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Deuterium release rates in a-C:D-layers during oxygen attack

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Abstract

A laboratory produced very homogeneous a-C:D-layer (DIARC, 3.5 μm of thickness, D/C = 0.1) is oxidised in oxygen (0.3–20 kPa) at temperatures of 523–723 K in order to generate D-releases; the results are used in development of a cleaning procedure of fusion reactor first walls from tritium. It is found, that the temperatures necessary for a continuous release are in the case of the DIARC specimen higher by about 100 K than for TEXTOR specimen examined earlier. Within the 50 K steps used, the burst-like D-release as observed for TEXTOR specimen at lower temperatures was not found for DIARC. Raman and SIMS spectra for both kinds of specimen are reported. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Accumulation of tritium on plasma facing components by codeposition with carbon has to be limited because of safety, maintenance and economical reasons [1]. In ITER a critical amount of tritium in these layers has to be expected already after about 50–1000 shots; accordingly, countermeasures have to be developed. One possible method applicable for codeposited a-C:H-layers is their controlled thermal oxidation with gaseous oxidants at temperatures as low as possible and removal of the product gases out of the vacuum vessel by pumping; an overview of existing data concerning thermal oxidation of a-C:D-layers is given in Ref. [2], indicating that there is still a significant lack of data on influence of temperature, oxidant partial pressure and composition (respectively microstructure) of the layer on D-release rates. Based on long-term experience with oxidation of C-based materials in oxygen and steam [3], our group contributes to the development of such a cleaning method, concentrating mainly on thermal reactions of oxygen with codeposited layers. In this paper we describe new D-release rate experimental results on laboratory produced a-C:D-films. These can be fabricated in a sufficient number of same quality specimens with well-defined characteristics (e.g. lateral and depth homogeneity of the film, defined D–C distribution profile across the sample depth, knowledge of impurity concentration, defined layer structure and exact knowledge of the D/C codeposition procedure and history). Using these layers is of great interest as one can produce reference D-rate data because of the layer starting condition relevance. In case of samples from fusion devices, the films are often not well characterised or defined, so the study can be affected by uncertainty related to the unknown sample status (in particular formation history and final state of the layer). This might also be the cause that the behaviour of specimen from fusion devices under oxidation treatment is far from unique [2]. Moreover, it has to be pointed out that DIARC specimens are examples of 'hard' a-C:D-layers (D/C ratio being = 0.1), to which many of the codeposited layers in fusion devices belong. This is also the case for a TEXTOR specimen we have measured (D/C ratio about 0.03), in order to compare the results.

2. Experimental

The facility DEREX has been developed for studies of oxidation on a-C:D-layers in Jülich [2]. Briefly, it

