CLEANING OF TOKAMAK WALLS BY RG-DISCHARGES IN HYDROGEN

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ABSTRACT

The efficiency for the deoxidation of SS 304 surfaces via the formation of H_2O in a combined rf- and glow discharge in hydrogen (RG-discharge) has been measured previously /11a/.
The observed dependency of the cleaning rate as a function of the wall temperature, the glow discharge current and the pumping speed can be described quantitatively in terms of a simplified model. Herein this rate is determined by the balance of the rates for H_2O formation and release from the wall, its dissociation in the plasma and the reoxidation of the wall. The model will be presented and compared with the experimental data.

1. INTRODUCTION

The presence of low Z impurities, mostly carbon and oxygen, influences strongly the temperature and the confinement of tokamak plasmas /1/. The concentration of C and O in stainless steel or inconel walls - generally used in fusion devices - is low; it is however well established /2, 3/ that the surfaces of these metals are covered with a layer of C- or O-rich compounds, which have a thickness of several tens of Å. It respresents a finite reservoir of C and O, if these substances can be released into the plasma.
As has been shown previously /4, 5/, chemical reactions between the surface impurity layer and the atomic hydrogen which has escaped from the plasma lead to the appearance of significant amounts of water, carbon oxides and hydrocarbons. Clearly, in situ prehandling procedures must be applied to remove the surface layers if oxygen and carbon free plasmas are to be obtained. A review /6/ has described the recent developments in this area.
Plasma discharges in hydrogen are well adapted to the cleaning task provided that the plasma temperature and density are maintained at sufficiently low values to avoid an appreciable dissociation and ionization of the released impurity molecules. Taylor discharge cleaning (TDC) /7/ and glow discharge cleaning (GDC) have been successfully, and an important reduction in the low Z contamination of tokamak discharges was obtained. Both led to appreciable release of hydrocarbons and CO. In TDC, the release of H_2O has been reported; in GDC, water release was practically undetectable in experiments such as ASDEX /8/ and PDX /9/, whereas significant H_2O release was reported in simulation experiments /5/ and in TFR 600 /10/.
The parametric variation of the cleaning efficiency in a glow discharge has been studied recently in an simulation experiment /11a/. Particular emphasis has been laid on the investigation of the deoxidation channel via water formation since it represents the only simple way to deoxidize a surface which has been decarburized beforehand. This will be the case of a tokamak which has been air-flooded after prolonged operation. The variables which determine the deoxidation effectivity via H_2O release have turned out to be the wall temperature T_W, the glow discharge current density j_{GD}, the pump speed S_p and the hydrogen pressure p_2. In order to operate a discharge at the desirable low hydrogen pressures, a combined rf- and glow discharge (RG-discharge) has been developed.
In the following chapters experimental results are summarized (they are described in more detail in /11a/). The variation of the H_2O cleaning efficiency as a function of the above mentioned parameters will then be discussed in terms of a simplified model. Here, the different production and destruction mechanisms of water in the discharge are considered.

2. DESCRIPTION OF THE EXPERIMENT

The apparatus wherein the simulation experiment had been performed consisted basically of a glow discharge vessel (GDV) of 45 cm diameter and 120 cm length, made from stainless steel 304 (inner area ≈ 2 m²).
A radiofrequency system allowed to initiate and maintain an rf-plasma discharge in H_2 at low pressures (10^{-3} torr). A dc voltage could be applied between the rf-coil and the vessel walls which modified the discharge into a hollow cathode glow discharge (RG discharge).
A residual gas analyzer which has been added via a connection tube to the GDV allowed to observe the volatile impurity compounds such as H_2O. In order to condition the RGA it could be heated up and pumped seperately.
The apparatus allowed to vary and to measure practically independently of one another

- the temperature T_W of the wall of the GDV up to 600 °C,
- the pump speed S_p using a throttle valve in general and lN_2 cryopump in the particular case of H_2O,
- the current density j_{RG} of the RG-discharge,
- the pressure p_2 of H_2 in the GDV.

