 20 nm thick layer, produced in a plasma experiment, it was shown, that even at room temperature oxygen exposure leads to a release of about

---

[*] Corresponding author. Tel.: +49-2461 616 234; fax: +49-2461 613 133; e-mail: s.alberici@fz-juelich.de.

0022-3115/98/$19.00 © 1998 Elsevier Science B.V. All rights reserved.
PII: S0022-3115(98)00113-5

20% of its H-content within 600 s with the hydrogen released as water. Continuous temperature increase (0.2 K/s) led to almost total H-release at about 573 K. The same procedure without oxygen resulted in a release of only 50% of hydrogen. A 200 nm thick laboratory produced a-C:H layer was exposed to oxygen at room temperature, leading to a release of 0.1% per day [10]. Comparison of codeposited layers from TFTR and layers produced in the laboratory by hydrogen implantation did not show significant differences during vacuum annealing and air attack. For both layers the thermal desorption becomes rapid at 673 K and the air oxidation induced release starts slowly at 473 K and proceeds rapidly at 573 K [11]. Layers (35 nm thick), formed by hydrogen implantation in graphite, were examined in oxygen and steam. Concerning oxygen (2 kPa) attack, no reaction occurred at 370 K, but at 570 K more than 90% of hydrogen was released within 20 h (layer erosion rate: 2 nm/h). At 770 K a nearly complete release occurred within 1 h (erosion rate about 80 nm/h) [12]. Comparison of measurements on chemisorbed and implanted hydrogen indicate, that oxygen is more effective for release of implanted, but steam for the chemisorbed hydrogen [12]. Erosion rates of codeposited a-C:D films of 2 nm/h are reported for oxygen (1 kPa) at 470 K: Reaction products measured by quadrupole mass filter (QMF) were $D_2O$, $CO_2$ and CO, whilst nearly no $D_2$ or $CD_4$ were found [13]. Wang [14] describes oxidation measurements in air for 2 kinds of specimens. Codeposited layers produced in laboratory (0.8 μm thick) and from ASDEX. Both specimens behave differently in air exposure at room temperature. The ASDEX specimens lose their D-content with a rate of about $10^{-3}$ $d^{-1}$ whereas the laboratory specimen is nearly stable. Release rates were nearly independent of layer thickness. At elevated temperatures (600–700 K) the ASDEX specimens emit at a rate about eight times higher than that of the laboratory specimens (complete D-release at 650 K within 1 and 8 h, respectively). Depth profiles indicate that during oxidation, oxygen is trapped near the surface (up to a depth of about 250 nm), and in parallel the D content decreases in this volume, whereas C is not attacked, perhaps D-release occurs before the carbon oxidation process.

Despite this substantial work there are still many questions to be answered, before an oxidation based cleaning method can be applied to big fusion machines. First, the structure of the codeposited films obviously influences the release rate in a manner which is not well understood. In detail, for different specimens the D-release rates scatter even for similar oxidation conditions within several orders of magnitude. Second, temperature and oxidant partial pressure as rate determining parameters have to be systematically studied. Also, the general hydrogen release mechanism is not completely understood. Based on experience in oxidation of carbon materials [15] we contribute here to an improvement of knowledge in the before mentioned field by examination of a-C:D TEXTOR specimens in oxygen at different temperatures and partial pressures.

## 2. Experimental

The experimental apparatus used for these measurements in Jülich, DEREX (Deuterium Release Experiment), is shown in Fig. 1. Basically it consists of a vacuum apparatus with a residual gas pressure in the range of $10^{-6}$ Pa. The reaction chamber CV, built in quartz, has a calibrated volume $V$ of $8.8 \times 10^{-4}$ $m^3$. The system is evacuated by means of a rotary pump plus a turbomolecular pump through the manual valve $v_1$. Oxygen of nominal purity of 99.9995% (impurities in vpm: $N_2 < 1.3$, $CH_4 < 0.05$, $CO_2 < 0.1$, $CO < 0.05$, $Ar < 2$, $H_2O < 0.5$) is supplied via a reservoir (volume $2 \times 10^{-3}/m^3$) by means of the manual regulating valve $v_2$.

