Thermo-oxidation to remove re-deposited layers and to release trapped hydrogen isotopes in HT-7 superconducting tokamak

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Abstract

Thermo-oxidation between 0.7 Pa and 32 Pa at wall temperatures of 400–470 K has been investigated in the HT-7 superconducting tokamak. During the oxidation process, deposited carbon layers were removed by the formation of CO and CO_2 and the incorporated hydrogen was released in the form of water molecules. A significant fraction of the injected oxygen was also absorbed on the walls. The overall amount of adsorbed oxygen is nearly linear with the filling pressure. The results of the thermo-oxidation experiment in HT-7 were similar to those in TEXTOR. High wall temperature and high oxygen pressure are helpful in removing carbon co-deposits and releasing trapped hydrogen.
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1. Introduction

The long-term retention of tritium fuel in the surface or bulk of plasma facing materials in fusion devices is one of the major problems in fusion technology. It has been concluded from various investigations that the dominant mechanism for hydrogen retention is co-deposition of carbon with deuterium with carbon walls [1,2]. The retention of a large fraction of input hydrogen isotopes was observed in TFTR [3], TEXTOR [4] and JET [5,6]. Tritium removal from amorphous tritiated carbon layers, a-C:T, co-deposited in the next generation tokamaks, such as ITER, will have an important impact on machine operation. If in situ co-deposit removal techniques are fast and effective, both in terms of T removal and plasma performance recovery after cleanup, the long term T retention/inventory problem could be mitigated [1].

The removal of T from thick a-C:T co-deposits may require the removal of the co-deposits themselves. This can be done by chemical and/or plasma assisted oxidizing reactions in the presence of oxygen or, alternatively, via abrasive/mechanical techniques [1]. Extensive laboratory studies of hydrogen isotope removal on exposing co-deposited films and D implanted graphite to air or oxygen have led to the following conclusions [7–12]: (1)

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the release of D occurs in conjunction with C erosion; (2) the D removal and C erosion rates depend strongly on the film structure; (3) the D release rate during oxidation is a critical function of annealing temperature and is significant well below 900 K, the temperature needed for thermal desorption in vacuum [13]. Significant oxidation rates could be achieved in the temperature range between 520 and 750 K, depending on the type of carbon film or carbon deposit [8–11,14]. At these temperatures, the graphite bulk material is not significantly attacked by the oxygen [17,18]. In laboratory experiments involving the oxidation of carbon films, it has been concluded that the film is removed by the formation of CO and CO_2 and the incorporated hydrogen is released in the form of water molecules [10]. No significant release of hydrogen molecules or hydrocarbons has been observed. Similarly, no release of molecular hydrogen by oxidation could be identified within the sensitivity of the present measurement. Release of hydrogen species in form of water was expected as H_2O (mass 18), HDO (mass 19) and D_2O (mass 20) in the case of ^{16}O injection [2].

Very few experiments involving the injection of oxygen directly into tokamak for the purpose of removing co-deposits have been reported. Oxidation of the TEXTOR torus with oxygen pressures between 0.7 Pa and 32 Pa and wall temperatures between 500 and 700 K has been reported by Philipps [2]. It was observed that a significant part of the injected oxygen adsorbed on the walls due to formation of stable oxygen compounds. The behavior of the CO_2/CO ratio was in agreement with laboratory observations [11]. A significant increase of the water partial pressure was also observed by the differential pumped quadrupole mass spectrometers.

The oxidation experiments that have been carried out in the HT-7 superconducting tokamak include oxidation associated with ion cyclotron resonance discharge and glow discharge cleaning (O-ICR and O-GDC) [19,20], and thermo-oxidation with molecular oxygen. The objective of the experiments is to compare the removal rate of hydrogen and carbon for the different oxidation procedures. Before the oxidation experiments, the HT-7 tokamak with the carbon limiter had been operated in deuterium for more than ten thousand plasma discharges. At first, the O-ICR experiments were done for about 196 min. Then after 50 min He-ICRF cleaning, the plasma discharges in deuterium were performed

for about 200 shots. Later, the O-GDC and thermo-oxidation experiments were carried out. After O-GDC and thermo-oxidation experiments, the HT-7 machine was shut down for maintenance without trying to recovery plasma discharge.