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consists of an ultra high vacuum calibrated chamber (about one litre volume) in which the sample is placed. The chamber walls, as well as the sample holder, are built in quartz in order to reduce the noise effect given by the outgassing of the walls. This quartz chamber is placed within the oven (maximum temperature: 1200 K). The system temperature is monitored via three axially placed thermocouples and the whole system is controlled by means of an automatic data acquisition system. The gas is analysed by a quadrupole mass filter (QMF), which scans over the mass to charge ratio range 0–100; the gas is admitted to the QMF via a pressure reduction device operating in molecular regime to reduce the pressure from the experimental value (up to 2×10^4 Pa) down to the pressure range of about 10^{-5} Pa, suitable for the QMF itself. It should be noted that the experiments were conducted under isobaric conditions, the pressure being fixed by means of a variable valve which compensates the gas consumption by pumping admitting gas from an oxygen reservoir. This means that we do not necessarily keep constant the oxygen partial pressure. In case oxygen is consumed by oxidation, gaseous reaction products are formed which (with respect to total pressure) compensate the oxygen consumption; accordingly, because refilling of oxygen into the system occurs automatically by total pressure decrease (due to pumping) only, there is some drop in oxygen partial pressure in such cases. The oxygen purity was 99.9995%; the QMF was calibrated using the main gases involved in these measurements: O_2, CO_2, CO, Ar, D_2, H_2, H_2O and D_2O. The calibration procedure simply consists of finding the correspondence among the gas partial pressure value present in the QMF head volume and the related ionic partial current detected at the QMF itself (linear correlation), this being made only after creating a very good base vacuum in DEREX and then filling the facility with the desired gas type (still thought the gas of extreme pureness). By the pressure reduction device [2], the partial pressure present in the QMF head is representative of the real pressure within DEREX, this leading to a direct measure of the actual pressure within the reaction chamber starting from the detection of the QMF ionic current. Object of first DEREX experiments was an a-C:D specimen generated in TEXTOR [2]: A graphite sample type EK98 (size 70 × 16 × 2.5 mm) was oriented perpendicularly to the toroidal magnetic field direction, positioned with its plane surface at 476–532 mm radial distance from the plasma centre on the electron drift side and 475–544 mm on the ion drift side, respectively. This sample was exposed to plasma discharges in deuterium for a total time of 57.8 s which caused a gradual growth of an a-C:D-film up to 2.5 μm by codeposition of D and C (average layer thickness 1 μm). Nuclear reaction analysis (NRA) has shown a pronounced non homogeneous distribution of deuterium within the specimen ($0–37 \times 10^{20}$ m^{-2}), the highest value being recorded in the middle of the surface; it is assumed that D/C is constant along the specimen, and that the D-amount varies linearly with the total layer thickness. A D/C ratio of about 0.03 was estimated for this sample. We oxidised this specimen in oxygen (0.3–0.6 kPa) at 523–673 K. Due to shortage of suitable TEXTOR samples, these experiments were performed on one single specimen, changing temperature and oxygen pressure stepwise, as described in detail in Ref. [2].

As a second experiment, we ran tests on specimens of 61 × 16 × 2.5 mm size fabricated in the following manner by DIARC Tech., Helsinki [4]: On a stainless steel type AISI 316 substrate, previously polished with Al_2O_3 paste, an Ar beam (500 eV, 10 μA mm^{-2}) is used to remove impurities from the surface by means of sputter etching. In order to improve the adhesion, a tungsten interlayer of approximately 70 nm is deposited. After that a tetrahedral amorphous carbon layer of about 50 nm thickness is deposited using a pulsed arc discharge source; by the same method the a-C:D-layer is formed. During the plasma pulse the D/C ratio in the coating chamber near the surface of the substrate was about 50 and the average carbon flux around 2×10^{18} C^+ cm^{-2} s^{-1}. The density of the DIARC a-C:D-film is 2600 ± 100 kg m^{-3}, as measured by Rutherford backscattering spectrometry (analysis performed using 2.7 MeV He^4 ions obtained from 2.5 MV van de Graaff accelerator) and the ratio of sp^3/sp^2 bonds is typically 70%, as electron spectroscopy results indicate [5,6]. The final thickness of the codeposited a-C:D-layer is about 3.5 μm (according to SIMS, [5]) and the resulting D/C ratio is nearly 0.1 (after nuclear resonance broadening analysis [5]); the layer thickness throughout one sample is higher by 10–15% in the middle than at the ends, due to the characteristics of the point source used. The general experimental procedure was as follows: After placing the sample into the chamber, a sufficient base vacuum of a few μPa is created by pumping for about one day. After that, the temperature is increased to the chosen value and a 'pre-run' of some hours is made to check for the deuterium release due to thermal outgassing. Then the vacuum chamber of DEREX is filled with oxygen up to the chosen value, which starts the oxidation process. Basically the run consists of time dependent recording of the partial ionic current associated with gases CO_2, CO, D_2O, HDO, D_2 and HD. To take into account the noise effect due to the outgassing of the walls, a "blank run" without specimen is also made, under the same conditions of temperature, pressure and time. During this blank run the same gas species previously listed are monitored, to be subtracted afterwards from the run with the sample. The duration of an individual run was between one day and two weeks. At first, temperature (523–723 K) and to some extent the initial oxygen partial pressure (0.3 and 0.55 kPa) are successively changed stepwise on a single DIARC specimen as done before for the TEXTOR specimen in order to compare both kinds of material (type A experiments). Starting at $T = 523$ K, $p_{O_2} = 0.3$ kPa the specimen was oxidised for 24 h; after this run, we have changed T and p (temperature steps of 50 K) and this procedure was repeated, at least for the temperature, until significant D-release rates were found.