Connected to CV is the QMF Leybold PGA100 (having an $Ir/ThO_2$ filament which is resistant against oxygen) which scans the mass to charge ratio ($m/q$) over the range 0–50. The QMF was calibrated beforehand with high purity gases (CO, $CO_2$, Ar, $D_2$, $H_2$, $^{16}O_2$,$^{18}O_2$). By an isothermal facility producing constant vapour pressures of $H_2O$ or $D_2O$ the QMF was calibrated also for these species, the calibration giving the linear relationship between the partial ionic current for present gas species actually measured by the QMF itself and the corresponding partial pressure. Since this system is calibrated, we will refer directly to the partial pressure instead of the measured partial ionic current. To reduce the gas pressure from its level in CV (300–600 Pa) to the QMF head working pressure of a few $10^{-3}$ Pa a pressure converter device $dw_1$ is placed between them. By adjusting the conductances $dw_1$ and $c_1$ in the UHV part a gas flow is created in a manner, that the pressure in the QMF head is $10^5$ times lower than in CV. Because flows

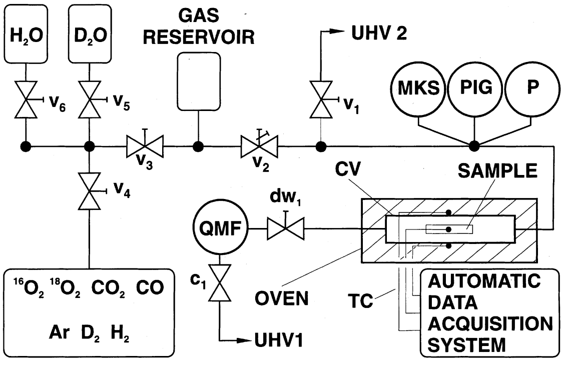

Fig. 1. Scheme of DEREX facility.

in $dw_1$ and $c_1$ are both in molecular regime their mass dependence is the same. This means that the composition of the gas mixture is not affected by the pressure reduction system. The temperature is measured by means of three chromel-alumel axially placed thermocouples (TC) and the pressure is read in the ultra high vacuum range using a Penning gauge (PIG), while for low vacuum a capacitive manometer (MKS) with range $10^{-1}$–$10^3$ Pa and a Pirani gauge (P) with range $10^{-1}$–$10^5$ Pa were used.

Graphite plates (EK98) of size 60 or 70 mm × 16 and 2.5 mm thickness were baked in vacuum at 1273 K and introduced into the limiter shadow of TEXTOR by means of the Stockholm-TEXTOR probe system. The plates were oriented perpendicular to the toroidal magnetic field direction and positioned with their plane surface in 476–532 mm radial distance from the plasma centre (plasma radius $r_a = 460$ mm) on the electron drift side and 475–544 mm on the ion drift side, respectively. The exposure to subsequent plasma discharges in D caused a gradual growth of an a-C:D-film up to several micronsby codeposition of carbon and deuterium ions which follow the field lines. After exposure the samples were dismounted and the thickness of the deposits determined by interference fringe analysis assuming $n = 2.0$ and $k = 0.005$ as optical constants [16]. As an example Fig. 2 shows a profile (boxes) across a sample A exposed to 23 discharges (total exposure time 57.8 s) in D. The maximum of 470 nm represents a carbon areal density of about $3 \times 10^{22}$ C/m$^2$ provided the density is $6.5 \times 10^{28}$ C/m$^3$ [17]. The deuterium distribution (scale to the right) has been determined by nuclear reaction analysis (NRA) [18] and corresponds to a ratio D/C = 0.22. The total D-amount considering the whole surface area turns out to be about $2.2 \times 10^{18}$ atoms. Fig. 2 also contains NRA analysis of the specimen B exposed to oxygen in our study. It corresponds to a total number of D-atoms of $1.4 \times 10^{18}$. Fringe analysis was very uncertain in this case, an average thickness of 1 μm was estimated, leading to D/C = 0.03. This is far less than the maximum, that can be found (≈0.4) in codeposits [17]. That might be due to the long time, nearly four years, the samples were stored in air before the oxidising experiment was carried out. Because of the similar history, we believe that D/C is homogeneous over the whole specimen B as shown for specimen A.

At first an experiment without a specimen present is necessary in order to scan the reacting gas and the species desorbed from the installation walls. One main point is to take into account different sources for $m/q = 20$: Not only $D_2O^+$, which is the main product gas signal, but also $Ar^{2+}$ and $H_2^{18}O^+$ (natural abundance of $^{18}O$: 0.204%) contribute to $m/q = 20$ and, as a result, corrections for the latter have to be done carefully. In addition, the production of $CO_2$ at the Ir/ThO$_2$ filament is a well-known phenomenon [19]; therefore the $m/q = 44$ peak also has to be recorded within the control experiment. Baking of DEREX was done for 24 h at 623 K under vacuum before running a control experiment without specimen. The ground level of the partial ion currents belonging to $m/q = 20$ and 44 (together with other 14 different peaks) was recorded under the same conditions as in the oxidation measurements (523–673 K, oxygen partial pressure 300–600 Pa). For the oxida-