The O-ICR experiment was performed in HT-7 in the presence of a permanent magnetic of field 1.5–2.0 T. The influence of ICRH power and filling pressure on hydrogen and carbon removal rates was analyzed. The highest removal rates of H, D and C-atoms up to 2.64×10^{22}, 7.76×10^{21} and 1.49×10^{22} atoms/h respectively were obtained in 40 kW 9×10^{-2} Pa O-ICR cleaning, corresponding to the removal rate of co-deposits of about 317 nm/day (7.2 g/day for carbon). After 50 min He-ICR cleaning followed the O-ICR experiment, normal plasma discharges could be recovered after a few tens of disruptive plasma discharges [19]. In the absence of magnetic fields, the O-GDC experiment had produced rapid, controlled co-deposit removal. Average removal rates, 5.2×10^{22} H-atoms/h, 5.65×10^{21} D-atoms/h and 5.53×10^{22} C-atoms/h, respectively, were obtained in 145 min O-GDC experiment in a pressure range of 0.5–1.5 Pa. The corresponding removal rate of co-deposited films was 1.19 μm/day (26.5 g/day for carbon) on an area of 12 m^2. The removal rate of H-atoms in He-GDC cleaning after O-GDC experiment was lower than that in He-GDC cleaning before O-GDC experiment, which indicates that the O-GDC wall conditioning had effectively reduced hydrogen retention on the walls [20].

In this paper, the results of thermo-oxidation experiments will be presented. Emphasis is on the formation of carbon oxides (CO and CO_2) and hydrogen release for various oxygen pressures. A short comparison with the oxidation of TEXTOR is presented in this paper.

2. Experimental set-up

HT-7 is a medium sized superconducting tokamak with a major radius of 1.22 m. The plasma is limited at $r = 27$ cm (minor plasma radius) by two toroidal limiters (located at top and bottom in the vessel) and one belt limiter (located at mid-plane on the high field side). The total plasma facing surface area of the HT-7 limiters is about 2.35 m^2. The materials of the limiters are made from doped graphite (GBST1308: 1%B, 2.5%Si, 7.5%Ti) with a 100 μm SiC coating [15,16]. The rest of the plasma facing surface (linear) is made of stainless steel with

a minor radial $r = 33$ cm. The effective plasma facing area of the limiters and liner is about $12 \, m^2$. The total volume of HT-7 is about $4.85 \, m^3$.

Oxidation experiments with all pumping turned off have been performed with filling the torus with pure oxygen (99.95%) to a given pressure. The time evolution of the total and partial pressures were monitored by differentially pumped quadrupole mass spectrometers. The pressure of oxygen in the filling tank was monitored with an APR262 compact Piezo gauge. Two PKR251 penning gauges were used to monitor the total pressure in the HT-7 vessel and the differential pumped chamber respectively. A needle valve was installed between the differential pump system and the HT-7 vessel. The differential pump system was connected to the main HT-7 chamber by a bellows tube, 1 m in length and 40 mm in diameter, which was baked to above 100 °C during the oxidation experiment. Temperatures in the limiter tiles and on the liner were measured by 12 thermocouples.

The procedure for oxidation in HT-7 was similar to that followed in TEXTOR. The liner was heated by direct current and the limiters were heated by thermal radiation from the liner. During the experiment, the temperature of the limiter was 402–425 K and that of the liners was 435–470 K. The initial oxygen pressures in the HT-7 vessel were filled to 0.7 Pa, 1 Pa, 9.3 Pa and 32 Pa, respectively.