3. SIMPLIFIED MODEL FOR THE DEOXIDATION REACTION IN THE RG DISCHARGE

The model presented here aims at the description of the water release as a consequence of the chemical reduction of metal oxides by the hydrogen dissolved in the wall as it occurs some time after the cleaning procedure has started. It seems reasonable to assume that the reducible oxides are then mainly bivalent and that the fractional coverage θ_0 of the surface with oxides is no longer close to one.
The rate v_{18} at which water is released from the surface is proportional to the exposed area S, to the concentration c_{MO} (cm^{-2} over the depth of the oxide) of the residual oxide MO and to the square c_0^2 of the hydrogen concentration:

$$v_{18} = S\, k_{18}\, c_{MO}\, c_0^2 \; . \tag{1}$$

The rate constant k_{18} for the water release has to be understood as an average over the different metals covering the surface. For the hydrogen concentration the validity

$$c_0^2 = \alpha\varphi_i / 2\sigma k_r \tag{2}$$

has been demonstrated /12, 13/ where $\alpha\varphi_i$ is the incoming flux density of hydrogen atoms into the wall and σk_r the rate constant for H_2 molecular release. It has further been shown experimentally /11a/ that $\alpha\varphi_i$ is a linear function of the measured current density j_{GD} of the glow discharge:

$$\alpha\varphi_i = (\alpha\varphi_i)_{RF} + A\, j_{GD} . \tag{3}$$

Here, $(\alpha\varphi_i)_{RF}$ is the flux density of hydrogen atoms originated by the rf discharge alone. From (1) - (3) we find the total rate of water release

$$v_{18} = S\, k_{18}\, c_{MO}\, (2\sigma k_r)^{-1} \left[(\alpha\varphi_i)_{RF} + A\, j_{GD} \right] \text{ (molecules } s^{-1}\text{)} \tag{4}$$

H_2O, once released leaves the vessel in three different ways:
- water vapor is pumped away at the rate

$$v_p = S_p n_{18} \quad \text{(molecules } s^{-1}\text{)} \tag{5}$$

with n_{18} as the density of H_2O molecules in the gas phase;
- water vapor reoxidizes the surface at a rate

$$v_{ox} = S(1 - \theta_o)\, k_{ox}\, n_{18} \quad \text{(molecules s}^{-1}\text{)} \qquad (6)$$

which is assumed to be proportional to the density n_{18} and to the still unoxidized surface $S(1 - \theta_o)$. k_{ox} is the temperature dependent phenomenological rate constant;

- water vapor can finally be ionized in the RG plasma. The resulting ions are accelerated by the cathode drop potential. Impact dissociation results leading to a water destruction rate v_I. In analogy with measurements made in methane and in ammonium /11a/ we write

$$v_I = S(\alpha_I + k_I\, j_{GD})\, n_{18} \quad \text{(molecules s}^{-1}\text{)} \qquad (7)$$

$S \cdot \alpha_I$ is the destruction rate for $j_{GD} = 0$. It seems likely that α_I and the proportionality constant k_I increase (because of the increasing electron density) when p_2 is raised.

Writing now the water particle balance and noting that the variation of n_{18} is slow, we obtain

$$v_{18} - v_p - v_{ox} - v_I \approx 0. \qquad (8)$$

Substituting equs. (4) - (7) into (8), solving for n_{18} and multiplying by S_p yields

$$v_p = S_p \cdot n_{18} = S_p \frac{k_{18}}{2\sigma k_r} \cdot c_{MO} \frac{(\alpha \varphi_i)_{RF} + A j_{GD}}{S_p/S + (1-\theta_o)k_{ox} + (\alpha_I + k_I j_{GD})} \;. \qquad (9)$$

v_p is the rate at which water leaves the vessel, i.e. the cleaning rate.

4. DISCUSSION OF THE PARAMETER VARIATION OF THE CLEANING RATE v_p

4.1. Variation as a function of the current density

Equ. (9) predicts that v_p should vary hyperbolically with j_{GD}.

$$v_p = (v_p)_{RF} \frac{1 + B\, j_{GD}}{1 + C\, j_{GD}} \;. \qquad (10)$$

$$(v_p)_{RF} = S_p \frac{k_{18}}{2\sigma k_r}\, c_{MO} \frac{(\alpha \varphi_i)_{RF}}{S_p/S + (1-\theta_o)k_{ox} + \alpha_I} \qquad (11)$$

is the cleaning rate in the presence of the rf discharge only,

$$B = A/(\alpha \varphi_i)_{RF}, \quad C = k_I \left[S_p/S + (1-\theta_o)k_{ox} + \alpha_I \right]^{-1} \;. \qquad (12)$$

When the current density is increased, the cleaning rate changes from $(v_p)_{RF}$ towards an asymtotic value

$$(v_p)_\infty = (B/C)\, (v_p)_{RF} \qquad (13)$$

which can be higher or lower than $(v_p)_{RF}$.
This can be seen quantitatively from fig. 1.

