WATER RELEASE FROM STAINLESS STEEL SURFACES EXPOSED TO .2 eV H ATOMS

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Keywords: stainless steel (AISI 304)
water release
surface deoxidation

ABSTRACT

The surface oxides of stainless steels and nickel base alloys have previously been observed to be reduced by hydrogen atoms. To improve the knowledge of the processes involved, v_{18}, the rate of water release from stainless steel 1.4301 (AISI type 304), has been measured in the temperature range of 350 K < T < 800 K. Relating v_{18} to the concentration of hydrogen atoms underneath the surface allows to deduce an activation energy of $1{,}41 \times 10^{-19}$ Ws (20.3 kcal/mol) for v_{18} from an Arrhenius plot.

I. INTRODUCTION

The walls of most magnetic confinement devices are made of stainless steels or nickel base alloys. The surface near layers of those materials are strongly oxidized (1, 2). The thickness of the oxide layer depends on the pretreatment but is usually of the order of 50 - 100 Å. Hydrogen atoms (including Franck-Condons) and atomic ions escaping from the confined plasma, interact with the wall and consequently with the surface-near oxides. Water is formed not only during the discharge (3, 4, 5) but also in between discharges due to the hydrogen implanted in the wall. The reaction rate is given by (6):

$$v_{18} = k_{18}\, c_{MO}\, c^2 \qquad (1)$$

where k_{18} is the reaction rate constant, c_{MO} the concentration of oxide and c the concentration of hydrogen underneath the surface. The water formed during the intervals between the discharges remains mostly in the wall-near layers as long as the wall temperature is well below 400 K. It can be released at the start of the subsequent discharge causing an initial oxygen contamination of the plasma. According to equ. (1), to lessen the oxygen contamination resulting from water formation, either the oxide concentration or the hydrogen concentration must be reduced. The first can be achieved by an elaborated discharge cleaning procedure under UHV conditions with hot walls (7), the second by burying the oxygen beneath a titanium layer (8) and simultaneously reducing the hydrogen concentration (9) due to the large recombination rate constant of hydrogen on the titanium surface layer compared to that on stainless steel.

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The aim of this work has been to study the water production and the subsequent release of H_2O from the surface of stainless steel 1.4301 (AISI type 304) during the exposure to hydrogen atoms with an energy of 0.2 eV. A better understanding of the processes involved, expecially of their temperature dependence, allows then an optimization of discharge cleaning procedures in tokamak devices with respect to wall temperature, flux density of hydrogen atoms and characteristic time for the pumping.

II. EXPERIMENTAL (For more details see (14))

The inner surface of the reaction chamber (R.C.), a hollow sphere of 156 mm diameter made of stainless steel 1.4301, has been exposed to hydrogen atoms. These have been produced by thermal dissociation of hydrogen molecules on a tungsten filament of 0.3 cm^2 area, kept on 2000 K. The filament is introduced into the sphere through a hole of 4.8 mm diameter which also serves as gas inlet. The hydrogen is supplied from an iron-titanium reservoir via a palladium filter. The gas flux can be regulated remotely by an ion gauge controlled valve. A second aperture of 4.8 mm diameter connects the sphere to the analyzer system, consisting essentially of a residual gas analyzer (RGA) and an ion gauge. The system is pumped by a turbumolecular pump. The wall temperature of the sphere which can be heated indepentently of the analyzer system and of the aperture have been measured with thermocouples.

The RGA has been calibrated using the ion gauge with its known sensibilities for hydrogen and water as a reference. The hydrogen pressure in the sphere can be calculated from the signal of the RGA, knowing the temperatures of the R.C., the area of the aperture of the analyzer system. From the pressure the flux density of the hydrogen atoms has been derived using Hickmott's formula (10) with a value of 0,2 for the sticking probability of hydrogen molecules on tungsten as proposed by other authors (11).

To obtain the release rate of water, the pumping speed S_{18} for water has been measured for water partial pressures p_{18} in the analyzer system ranging from 10^{-9} Pa to 10^{-3} Pa. The inaccuracy of the pumping speed is the main source of error in the evaluation of the water release rate v_{18}. For quasistationarity

$$v_{18} = S_{18}\, p_{18}/A_2 \qquad (2)$$

where A_2 is the real area of the inner surface of the sphere.

The system has been baked initially at 750 K for five hours. After cooling to 357 K with the filament on, the residual gas analysis yielded (the indices indicate the mass numbers): $p_2 = 1{,}4 \times 10^{-7}$ Pa, $p_{16} = 1{,}3 \times 10^{-9}$ Pa, $p_{18} = 3 \times 10^{-9}$ Pa, $p_{28} = 5{,}4 \times 10^{-9}$ Pa, $p_{44} < 5 \times 10^{-10}$ Pa.