3. Experimental results

3.1. Low pressure oxidation

In both low pressure oxidation experiments, 0.7 Pa and 1.1 Pa, the oxidation behavior was similar. Fig. 1 shows the typical evolution of the total pressure and the partial pressures (defined as P.P) of O_2, CO and CO_2 following the filling with O_2 up to a pressure of 1.1 Pa. This oxidation, lasting 104 min, immediately followed the oxygen injection at 0.7 Pa. The P.P of CO and CO_2 increased simultaneously with oxygen filling. At about 10 min after oxygen admission, the P.P of CO and CO_2 rise only slowly. Within 104 min after the oxygen admission, the P.P of CO and CO_2 reached about 0.21 Pa and 0.13 Pa respectively. The rate of oxygen consumption was faster than the decrease in total pressure. The strong decrease of the oxygen pressure showed that at these conditions (low filling pressure), most of the oxygen was adsorbed on the walls. Of the 1.87×10^{21} oxygen atoms injected, about $1.42 \times$
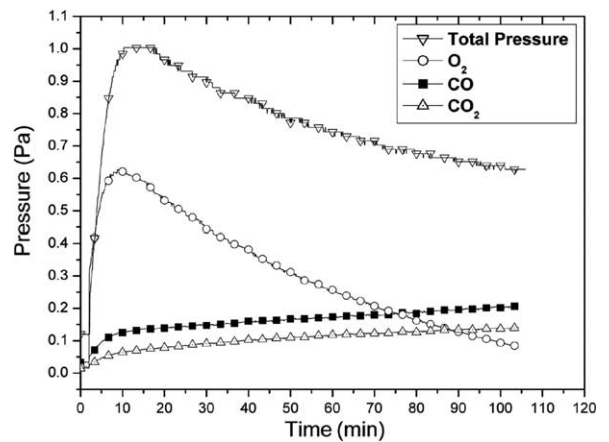

Fig. 1. The evolution of the total and the partial pressures of oxygen, CO and CO_2 following the filling with O_2 up to a pressure of 1.1 Pa (this oxidation immediately followed an oxidation at 0.7 Pa).

10^{21} was absorbed on the walls, 1.25×10^{20} and 1.82×10^{20} were converted into CO and CO_2 respectively (as shown in Table 1). 3.9×10^{19} O-atoms were converted into H(D)–O compounds and 1.08×10^{20} O-atoms were remained as oxygen molecules (O_2) in the HT-7 vessel, as listed in Table 1.

Fig. 2 shows the typical evolution of the P.Ps of the CO, H_2O, D_2O and HDO during 1.1 Pa oxidation experiment. The O_2 injection caused a rapid increase of H_2O, HDO and D_2O within the first few minutes. Although the CO, CO_2, HDO and H_2O signals continue to increase, the P.P of D_2O stayed nearly constant or even decreased with time. The decreasing P.P of D_2O meant that it was being absorbed on the wall surfaces (all pumps are closed!), most probably on cold surface of the HT-7 first wall [vacuum wall and in particular port holes, valves etc., which are kept in much lower temperatures (<320 K)]. Although oxidation clearly produced amount of water molecules, it was difficult to calculate hydrogen or deuterium released because some fraction of the produced water was absorbed on the wall. Assuming no re-absorption of water on the walls, of the 1.87×10^{21} O-atoms injected, about 3.88×10^{19} O-atoms were converted into H(D)–O.

Fig. 3 shows the temporal evolution of CO, CO_2 production rates and O_2 filling rate and consuming rate for the 1.1 Pa experiment, evaluated from the derivative of the pressure rise. A rapid decrease of the reaction occurs during the first 10 min when the oxygen filling showing that the reaction is only transient. The highest production rates of CO and