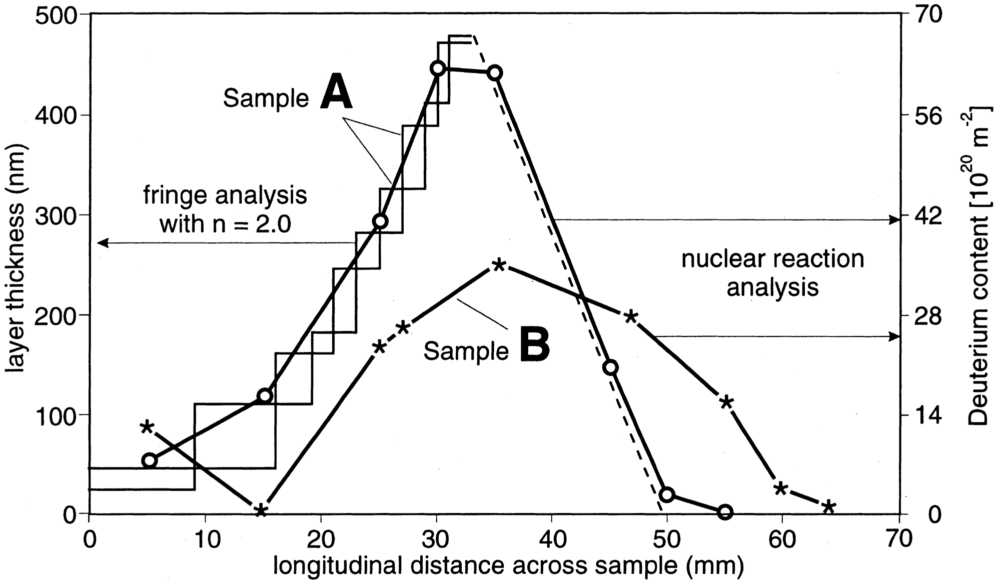

Fig. 2. D-content for 2 TEXTOR specimens (exposed in the scrape-off layer) as measured by nuclear reaction analysis; for specimen A also layer thickness measured by fringe analysis is given.

tion measurements the peak at $m/q = 20$ of was corrected by subtraction of the corresponding ground level. The same was done for all the different gas species in order to eliminate the parasite contributions of the installation walls.

The isothermal measurements with a-C:D-sample, which started at 523 K, consist of 2 steps, thermal outgassing and oxidation. During the outgassing tests under vacuum $m/q = 4$ and 3 were measured in order to quantify the thermal desorption of D ($D_2$ and HD). Oxidation was started without changing the temperature by filling CV with oxygen within about 30 s. Most oxidation runs were stopped, when the $m/q = 20$ peak was back to the ground level. After that the temperature was increased by 50 K (after pumping down DEREX) and the procedure was repeated using the same (due to the limited number of TEXTOR samples of this kind). In some cases the oxidation was even stopped when a stationary D-release rate was established. Detecting $m/q = 20$ the QMF worked in its highest sensitivity range, which implies some instabilities. The latter however vanished to a large extent by applying the correction procedure.

In order to calculate the D-release, the flux balance of the System has to be considered. With $\varphi_{\text{in}}(t)$ as $D_2O$ flux generated at the sample surface and $C_{\text{dw}}$ the admitting conductance at the QMF head this balance equation is ($p(t)$ here is the pressure of $D_2O$ in the volume $V$):

$$-V\frac{\mathrm{d}}{\mathrm{d}t}p(t) = C_{\text{dw}}p(t) - \varphi_{\text{in}}(t). \quad (1)$$

Integrating this equation and solving for $\varphi_{\text{in}}(t)$, one obtains the following relation:

$$N_{\text{D}} = \frac{2N_{\text{A}}}{RT}C_{\text{dw}}\int_0^{\tau} p(t)\mathrm{d}t + Vp(\tau), \quad (2)$$

where $N_{\text{D}}$ is the number of D atoms outgassed from the sample as $D_2O$ within time interval $\tau$, $R$ is the gas constant and $N_{\text{A}}$ is Avogadro's number. This simple model holds for any of the other gas species in a similar manner. The QMF measures the pressure in the low pressure stage of our installation; however, due to the well known efficiency of the pressure reduction system the real pressure $p(t)$ within CV is also known.