At the start of each experimental run, the inner surface of the sphere has been oxidized by exposing it at 470 K for two hours to dry air at 10^5 Pa. Thereafter, the R.C. has been baked out at 720 K for twelve hours. This procedure reconstitutes the surface near oxide layer leading to the same average oxygen concentration and thickness (≈ 75 - 100 Å) of the oxidized zone (1). The temperature controls have than been adjusted to the desired

value and the filament heated up. After obtaining temperature equilibrium, hydrogen has been introduced into the sphere at some preset pressure, (e.g. 10^{-5} Pa in the analyser chamber), which was maintained constant using a feed back loop. The value of the hydrogen pressure and the flux density of atoms reaching the wall ($5 \times 10^{11} < \varphi < 5 \times 10^{12}$/cm^{2}s) were evaluated, taking the wall temperature into account. The evolution of v_{18} was measured until its quasi-stationary value was reached. The gas inlet valve has then been closed, the temperature maintained constant and the decrease of v_{18} followed until it again became stationary. The difference of v_{18} in the presence and absence of hydrogen is the release rate caused by the H atoms. The temperature was modified and a new measurement carried out.

III. RESULTS

As observed earlier, v_{18} does not rise immediatly to its final value after the start of the irradiation but increases gradually. The quasi-stationary value, in the lower range of temperature domain and at the moderate flux densities used here, is first reached after some hours. Thereafter, v_{18} remains practically constant over long periods of time. The initial transient phase will be discussed in another article (14). We limit ourselves here to the discussion of the quasi-staionary v_{18} values

The constancy of v_{18} in this quasi-stationary domain shows that c_{MO} and c can practically be considered as constant. As a consequence of multiple reflexions in the hollow sphere and since recombination in the gas is negligible, the flux density of atoms sticking to the wall is equal to that φ of primary atoms to the wall. As mentioned earlier, φ is deduced from the dissociation rate at the filament (10, 11).

In fig. 1, these v_{18} values, normalized with respect to φ, are plotted as a function of 1/T. In agreement with our earlier results (H_2O production mainly by dissolved H in the surface near layer), the fraction of water molecules released per incident atom depends strongly on the wall temperature. From 370 K to 570 K, it increases by a factor of 40. It then tends to saturate at 0.17 at a temperature of about 670 K. The difference between the three runs lies within the limits of experimental errors indicating, in agreement with the measurements of Betz et al. (1), that the thickness and composition of the oxide layer can be reproduced after an adequate exposure to air at 470 K. The variation of v_{18} with temperature does not follow an Arrhenius plot; this results from the large surface concentration of oxides in the present experiment.

The model used earlier for measurements at lower c_{MO} values is therefore expanded to the case where, besides hydrogen molecules, an appreciable amount of water is released from the surface. In the stationary state the diffusion of hydrogen into the bulk has become negligible and the number of atoms sticking to the surface must be twice the number of H_2 and H_2O molecules released:

$$A_1 \varphi = 2 A_2 (k_r c^2 + k_{18} c_{MO} c^2). \qquad (3)$$

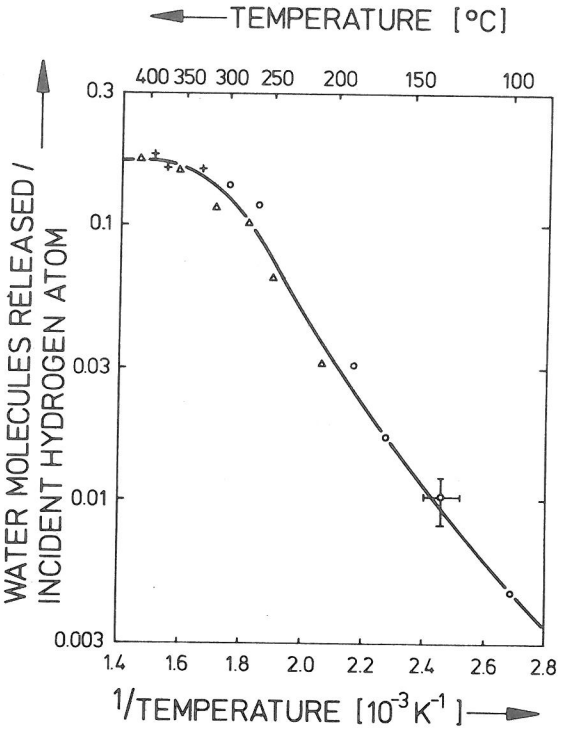

Fig. 1: Released water molecules per incident hydrogen atom in dependence of the increase temperature. Surface oxidised at 470 K, then first run Δ , surface treated as described above, then second run o, surface treated as described above, then third run +.