Table 1
Summary of thermo-oxidation experiments performed at the liner temperature of 450 K in HT-7

| Filling pressure (Pa)	Injected O-atoms $\times 10^{20}$	Exposure time (min)	O-atoms $\times 10^{20}$ and percent of injected O-atoms					Corresponding coverage (10^{16} O-atom/cm^2)
			Adsorbed	O in CO	O in CO_2	O in H(D)–O	O in O_2	
0.7	12.5	46	11.8 94.4%	0.16 1.29%	0.196 1.57%	0.034 0.27%	0.311 2.48%	0.98
1.1	18.7	104	14.16 75.7%	1.25 6.69%	1.82 9.77%	0.388 2.07%	1.08 5.76%	1.18
9.3	222	127	139.6 62.9%	4.45 2%	2.8 1.26%	4.65 2.01%	70.5 31.7%	11.6
32	630	121	306 48.6%	3.13 0.5%	5.67 0.9%	3.33 0.53%	312 49.5%	26
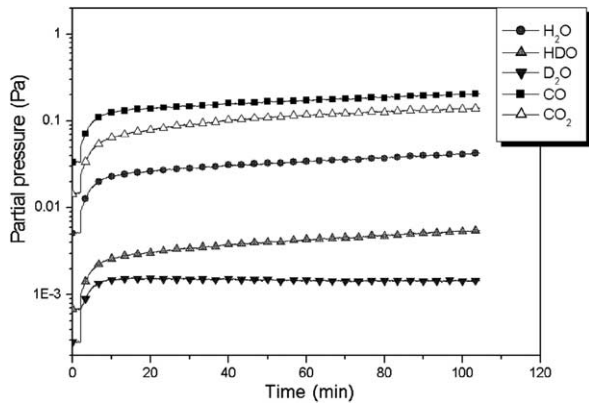
Fig. 2. Typical behavior of partial pressures of CO, CO_2, H_2O, D_2O and HDO during the 1.1 Pa oxidation experiment.
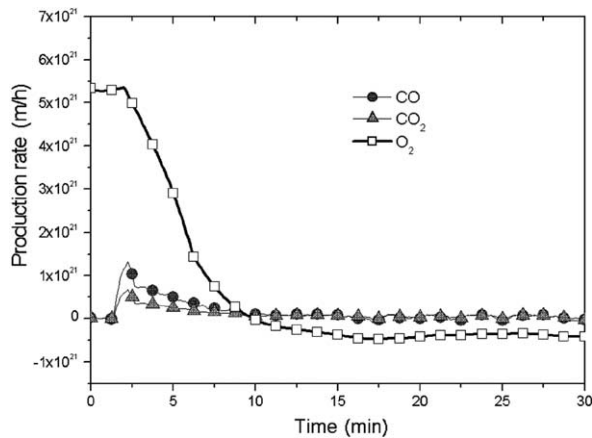

Fig. 3. Temporal evolution of CO, CO_2 production rates and O_2 filling rate and consuming rate for the 1.1 Pa oxidation, evaluated from the derivative of pressure rise.

CO_2 were 1.3×10^{21}, and 6.5×10^{20} molecules/h, respectively in 1.1 Pa oxidation at 2.5 min after the admission of oxygen.

3.2. High pressure oxidation

In the high pressure oxidation experiments, 9.3 Pa and 32 Pa, the oxidation behavior is similar to those at lower pressures. Fig. 4 shows the typical the evolution of the P.Ps of the important molecules following the filling with O_2 up to a pressure of 32 Pa. In this oxidation, the oxygen partial pressure decreased very slowly. During the 120 min of the experiment the O_2 pressure decreased from 32 Pa to 25 Pa, and the CO and CO_2 partial pressure increased to 8.2 and 7.3 Pa respectively. The H_2O and D_2O partial pressure increased to 0.49 and 0.04 Pa respectively.

