Studies of Mechanisms of Hydrogen Recycle Using a Plasma-Wall Interaction Experiment*

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Abstract

It is shown that for type 304L stainless steel at room temperature and ion energies of 100 eV a large part of the recycling occurs with hydrogen residence times in the wall of about 100 ms. The use of wall temperatures from 80 to 500 K permits differentiation between thermally activated processes and ion bombardment-induced phenomena. For low energy ions (100 eV) onto 300 K stainless steel walls recycling increases to more than 90% in a few tenths of a second at 3×10^{16} ions $\text{cm}^{-2}\text{s}^{-1}$. For ions up to 300 eV at this flux there is little energy dependence. Both thermally and ion induced processes can be important at room temperature, but under the conditions of this study thermal processes greatly enhance the recycle rates at 300 and 500 K. Preliminary results indicate that recombination of atomic hydrogen to molecular hydrogen can be rate controlling in some practical regimes.

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1. Introduction

Recycling in plasma devices is a term which deals with the processes responsible for the return to the plasma from the confining walls those constituents which would otherwise be lost. Recycling plays a fundamental role in present day tokamaks and will assume an even greater role in future devices fueled with tritium. Particle containment time in the plasma is shorter than plasma pulses by a factor of 5 to 20. Thus, on the average, particles are recycled many times between the plasma and the wall and/or limiters which confine the plasma. Other important facets related directly to hydrogen recycle include, plasma edge cooling, fuel cycle, tritium inventory control and materials problems related to stability of coatings and metal surfaces and to bulk effects of hydrogen in metals.

Although the general nature of recycling has been modeled [1,2] and much experimental information exists concerning the various physical processes involved [3,4], there continues to be a need to determine which processes are most important, i.e., rate controlling in a particular circumstance. We [5,6] and others [7] have shown that surface composition and temperature are very important parameters for technical surfaces. Perhaps even more importantly we have shown that recycling rates change very rapidly near the beginning of a plasma discharge [6] for fluxes of interest for tokamak walls. The recycling can increase from less than 50% to more than 90% in fractions of a second. This means that most of the hydrogen returns to the plasma after only a very short time in the wall. The study of these "prompt" processes also offers the opportunity to separate out some of the physical processes involved and to test recycling models.

The following sections describe recent work in which we have been able to improve the time resolution of our measurements to better than 10 ms and to examine the transient phenomena at the beginning of the hydrogen recycling processes.

2. Experimental Technique

The apparatus is little changed from that previously described [6]. A plasma column which fills a 3.8 cm diameter type 304L stainless steel tube is obtained between a hot tungsten wire cathode and a remote anode. An electrical potential may be applied between the plasma and the wall to accelerate ions from the plasma across the sheath into the wall. Current densities up to a few mA/cm² can easily be obtained on wall areas of about 350 cm². Ion energies of several hundred electron volts may be obtained. The system was preconditioned to provide a known surface composition (by glow discharge cleaning). The composition of the surface could be determined by Auger electron spectroscopy after transferring a removable section of the wall to an integral surface analysis chamber. All parts of the system are of standard UHV construction.

A high speed capacitance manometer is used to measure gas pressure in the discharge chamber and provides the primary data.

3. Short Plasma Pulse Technique

Before each discharge the cell was filled with hydrogen to 3.3 Pa and the hot cathode brought to operating temperature. All valves were closed so that no hydrogen entered or left the chamber during the plasma pulse. Figure 1 shows the pressure changes in the discharge chamber as the result of a short plasma pulse with stainless steel walls at 500, 300 and 80 K.

At time t_1 the discharge is initiated and the pressure falls as hydrogen is buried in the wall. At time t_2 the discharge is turned off and the pressure rises as gas buried during the plasma pulse is desorbed back into the volume of the cell. The amount of hydrogen in the wall at any time $t_1 < t < t_2$ is given by $Q = Q_0 + (\Delta P)V$. The amount of hydrogen in the wall prior to the plasma pulse, Q_0 , can be made very small by outgassing the walls prior to the pulse and is negligible in the experiments reported here (except as noted in the second through tenth pulses on Fig. 2). ΔP is the measured difference between the initial and instantaneous hydrogen pressure in the closed discharge cell and is a function of time, t .

It is useful to differentiate these data and define $q \equiv \frac{dQ}{dt}$ where $q(t) = (-\frac{dP}{dt})V$. $q(t)$ is the net rate of hydrogen storage in the wall. It can be written as the sum of the rates of influx (index i) and the rates of outflux (index o), $q(t) = q_{ip} + q_{op} + q_{it} + q_{ot}$.

Here we also distinguish between processes caused directly by the plasma-wall interactions (index p) such as trapping and ion-induced desorption and those which are thermally activated (index t) such as normal diffusion, recombination and desorption. In all cases thermally activated influxes are assumed to be negligible by comparison with plasma induced processes, i.e., $q_{it} = 0$.