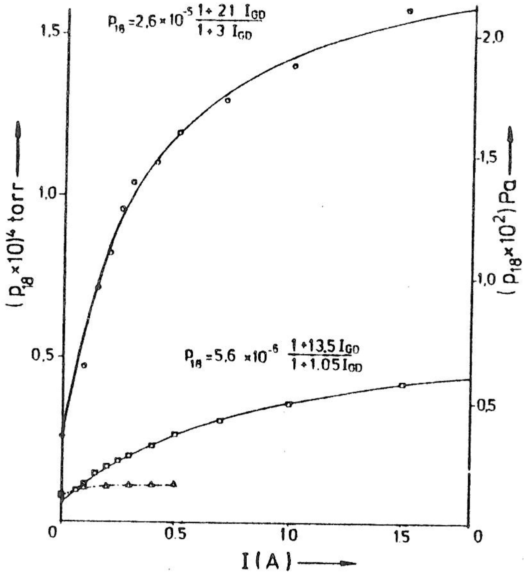

fig. 1 Variation of the partial pressure of water p_{18} as function of the glow discharge current I ; T_W = 200 °C
○ $p_2 = 2.8 \times 10^{-3}$ torr; wall freshly oxidized
□ $p_2 = 2.8 \times 10^{-3}$ torr; wall partly deoxidized
△ $p_2 = 1.2 \times 10^{-2}$ torr; wall partly deoxidized

The figure shows the experimental values (symbols) of the partial pressure p_{18} for different experimental conditions as function of the total current I. The water pressure p_{18} is proportional to the cleaning rate v_p, and $I = Sj_{GD}$. In all cases a good fit of the data by equ (10) is obtained. The difference between the B values deduced from the two measurements at $p_2 = 2.8 \times 10^{-3}$ torr results mainly from the reduction of the rf power from 72 to 32 W which lowers $(\alpha\varphi_i)_{RF}$. The different C values might result from the different surface coverage ratios θ_0 during the two runs.

When p_2 is raised, k_I is expected to increase; S_p decreases. This leads to a rapid increase of C. Already at a pressure of 1.2×10^{-2} torr (lower curve) the state C = B is reached where the cleaning rate is independant of the glow discharge current.

At even higher pressures and lower S_p a decrease of v_p with increasing j_{GD} can be expected. This has indeed been observed in this simulation and other experiments (DITE, ASDEX).

When the pump speed S_p is strongly enhanced, e.g. by activating a cryopump, the cleaning rate increases (equ. (9)) and reaches at very large S_p:

$$v_p = S \frac{k_{18}}{2\sigma k_r} c_{MO} \left[(\alpha\varphi_i)_{RF} + A\, j_{GD} \right] = v_{18}\,. \qquad (14)$$

The cleaning rate cannot become larger than v_{18}, the rate of production of water molecules. The increase of S_p should broaden the domain wherin the cleaning rate varies linearly with j_{GD}. This has been varified experimentally. Fig. 2 compares the variation of p_{18} with I (T_W = 200 °C) without and with liquid nitrogen in the cryopump. In the latter case, the variation is practically linear ($v_p = v_{18}$) up to 1.5 A.

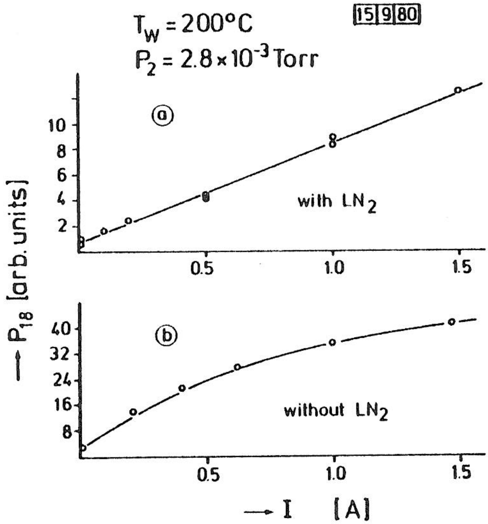

fig. 2 Variation of p_{18} as function of I with and without activated cryopump

4.2. Variation as a function of the wall temperature

Fig. 3 shows the experimentally observed variation of p_{18} as a function of the wall temperature T_W. The outgasing of H_2O at the measuring temperature has been taken into account. No water release as a consequence of the discharge could be detected at room temperature. It increases exponentially and rapidly between 100 and 350 °C and starts decreasing beyond 400 °C. This agrees with earlier observations /5b/.

The existence of an optimum wall temperature is a straight forward consequence of the model. Three coefficients in equ (9) are strongly (exponentially) temperature dependent. These are

- $k_{18} \propto \exp(-Q_{18}/RT)$, the rate constant for the water production $MO + 2[H] \rightarrow M + H_2O$ where $[H]$ is the concentration of H dissolved in the lattice,
- $2\sigma k_r \propto \exp(-Q_r/RT)$, the phenomenological rate constant for the recombination of two solved atoms and the release of H_2 molecules from the metal surface,
- $k_{ox} \propto \exp(-Q_{ox}/RT)$, the rate constant for the reoxidation $M + H_2O \rightarrow MO + [H]2$.