Similar to the low pressure cases, the P.Ps of HDO and D_2O stayed nearly constant or decreased during the 32 Pa oxygen ventilation. The decrease of P.Ps of HDO and D_2O showed that the water molecules were being absorbed on the wall surfaces,
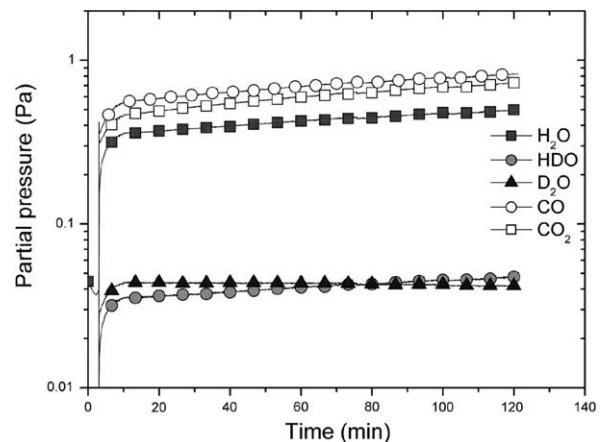

Fig. 4. Typical behavior of the evolution of the P.P of a few molecules following the filling with O_2 up to a pressure of 32 Pa (this oxidation immediately followed an oxidation at 9.3 Pa).

most probably on colder areas of the HT-7 first wall. Assuming no re-absorption of water on the walls, of the 6.3×10^{22} oxygen atoms injected, about 3.06×10^{22} were absorbed on the walls, 3.13×10^{20} and 5.67×10^{20} were converted into CO and CO_2 respectively. 3.33×10^{20} atoms were converted into hydroxides and 3.12×10^{22} O-atoms remained as O_2 in the HT-7 vessel, see Table 1.

The highest production rates of CO and CO_2 were 7.1×10^{22} and 5.4×10^{22} molecules/h, respectively during oxygen filling. In contrast to the 1.1 Pa oxidation experiment, a rapid decrease of the reactions occurred after only a few tens of seconds in the 32 Pa experiment.

3.3. Comparison of the HT-7 and TEXTOR thermo-oxidation experiments

HT-7 and TEXTOR (both carbon limiter toka-mak devices) have performed thermo-oxidation experiments with similar pressure pure oxygen in both tokamak. The liner was heated by direct current and the limiters were heated by thermal radiation from the liners; The temperature of the limiters were typically 30 K lower than that of the liner. Differences between the devices are: the area of plasma facing surface of the carbon limiters in HT-7 is $2.35 \, m^2$ whereas it is $3.5 \, m^2$ in TEXTOR, while the effective area of plasma facing surfaces of the limiter and liner in HT-7 is about $12 \, m^2$ whereas it is $35 \, m^2$ in TEXTOR. Also, the wall temperature in the thermo-oxidation of TEXTOR was about 500–700 K compared to 400–470 K in HT-7. Table 1 summaries the results from the oxidation experiments of HT-7; Table 2 gives the summary of the oxidation experiments performed at a liner temperature of 610 K in TEXTOR [2].

In general, the time evolution of various partial pressures followed the same trends in both HT-7 and TEXTOR, with the P.Ps of all oxides increasing rapidly following the admission of oxygen. A significant part of the injected oxygen was absorbed on the walls or formed stable non-volatile compound. The absorption of O_2 on the walls of TEXTOR appears to saturate at high pressures. However, this effect was not observed in HT-7. This may be due to the lower volume to surface area ratio and lower wall temperature in HT-7.

The temperature in TEXTOR was somewhat higher and surface area of the walls is larger, possibly contributing to the increased CO and CO_2 production. Especially during high pressure oxidation, the formation of CO_2 was greater than that of CO in the TEXTOR experiment, whereas the formation of CO was higher than that of CO_2 in the HT-7 experiment. It seems that the higher wall temperature leads to the CO transferring to CO_2. It was also found that in the TEXTOR experiment, the higher the filling pressure, the higher the ratio of CO_2 to CO formation. In the 32 Pa oxidation, the ratio is 3.15 whereas at 0.7 Pa that the ratio is 0.76 in TEXTOR. Similar results were found in HT-7; at 32 Pa, the ratio is 0.9 whereas at 0.7 Pa that the ratio is 0.63. The phenomenon was also observed in the formation of HDO and D_2O.