Because the amount of hydrogen in the wall has been made small, ion-induced desorption processes are negligible at the beginning of the discharge, and only the plasma related influxes are operating: $q_{ot} = 0$, $q_{op} = 0$ and $q = q_{ip}$. Thus the flux of hydrogen from the plasma into the wall caused by plasma-induced processes can be measured directly for the first instant. We further assume that the processes which contribute to the plasma-induced influx are constant for short pulses.

After t_1 the hydrogen concentration in and on the wall increases, the desorption processes begin to operate and for $t_1 < t < t_2$, $q = q_{ip} + q_{op} + q_{ot}$.

When the plasma pulse is terminated suddenly at time t_2 the plasma induced processes vanish so that for $t > t_2$ $q_{ip} = 0$ and $q_{op} = 0$ and $q \rightarrow q_{ot}$. The magnitude of q then decreases as the hydrogen concentration in or on the surface is depleted. At the first instant after the pulse is terminated q_{ot} can be measured directly; this will approximate $q_{ot}(t_2)$.

A special case occurs as q approaches zero, i.e., when the wall approaches a steady state where influx rate equal outflux rate (100% recycling). For this circumstance no more hydrogen is accumulating and $q_{ip} = -(q_{op} + q_{ot})$.

We use two functional definitions for the recycle coefficient.

$R_I \equiv \frac{\text{Rate of hydrogen leaving the wall}}{\text{Rate of hydrogen hitting the wall as ions}} = \frac{q_{ii} - q}{q_{ii}}$, where the ion current to the wall is measured and the hydrogen influx, q_{ii} , calculated from this source. This definition has the problems of ignoring atomic hydrogen and uncertainty in determining the particle flux from the ion current. It does include reflected particles, however, by assuming they are returned to the plasma as neutrals.

In order to access or avoid these problems a second definition is introduced. $R_W \equiv \frac{q_{ip} - q}{q_{ip}}$ where $q_{ip} = q(t_1)$.

The atomic hydrogen which enters the wall is included in the measurement of q_{ip} . R_W does not include reflection at the wall, nor does it use calculations based on the ion current. The differences due to atomic hydrogen effects, the use of ion current to determine hydrogen fluxes and the inclusion of reflection can thus be seen by comparing R_I and R_W .

4. Experimental Results and Discussion

The experimental results obtained at three temperatures are shown in Fig. 1. The upper curves show the changes in pressure which occurred as a function of time during 200 ms plasma pulses. The initial pressure was 3.3 Pa. At 500 K this dropped in about 50 ms to 2.8 Pa and decreased only very slowly for the last 150 ms of the pulse. At the end of the plasma pulse the pressure recovered nearly .3 Pa in the first 75 ms. Although not shown here, virtually all of the adsorbed hydrogen was reemitted within one minute. The current of ions to the wall, I_{pw} , is shown in the lowest curve and was 1.8 amps for all temperatures. This gives a current density of about 5 mA/cm² (8×10^{16} H/cm²s if the average ion has 2.7 H nuclei [8]). The middle set of curves shows the rate at which gas is being absorbed by the sample during the plasma pulse, q . At the end of the pulse gas is desorbed and q becomes negative.

At 300 K the pressure drops by almost 1.3 Pa in the first 50 ms of the plasma pulse indicating that much more gas is absorbed in the wall

than at 500 K before the reemission processes begin to compete significantly with the absorption of gas. After 200 ms hydrogen is being absorbed in the sample at a rate of only 2×10^{15} atoms/cm²s. At the end of the discharge the magnitude of the desorption rate due to thermal processes is about a factor of 10 larger than this.

The results obtained at liquid nitrogen temperature are also shown in Fig. 1. This data was from the first plasma pulse on the cold surface after thorough degassing at 500 K. Thus no hydrogen is present from previous pulses. The very fast increase in pressure when the discharge is initiated is due primarily to the heating of the hydrogen in the plasma column (an increase of perhaps 30 K above ambient). This effect does not produce any error in

q after the first few ms, and Q values are easily corrected. The initial sorption rate, q, is high and remains high for the entire pulse at 80 K. At the end of the discharge the pressure falls as the gas cools. The effects of repeated pulses at liquid nitrogen temperature are shown in Fig. 2. The gas pressure was brought to 3.3 Pa before each pulse by admitting gas. By the tenth pulse (which is after about 2 s of accumulated plasma time) the recycling coefficient R_W is about 90%. Since the desorption rates at the end of the pulse are small, thermal diffusion and desorption are not contributing significantly to the recycling at liquid nitrogen temperatures. At the end of the tenth pulse ion induced desorption processes are able to recycle about 90% of the gas that goes into the wall, but nearly 4×10^{16} atoms/cm² of hydrogen have been adsorbed into the sample. This is about one-fourth the total hydrogen hitting the surface as ions during 2 s (assuming 2.7 atoms per ion [8]).