At low wall temperature where $k_{ox} \ll S_p/S + \alpha_I + k_I j_{GD}$, the apparent activation energy of the cleaning rate should be

$$Q^{(1)} = Q_{18} - Q_r \quad .$$

From the initial slope of the curve in fig. 3 a value of $Q^{(1)} \approx 5.8$ kcal/mole could be deduced which agrees well with that of 6.8 kcal/mole previously reported /5b/. The value of Q_r for this stainless steel has been determined in recent experiments /15/ to be

$$Q_r = 16 \text{ kcal/mole.}$$

Thus an activation energy of water formation

$$Q_{18} = 21.8 \text{ kcal/mole}$$

results, in fair agreement with the 20.3 kcal/mole given in the literature /16/ for the "water desorption" from stainless steel.

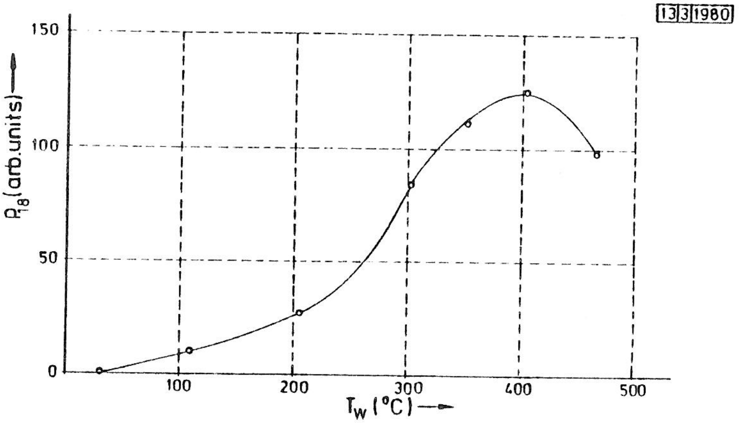

fig. 3 Variation of the partial pressure p_{18} of water in the discharge as function of the wall temperature T_W ($p_2 = 2.8 \times 10^{-3}$ torr, $I = 0.5$ A, $W_{RF} = 32$ W)

At high wall temperatures, when $k_{ox} \gg S_p/S + \alpha_I + k_I j_{GD}$, Q should decrease down to

$$Q^{(2)} = Q_{18} - Q_r - Q_{ox} .$$

Q_{ox}, the activation energy for the reoxidation process has been estimated /11a/ to be in the order of 10 to 20 kcal/mole. Therefore, the value of $Q^{(2)}$ should lie within the range of - 5 to - 15 kcal/mole, i.e. the observed change of the sign of Q (fig. 3) agrees with the model.
Similarly, from the observed value of Q_{18} and Q_{ox}, we deduce the enthalpy

$$\Delta H_{ox} = Q_{ox} - Q_{18} \text{ for the reaction } MO + 2[H] \longrightarrow M + H_2O + \Delta H_{ox}$$

within the range + 1.8 to - 11.8 kcal/mole. Since the reaction enthalpies at 200 °C are 5 kcal/mole for Ni, - 1.5 kcal/mole for Fe and - 29kcal/mole for C the experimental value for ΔH_{ox} indicates that it is probably iron oxide which is reduced during the main clean down phase. This supports the conclusions of Dylla /6/ and Staib /17/.

CONCLUSION

The earlier observed variation of the water partial pressure in stainless steel vessels in the presence of RG-discharge in hydrogen /11/ is very well described by a phenomenological model, presented in this paper. Water is formed through the reduction of metal oxides by hydrogen dissolved in the wall. Its further way is determined by several mechanisms. We have found that the following reactions are of importance in a RG-discharge:

- release of H_2O from the wall,
- dissociation of H_2O in the discharge,
- reoxidation of the wall material,
- pumping H_2O-vapour out of the system.

The predictions of the model with respect to experimentally accessible parameters as are the wall temperature, pumping speed and glow discharge current density are compared to the experimental data. Its direct application is certainly limited to systems having roughly the same ratio $S_p/S \approx 0.1\ ms^{-1}$ as in the earlier experimental study. We feel however, that equ. (9) can be used with confidence to the phenomena as a function of the available parameters. This is of particular importance for fusion plasma devices.

ACKNOWLEDGEMENTS

The measurements have been made by technical assistance of MM. Banno, Gervelmeyer, Grobusch, Korr, Peuser and Waelbroeck, jr. Discussions with R.E. Clausing and H.F. Dylla on various aspects of this work were very usefull.

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