The maximum production rates in HT-7 were sustained for a shorter time than that in TEXTOR. The total production of oxides in TEXTOR was formed also higher than that in HT-7. For example, within 2 h 32 Pa oxidation experiment, the amounts of CO and CO_2 were 3.3×10^{21} and 1.04×10^{22} molecules in TEXTOR whereas there were 3.13×10^{20} and 5.67×10^{20} molecules, respectively, formed in HT-7.

Table 2
Summary of thermo-oxidation experiment performed at liner temperature of 610 K in TEXTOR [2]

| Filling pressure (Pa)	Injected O-atoms $\times 10^{21}$	Exposure time (min)	O-atoms $\times 10^{20}$ and percent of injected O-atoms			Corresponding coverage (10^{16} O-atom/cm^2)
			Absorbed O-atoms	Formed CO	Formed CO_2	
0.7	2.88	7	27.2 94.4%	0.63 2.2%	0.48×2 3.3%	0.77
1.1	4.6	20	37 80.4%	0.87 1.9%	1.2×2 5.3%	1.0
9.3	38	100	228 26.3%	5.13 1.35%	9.3×2 4.9%	6.5
32	130	120	280 21.5%	33 2.6%	104×2 16%	7.0

4. Discussion

The experimental conditions for the oxygen experiment in the HT-7 are very complex, but similar to the TEXTOR experiment [2]. The heated area of the wall components facing the plasma is about 12 m^2 with a similar area not facing the plasma. The temperatures of the components facing the plasma, limiters and liner varied from 410 K to 490 K among graphite tiles on the limiters. Additionally, the vacuum vessel has an even larger area reaching a temperature lower than 370 K. Before the oxidation experiment, the distribution and the character of the carbon deposit was not clear. After the oxidation experiments carbon deposits were observed mainly on the surface of the graphite tiles; very little deposition was observed on the liner.

In the thermo-oxidation experiments, it can be concluded that carbon deposits are removed by formation of CO and CO$_2$ and the incorporated hydrogen is released in the form of water molecules. No significant release of hydrocarbons has been observed. The release of hydrogen species was in form of water (H$_2$O (mass 18), HDO (mass 19) and D$_2$O (mass 20)) similar to laboratory oxygen results [7–12].

The decreasing partial pressures of HDO or D$_2$O indicate the absorption of water on wall components with lower temperatures. Because this absorption is not easy to estimated, the amount of hydrogen released during the experiments could not be calculated with certainly. In the thermo-oxidation experiment of HT-7, the calculated formation of water species was only from gas status. The absorption of water on the walls is the main obstacle to understanding the release of hydrogen.

During the oxidation experiment, the influence of oxygen pressure and wall temperature on the formation of oxides depends on the free energy changes of following reactions:

$$C + \frac{1}{2}O_2 \rightarrow CO, \quad C + O_2 \rightarrow CO_2$$

$$CO + \frac{1}{2}O_2 \rightarrow CO_2$$
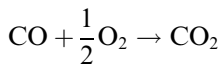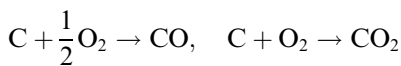
The free energy change is related to the P.P. of oxygen, carbon mono-oxide and carbon dioxide

$$\Delta G = -RT \cdot \ln[P(CO_2)/(P(CO) \cdot P(O_2)^{1/2})].$$

This indicates that a higher P.P. of O$_2$ increases CO$_2$ production and that the consumption of O$_2$ decelerates the CO$_2$ production. Taking the former two

Eqs., the ratio of CO$_2$/CO production depends on the temperature and P.P. of O$_2$. The formation of CO$_2$ is possible from CO given a high enough oxygen pressure, as shown in Fig. 5. In HT-7, the formation of CO was always higher than that of CO$_2$; however, the higher the oxygen pressure, the closer the P.P of CO$_2$ is to that of CO consistent with this mechanism. The influence of wall temperature during oxidation on the formation of oxides and on the amount of oxygen absorbed may also be drawn from a comparison between the experiments in HT-7 and TEXTOR. The high wall temperature favored the formation of CO$_2$, as noted in Section 3.3.