A_1 is the geometric, A_2 the real surface, k_r the rate for the recombinative H_2 release. The water production is the main impurity release process (the CO release - the second largest contribution - is by about one order of magnitude samller). Combining equ. (3) and (1) yields, with $\sigma = A_2/A_1$ the roughness factor:

$$k_{18}\, c_{MO} = \frac{2\sigma k_r\, v_{18}}{\varphi - 2\sigma v_{18}} \qquad (4)$$

In ref. (12) a value of $k_r \approx 8.4 \times 10^{-18}$ exp (-13 600/RT) has been proposed; whence

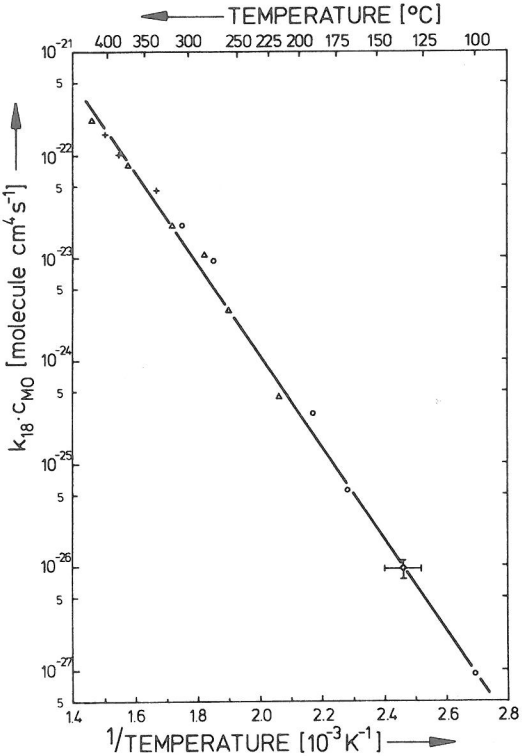

Fig. 2: The reaction rate constant times the oxygen concentration as a function of the inverse temperature. Wall treatment as described in fig. 1: Δ first run, o second run, + third run.

$$k_{18}\, c_{MO} = \frac{4.4 \times \sigma v_{18}}{\varphi - 5.3 \times 10^{17} \sigma v_{18}} \exp(-6800/T) \qquad (5)$$

($k_{18}\, c_{MO}$ in molecule $cm^4 s^{-1}$, σv_{18} in Pa l $s^{-1} cm^{-2}$, T in K).
From this equation and the measured quantities σv_{18} (equ. (2)) and φ the logarithm of $k_{18}\, c_{MO}$ has been calculated and plotted as function of 1/T (fig. 2). In contrast to the presentation in fig. 1, an Arrhenius plot now results, yielding an activation energy of 1.41×10^{-19} Ws (20.3 kcal/mol) for k_{18}. This value is in relatively good agreement with that (1.56×10^{-19} Ws) given in the literature (13) for the water desorption from stainless steel.

CONCLUSION

It is shown that the water production in stainless steel 1.4301 is an activated process. An activation energy of 1.41×10^{-19} Ws for the reaction rate constant k_{18} is derived, using the activation energy for the recombinative H_2 release proposed in (12). The agreement with the value of the literature for the water desorption from stainless steel shows that assumptions made are plausible.

The measurements, including the observation of a long transient phase before quasi staionarity is reached, support the model in which the water production rate is proportional to the square to hydrogen concentration in the solid. This concentration decreases with increasing wall temperature T_W. Two competing processes are involved: water production and recombinative release of H_2. Since the activation energy of the first is larger, one expects and observes that at constant flux densities of hydrogen atoms the ratio v_{18}/φ increases with T_W and tends to saturate.

Wall cleaning methods using chemical reactions between hydrogen atoms (or H^+) and surface impurity layers (3, 4, 5) on stainless steel should thus be applied as far as feasible at elevated T_W, but little is gained by increasing T_W beyond 600 - 700 K.

Similar measurements should be carried out on nickel base alloys and other candidate wall materials; additionally informations on the rate constant for the recombinative H_2 release on these materials are urgently needed.

The assistence of MM Grobusch, Korr, Peuser, Gervelmeyer in building up the apparatus and carrying out measurements is greatfully acknowledged.

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