$D_2$ measured during the thermal outgassing amounts to <1% of the total D content, most of it outgassed at 523 K, with negligible formation of HD. It has to be assumed that this D is desorbed from the very first atomic layers. In Fig. 3 the integral oxidation induced D-release is plotted as a function of time. The ordinate corresponds to the percentage of the total D-release we have measured; the latter has been estimated to be $9.5 \times 10^{17}$ D-atoms, being in sufficient agreement with that one of $1.4 \times 10^{18}$ assessed by NRA (considering that, as shown below, our oxidising treatment leads to a nearly complete release). At 523 K a small and at 573 K (300 Pa) a significant D-release occurred, which was initially fast but decreased virtually to zero after some hours (i.e. the integral release remains constant). Further significant release rates were not observed at $T < 623$ K. It is not clear, whether constant release rates without complete slowing down (as observed at $T \geqslant 623$ K) might also be possible at lower temperatures and higher oxygen partial pressures. The measurement duration for 573 K and 600 Pa was not sufficient for clarification of this problem. It is important to note, that the doubling of oxygen partial pressure has a more pronounced effect on D-release at $T > 573$ K than temperature increase by 50 K (Doubling partial pressure increases D-release rates by up to factor of 5 at 623 K). This does not simply correspond to the well known oxidation kinetics of pure carbon in oxygen, where a reaction order of 1 has to be expected at low oxygen partial pressures (i.e. a proportionality of oxidation rate and partial pressure). Furthermore, an activation energy of about 200 kJ/mol has to be assumed for the $C/O_2$-reaction, which should lead to a rate increase by a factor of about 10–50 for a temperature increase of 50 K [15,20]. Whether the oxidation kinetics of a-C:D-layers is very different from pure carbons or D-release rate is not simply proportional to carbon oxidation rate has to be clarified in future by stepwise SIMS-analysis of oxidised specimens. The maximum release rate we observed was $1.2 \times 10^{-4}$%/s (10%/d) at 623 K and 600 Pa. At 673 K the D-release rate slows down a bit, indicating that the specimen became empty of D. This was confirmed by NRA post examination showing D-concentrations of $<1.4 \times 10^{20}$ $\text{m}^{-2}$ or <10% of the initial content. In general it should be noted, that the QMF operated within its highest sensitivity range during our measurements, which increases the experimental error. Due to the non uniform layer thickness (Fig. 2), a reliable value for the C-removal rate, which is often used to characterise the effectiveness of a tritium cleaning method, cannot be given.

Reaction products we detected were $CO_2$, CO and $D_2O$ (HDO being below the detection limit of QMF). Concerning $CO/CO_2$ relation we found values always <1 with a tendency to increase with temperature. This is in line with experience from carbon oxidation for low temperatures. Carbon mass balance by comparing weight loss (1.65 mg) with gasified amount calculated from CO and $CO_2$ (1.80 mg) agrees fairly well. The relation $(CO+CO_2)/D_2O$ is >100, which is not surprising, because the a-C:D layer covers only part of the TEXTOR specimen and the EK98 graphite itself has a much larger (inner) reactive surface than the dense layer. It is well known, that thermal reactions of oxygen with nuclear grade graphites like EK98 start to become measurable at about 573 K.