3. Results and discussion

Fig. 1(b) contains a SIMS-spectrum (C, D, H, O, metal) of DIARC layer in comparison with one of the before mentioned TEXTOR specimen, shown in Fig. 1(a). The crucial advantage of the laboratory produced specimen, the very homogeneous layer, appears clear; in contrast to that, there is a complicated depth profile of the relevant isotopes in the TEXTOR specimen, which results from strong variations in TEXTOR operation conditions. Regarding O and H profiles in the SIMS spectrum of the TEXTOR sample, one notices a high concentration, in particular on the outside, for H being even significantly higher than for D; O, H and D are going nearly parallel. We heated the specimen for several hours in vacuum at 523 K, because we wanted to prove, whether ad/absorbed water (penetrated during long term storage in air into the specimen) might be the cause for the O and H content, whose presence in such large amounts in relation to D is difficult to understand from formation history. At this temperature, all physisorbed and a substantial part of chemisorbed water should desorb, as it is known for steam/graphite interaction [7]. SIMS spectrum obtained after this vacuum heating did not show differences with respect to the spectrum of the untreated sample, so it has to be assumed that H and O are really ‘incorporated’ within the film; a similar observation was made in Ref. [8], showing significant H and O concentrations in an a-C:D-film up to a depth of 250 nm. Fig. 2 shows Raman spectra, which are often used for characterisation of these kinds of layers, of a DIARC specimen (one broad peak at about 1500 cm^{-1} with a shoulder at lower wave numbers, as it is typical for ‘diamond’ like carbon layers [9]), revealing significant differences with the spectrum of the TEXTOR specimen (consisting of two separate peaks at 1350 and 1580 cm^{-1}); the latter looks more like a spectrum of a graphitic material; Raman spectrum of polycrystalline graphite has two sharp peaks, the G-peak at 1585 cm^{-1}, originating from lattice vibrations in the plane of the graphite-like rings, and the D peak at about 1350 cm^{-1}, which occurs only in graphites with sufficient small crystal size and is forbidden in single crystals [9]. In addition, it should be noted that DIARC specimens are more sensitive on changing of the laser power (which induces the Raman emission and leads to a local tem-