Most oxides were formed on the admission of oxygen in short transients. In contrast, oxides were continually formed during O-ICR and O-GDC wall conditioning [19,20]. Thermo-oxidation with molecular oxygen will clearly have a smaller effect on the removal of co-deposits than O-ICR and O-GDC wall conditioning. However, thermo-oxidation has
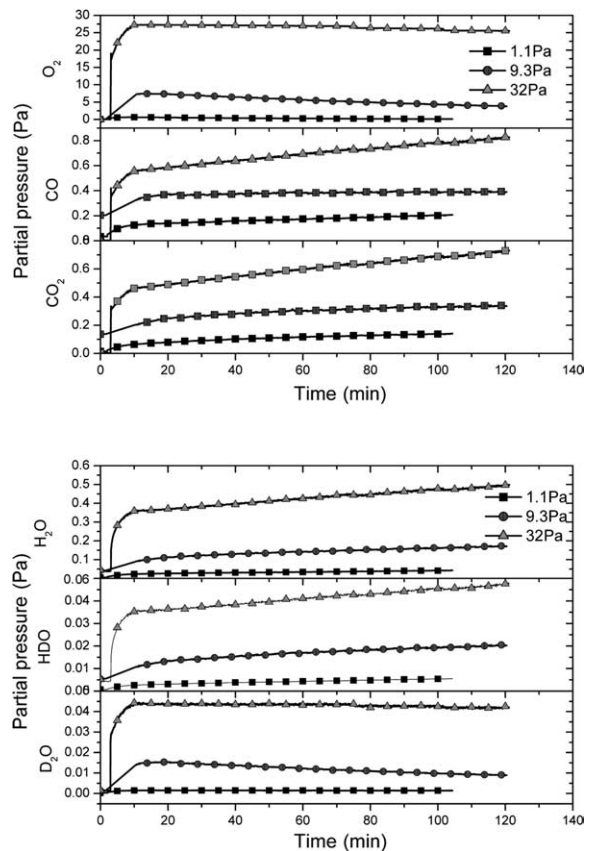

Fig. 5. Comparison between oxidation experiments with 1.1 Pa, 9.3 Pa and 32 Pa oxygen.

the advantage of being equally effective on all wall surfaces, whereas the O-ICR and O-GDC are most effective on surfaces with line-of-sight to plasma. Thus thermo-oxidation may be required to remove co-deposits on the less accessible places, such as tile gaps and other non-plasma facing surfaces. Additionally, thermo-oxidation could be carried out in high oxygen pressure whereas the pressure was limited during O-ICR and O-GDC wall conditioning. For example, during O-ICR in HT-7 the total pressure was required lower than 0.1 Pa to avoid wave reflection; and during O GDC in HT-7 the total pressure was required lower than 1 Pa to avoid influence the turbo-pump operation.

Before oxidation experiments, the HT-7 has been operated largely with deuterium, however, more H than D was observed in the released species in different oxidation procedures, including O-ICR, O-GDC and thermo-oxidation. The possible reason is that deuterium may be only concentrated in the co-deposits or carbon limiter whereas hydrogen would come from all walls, especially stainless steel components would provide a permanent H source.

5. Summary

Oxidation of the HT-7 tokamak was carried out with oxygen pressures between 0.7 and 32 Pa, at wall temperatures of 400–470 K.

During thermo-oxidation, the productions of CO, CO_2 and water were observed; hydrocarbons were not observed. The deposited layer was removed by the formation of CO and CO_2 and the incorporated hydrogen was released in the form of water molecules. The P.Ps of all oxide transient increased at the admission of oxygen. The thermo-oxidation could remove the co-deposits on a broad surface of walls.

The largest effect was the absorption of oxygen on the walls of the vessel, accounting for as much as 94% of the O_2 admitted to the vessel. The wall coverage increased approximately linear with the filling pressure.

The temperature and surface of the walls, possibly contributing to the CO and CO_2 production,

which maybe the main reasons of the difference between results in HT-7 and TEXTER.

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