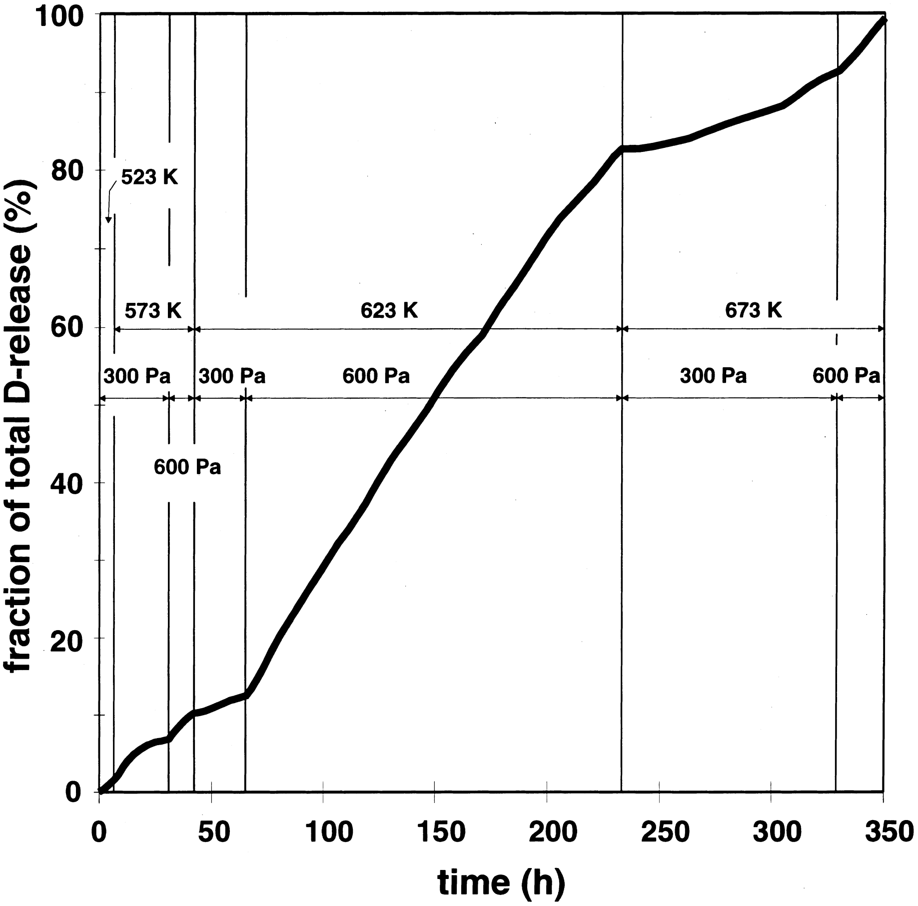

Fig. 3. Fractional D-release depending on oxygen exposure time for TEXTOR specimen B.

## 3. Discussion and conclusions

As D-release rates from our first DEREX measurements and NRA analysis indicate, oxygen can be used as cleaning agent for TEXTOR a-C:D layers. At oxygen pressures ⩽ 600 Pa, temperatures of at least 600 K seem to be necessary for getting an almost complete D-release within several days. However, the oxygen pressure influences D-release rates more than proportional and it might be possible, that by increasing the partial pressure the reaction temperature to be used in the cleaning procedure can be substantially decreased. This will be a task of further research (i.e. to find the optimal conditions for controlled removal of tritium, also bearing in mind that the amount of damage to the vacuum vessel interior by the oxygen treatment must be kept as low as possible). Future work to understand the detailed kinetics of the D-release will be done at first on laboratory produced a-C:D-layers (of which a sufficient specimen number of same quality can be obtained) and later on other kinds of a-C:D-specimens. The use of different kinds of specimens gives information on the influence of the layer structure on the D-release kinetics. Further plans include the study of the influence of additional elements such as Si in the codeposited layer on the D-release kinetics. This is needed, because parts of ITER first wall liner consist of CFC NS31, which contains some Si. Finally, other reacting media ($H_2O$, $CO_2$, $O_3$ etc.) will be examined in comparison with oxygen.

## References

[1] G.M. McCracken et al., J. Nucl. Mater. 162 (4) (1989) 356.
[2] J.C. Angus et al., in: J. Molt, F. Jansen (Eds.), Plasma deposited thin films, CRC, Boca Raton, 1986.
[3] G. Federici et al., Fus. Eng. Des. 26 (1995) 136.
[4] M. Mayer et al., J. Nucl. Mater. 230 (1996) 67.
[5] C. DeMarino et al., Diamond Relat. Mater. 4 (1995) 996.
[6] J. Robertson, Diamond Relat. Mater. 6 (1997) 212.
[7] E. Vietzke, A.A. Haasz, in: W. Hofer, J. Roth (Eds.), Physical Properties of the Interaction of Fusion Plasmas with Solids, Academic Press, New York, 1996.

[8] W.L. Hsu, J. Vac. Sci. Tech. A 7 (3) (1989) 1047.
[9] D. Mueller, W. Blanchard et al., J. Nucl. Mater. 241 (3) (1997) 897.
[10] R.A. Causey et al., J. Vac. Sci. Tech. A 7 (3) (1989) 1078.
[11] R.A. Causey et al., J. Nucl. Mater. 220 (2) (1995) 823.
[12] S. Chiu et al., J. Vac. Sci. Tech. A 9 (3) (1991) 747.
[13] A.A. Haasz et al., J. Vac. Sci. Tech. A 14 (1) (1996) 184.
[14] W. Wang et al., Lecture on Jahrestagung der Deutschen Physikalischen Gesellschaft, 1997, Mainz (submitted to J. Nucl. Mater.).
[15] H.-K.Hinssen et al., Jül 1875 (1983).
[16] P.Wienhold et al., Vacuum 47 (1996) 919.
[17] P.Wienhold et al., J. Nucl. Mater. 162 (4) (1989) 369.
[18] J.P.Coad, Joint European Torus Report JET-R (95)10, Appendix A, 1995.
[19] J.F. O'Hanlon, A User's Guide to Vacuum Technology, 2nd ed., Wiley, New York, 1989, p. 141.
[20] R. Moormann et al., J. Nucl. Mater. 212 (5) (1994) 1178.