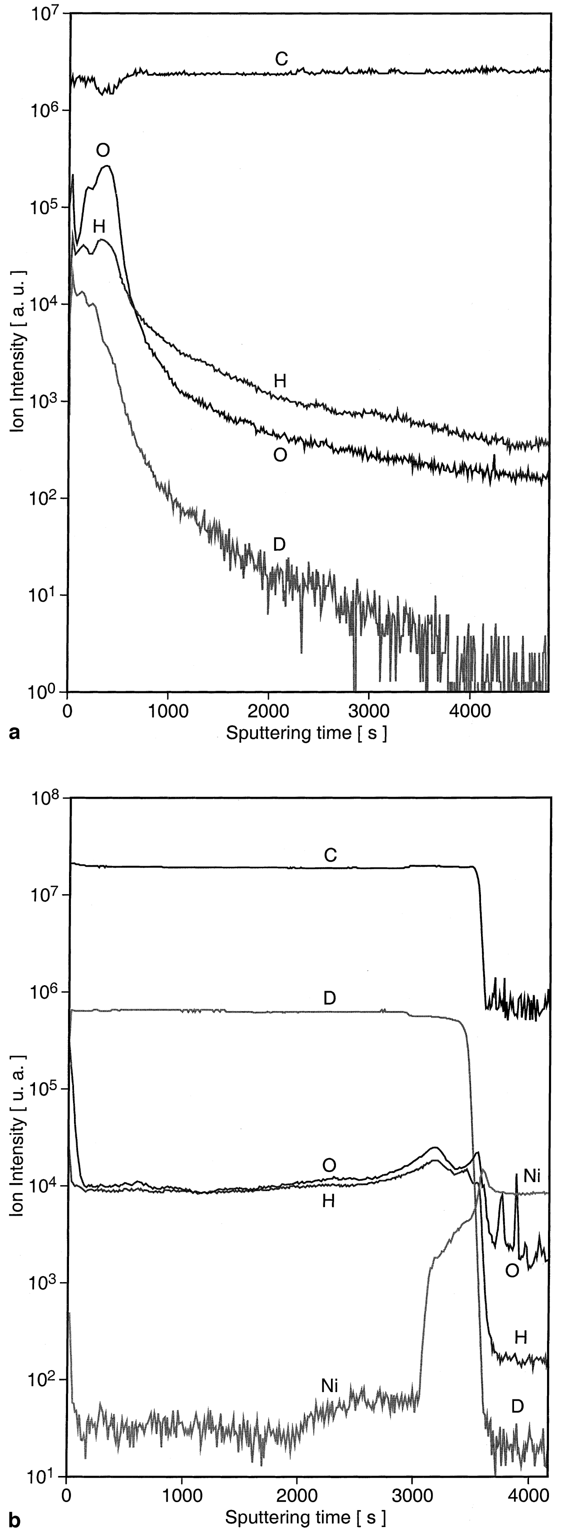

Fig. 1. (a) SIMS-spectra of virgin TEXTOR specimen, (b) SIMS-spectra of virgin DIARC specimen.

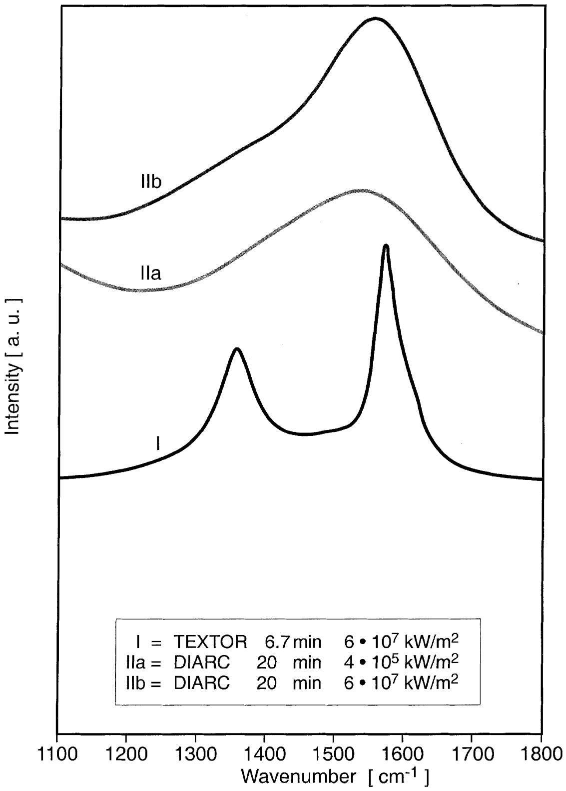

Fig. 2. Raman-spectra of virgin specimens.

perature change) in comparison with the TEXTOR specimen. Whereas the shape of the TEXTOR spectrum remains nearly unchanged when laser power is increased (except for slight reductions of band widths), a more remarkable change for DIARC specimen is observed, in the sense that it becomes more narrow. However, because the D/C ratio in the TEXTOR specimen examined was only about 0.03 in comparison with 0.1 for DIARC specimen, this result should not be generalised. Nevertheless, the differences in Raman spectra might be taken as an indication that sp^3/sp^2-ratio in DIARC is higher than in TEXTOR. It should be noted here that, with respect to classification of a-C:H-films, given in Ref. [10], TEXTOR specimen belongs, because of its Raman spectrum, probably to the GLHC (graphite-like hydrocarbon) layers, characterised by low H-content and low sp^3/sp^2-ratio, whereas DIARC specimens belong obviously to the diamond like hydrocarbons (DLHCs), characterised by high sp^3/sp^2-ratio but low H-content (hard films). The third group of films (polymer like hydrocarbons PLHCs) with low sp^3/sp^2-ratio but high H-content ($H/C \geqslant 1$), are rarely found in codeposited layers. Although there are no systematic examinations concerning the reactivity of these a-C:H-groups in oxidising gases up to now, the general tendency indicates a higher reactivity of layers with low sp^3/sp^2-ratio in comparison with those of high sp^3/sp^2-ratio.

Regarding TEXTOR, no significant D-release was found at $T < 573$ K; the maximum D-release rate at 623 K was 12% (of the total previous inventory)/day; oxygen partial pressure seems to be an important parameter, because it influences the D-release rate more than linear [2]. Even at lower temperatures (573 K) oxidation of the TEXTOR specimen resulted in a D-release of 5%/day which however did not last for longer than about 20 h.

Regarding the stepwise run, main parameters of this (type A) experiment are presented in Table 1; the results can be summarised for different temperature regimes. From 523 to 573 K gaseous reaction products of oxidation (HDO, D_2O, CO, CO_2) are not measurable, leading to the conclusion that in these conditions of temperature and pressure no oxidation occurred. In the second range 623–673 K a slight production of carbon oxides is measured, D_2O and HDO however still remain within or just over the detection limit. From production of CO_2 (though CO normally being only about 10–20% of CO_2), the reduction rate of the layer can be roughly estimated. By the CO_2 partial pressure curve measured with the calibrated QMF, the CO_2 related molecular flow is evaluated, taking the nearly linear beginning stage of the curve (Fig. 3, first 20 h). With reference to this point, it should be noted that, in case of carbon materials without pores, there is a small increase of gasification rate with burn-off only at the very beginning of the oxidation process; however, when equilibrium roughness is reached, the rate remains constant [11] and the strong dependence of rate on burn-off, as for porous carbons, is not found. Stated another way, the nearly constant rate assumed (and found) for DIARC, is in line with the expected behaviour for nonporous carbon materials. Now, by least square fitting and curve derivation, the related equivalent CO_2 molecular flow is obtained, which leads to a layer corrosion rate of a few nm/h in the experimental condition mentioned above (with some uncertainties, due to QMF calibration errors, gas-surface interaction processes and delays in gas transport to the QMF head). Interpreting the curves in Fig. 3 one should bear in mind, that the gas admission to QMF proceeds via differential pumping: At the first 20 h, the oxidation induced flow is higher then that one which is pumped away through the QMF (this one being limited by the QMF conductance); after that the former decreases, because a substantial part of the layer is already oxidised and in some parts the metal substrate is reached.

A significant D-release was found at 723 K, 0.55 kPa. The partial pressures of the gaseous reactants in the vacuum chamber of DEREX are shown for this run in Fig. 3. Because of the pronounced effect, we prolonged the measuring time for these conditions to 200 h. D_2O was well detectable by the QMF but HDO was the main

Table 1
Experiments on DIARC specimens

Temperature (K)	p_{O_2}[a] (Pa)	Time (h)	D_2O release	HDO release	CO release	CO_2 release
Type A: Stepwise						
523	300	24	not measurable	not measurable	not measurable	not measurable
573	300	24	not measurable	not measurable	not measurable	not measurable
573	550	24	not measurable	not measurable	not measurable	not measurable
623	300	24	not measurable	not measurable	not measurable	not measurable
623	550	24	not measurable	not measurable	not measurable	not measurable
623	550	24	in the detection limit	in the detection limit	little	little
673	550	24	in the detection limit	little	little	little
723	550	200	release	strong release	strong release	strong release
773	550	72	going down	going down	going down	going down
823	550	24	in the detection limit	in the detection limit	going down	going down
Type B: Constant conditions						
523	4500	376	not measurable	not measurable	in the detection limit	in the detection limit
523	9000	261	not measurable	not measurable	in the detection limit	in the detection limit
623	4500	70	not measurable	little	little	release
623	9000	136	in the detection limit	little	embrittlement of the layer	
673	4500	200	release	strong release	strong release	strong release

[a] Initial $p_{O_2} = p$

D component generated; under the aforementioned conditions the HDO pressure was about one order of magnitude higher than the D_2O one. This is different from former measurements on the TEXTOR specimen, where D_2O was the main oxidation product of D. This difference is probably due to the fact that we did not bake DEREX before the run on the DIARC specimen (as it was done in experiments on TEXTOR samples); accordingly, the H_2O concentration in the runs on DIARC samples was around 1–2%, while for TEXTOR it was about 0.2%. HDO is probably formed via isotope exchange reactions from D_2O and H_2O; chemical equilibrium rules require that an increase of H_2O concentration will lead to an increase of HDO concentration too, as found in our experiments. It should be noted that a high H_2O concentration (as in the experiments on DIARC specimen) is more near to the conditions of a real fusion reactor cleaning procedure; this more realistic H_2O concentration might lead to more realistic results, because it is known that water concentration can influence oxidation processes (via the OH radical formed). There are even some speculations, that the hydrogen release from codeposited carbon/hydrogen layers in air of normal humidity is mainly caused by the moisture content and not by oxygen [12]. A CO/CO_2 ratio of about 0.19 was detected for the DIARC specimen at 723 K, 0.55 kPa. The layer reduction rate was estimated to be 55 ± 25 nm/h for this particular experiment, while the D-release was in the order of 10 ± 4%/day (the uncertainty scatter of these values will be reduced by NRA post analyses, which are under way). Comparing this value with such for TEXTOR specimen one should bear in mind that the D content per surface is, on an average, higher by (at least) a factor of 3 in DIARC specimen. After this run the temperature was increased two times by 50 K in order to show that the D-release was complete. In both cases the D-release rate went down significantly with time, indicating that most D was gone. As additional information, only very little amount of HD and D_2 were recorded, the D oxides being the most favourite products in this processes. Compared with the TEXTOR sample, the DIARC specimen needs temperatures higher by about 100 K in order to induce a significant release. This different behaviour might be due to the different characteristics of both kind of specimens, which are documented in the earlier sections. A sufficient correlation between structure parameters of the layer and oxidation cannot however be given at the moment. Another experimental difference is found for the CO/CO_2 ratio, which in case of the TEXTOR specimen was about a factor of 2 higher; this might be due to the aforementioned smaller

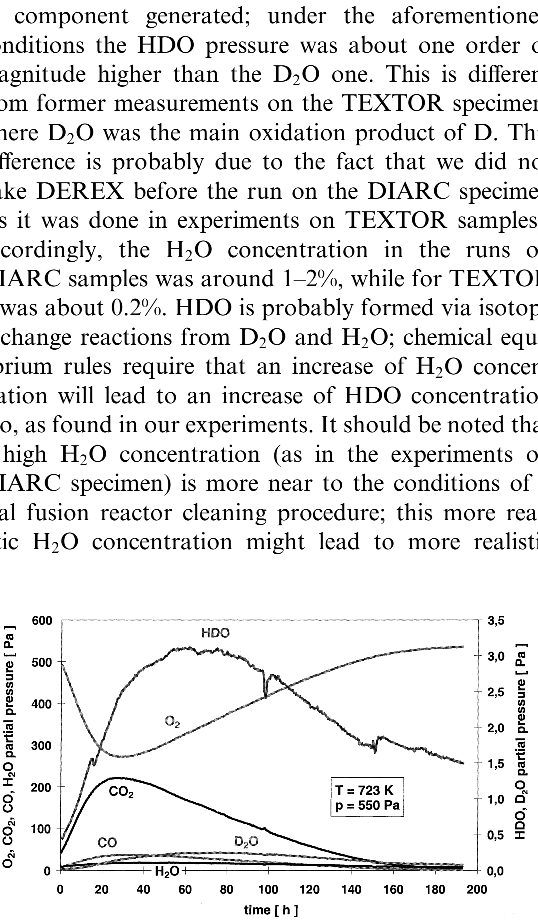

Fig. 3. Time dependence of the gaseous reactants.

concentration of H_2O during the measurements on TEXTOR specimen, because it is well known that water catalyses the oxidation of CO to CO_2 [13]. Regarding the HDO release curve, whose maximum occurs delayed in comparison with the minimum of O_2 (this one coincident with the maximum of CO_2 and CO) as shown in Fig. 3, two reasons are possible: (a) The HDO transport is affected by ad/desorption at the QMF head (being at room temperature during the run). (b) HDO formation proceeds non simultaneous to the carbon oxidation; a non simultaneous release of D and C was indeed found in Ref. [14], but, in contrast to this, with a delayed release of the C components. A deeper investigation with respect to this aspect must be performed in order to understand this delay.

A second set of experiments were conducted under fixed T–p conditions for each DIARC sample, allowing a more detailed analysis due to the fact that starting conditions are always the same (Table 1 type B). At $T = 523$ K and $p = 4.5$–9 kPa no product gases of oxidation were detectable, even though the run was performed up to 376 h. The first, although little, D-release was detected not earlier than at 100 K higher temperature, whereas a significant CO_2-release was observed within an experimental time of 70 h. This run was repeated with another sample for 136 h at 20 kPa, but here also the HDO release rate was just a little bit higher than the detection limit of the quadrupole. However, after this run the surface of the film (which in the virgin state looks nearly 'mirror-like') was clearly embrittled, with very little amount of black powder left on the sample holder. To prove whether this embrittlement was due to the oxidation process or due to the temperature exposure itself, an additional experiment on a new specimen was performed for four days in the same condition of temperature but under ultra high vacuum conditions. As a result, the film surface was still mirror-like as it was at the beginning, indicating that the embrittlement/powder formation phenomenon clearly arises from oxidation under high oxygen pressure conditions. It appears quite obvious that this embrittlement may affect the detection of the gas species, as indicated in Table 1. The final analysis was performed at $T = 673$ K and $p = 4.5$ kPa for 200 h. The embrittlement/powder formation was observed too, but, due to the higher oxidation rate obtained here, well defined ion partial current was recorded. A layer reduction rate of 7 ± 3 nm/h was calculated from the gasified carbon and a corresponding D-release rate of about 5 ± 3%/day was found, being about one half of that found for type A experiments at $T = 723$ K, $p = 0.55$ kPa. A CO/CO_2 value of 15% was detected for this run. The burst-like release observed for TEXTOR specimen in oxygen [2] at 50 K below the temperature where continuous release occurred, was not observed for DIARC specimen; however, it is not yet clear whether this is a general different behaviour or if such a burst-like release occurs perhaps within the temperature step of 50 K. Nevertheless, this is in line with the homogeneous structure of DIARC samples. Burst-like release has to be expected if, within the material, exist fractions with significant different activation energies concerning the oxidation or release process. This explanation has to be supported by additional experiments. Also, during these experiments the formation of HD and D_2 was seen just within the limit of detection, coherently on what it has been observed for the stepwise runs.

4. Conclusion

Comparison of oxidation data for a sample from TEXTOR with laboratory created DIARC specimen indicates that the latter requires 100 K higher temperature than the TEXTOR specimen for a high, constant D-release; this is probably due to difference in the microstructure of the layers, with DIARC specimen probably being more diamond like (larger sp^3/sp^2-ratio) than the TEXTOR sample. However, more extensive examinations are necessary in order to understand the D-release rates in relation to microstructural parameters. Accordingly, other kinds of specimen should be examined in DEREX, too. We plan to measure in the future, specimen from TFTR, carbon flakes from TEXTOR and TEXTOR specimen containing some Si in the a-C:D-layer also.

Concerning minimum temperatures for total release of D from a-C:D-layers in oxygen, it becomes more obvious that even at high oxygen partial pressures, at least 623 K is necessary. Because lower temperatures are more easy to handle in a machine like ITER during a cleaning procedure, it seems worthwhile to examine more reactive gases like ozone too.

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