We have examined the influence of ion energy on the recycling rates and over the ion energy range 100 to 300 eV there is no significant energy dependence of the recycling phenomena for fluxes of 3×10^{16} ions/cm². This is not surprising since the penetration depth of the plasma particles is very small at these energies.

Several results are immediately apparent from Fig. 1 and the data summarized in Tables 1 and 2.

1. Recycling of low energy ions is very fast at 500 and 300 K. The average lifetime of a particle in the wall at 500 K must be less than 50 ms since the recycling rate, R_W , has reached ~100% at this time (with only about 3×10^{15} hydrogen atoms/cm² absorbed in the surface region). At 300 K the recycle rate, R_W , is greater than 85% at 80 ms (with about 6×10^{15} hydrogen atoms/cm²) and at 200 ms R_W is greater than 97% (with about 8×10^{15} hydrogen atoms/cm²).

At liquid nitrogen temperature, on the other hand, the recycle rate R_W at 200 ms is $\approx 70\%$ (with about $1.7 \times 10^{16}/\text{cm}^2$ hydrogen atoms/ cm^2 absorbed). This is about 60% of the hydrogen incident on the surface during the 200 ms.

2. The differences in the curves at the three temperatures suggest that at 300 and 500 K thermal effects greatly enhance the recycle rates. Ion induced effects should increase as Q increases. Q is much larger at lower temperatures and since the initial plasma conditions and sorption rates were not grossly changed by the wall temperature, it is argued that for the conditions used here the rate controlling desorption processes at 300 and 500 K are thermally activated.

3. Data in Table 2 indicate that the amount of hydrogen in the wall depends upon the hydrogen ion current density in a manner which suggests that recombination is the rate controlling step in some cases. The data is preliminary and the analysis given below is simplistic; further experiments and more complex modeling must be done. However, because of the importance of understanding which processes are rate controlling, we present the following.

The rate of evolution of hydrogen from a surface is dependent on the first power of the concentration if diffusion in the wall to the surface, is rate controlling [3] and follows Fick's first law, $q_{ot} = D \frac{dc}{dx}$, where D is the diffusion coefficient, c the concentration and x the distance from the surface. In this case $\frac{dc}{dx}$ is proportional to c if the source of c is hydrogen implanted below the surface and the surface concentration is zero, i.e., no barrier for desorption exists. (It can be shown that diffusion into the bulk is small in 200 ms but that diffusion through a few atom layers to the surface is possible.)

If recombination is rate controlling, $q_{ot} = \sigma K_r c^2$ [3], where σ is a surface roughness factor and K_r is the recombination coefficient.

Outflux must equal the influx when the recycle coefficient is near 100% as it is at 200 ms at 300 K. It follows that the concentration near the surface will increase as a linear function of current density if diffusion is rate controlling and as the square root of current density if recombination is rate controlling. For short times, c near the surface is proportional to the amount of hydrogen Q in the wall, which is easily measured. This simple model suggests that if Q increases linearly with current density (or I_{pw}), diffusion is rate controlling; if Q^2 increases as I_{pw} , recombination is rate controlling.

Both effects have been observed at room temperature. Data obtained at 300 K are given in Table 2 which show that on a moderately clean type 304L stainless steel surface the concentration at the end of 200 ms is proportional to current up to 7×10^{16} H atoms/cm²s ($I_{pw} = 1.6$ A) and then becomes less than linear. Runs with samples having more oxygen on the surface give increases in concentration which are more nearly proportional to the square root of current density as shown. (The last sample also used a longer pulse length which will tend to increase the role of recombination.)

These results suggest that for clean stainless steel surfaces at 300 K and for fluxes up to about 10^{17} H/cm²s, diffusion processes dominate recycle. If the surface has more oxygen on it, recombination may dominate for fluxes above a few times 10^{16} H/cm²s.

5. Conclusions

Much of the recycling from 300 and 500 K stainless steel walls is very fast when fluxes are high. The recycle coefficient approaches unity in less than 100 ms with fluxes in the range of 8×10^{16} H/cm²s.

By contrasting recycle at 80 K with that at 300 and 500 K it appears that recycling at the higher temperatures is greatly enhanced by thermal processes, while recycling at 80 K is dominated by plasma induced processes.

Preliminary results indicate that for 200 ms pulses the amount of gas in the wall is proportional to the ion flux at low current densities on moderately clean walls but departs toward $Q^2 \propto I_{pw}$ for higher fluxes, oxygen contaminated surfaces and longer pulses. This suggests that recombination becomes the rate determining step for these latter conditions and prepares the way for future more detailed studies of the variables affecting recombination using the simulator.

The above conclusions are based on rather simple arguments. More complex models will be required for a detailed understanding of the relationships between recycling processes and plasma exposure parameters.

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Table 1. Summary of Measurements at 500, 300 and 80°K

Time (ms)	15	200	200	215	15	200	200
Quantity	q_{ip}	q	Q	q_{ot}	$R_I^{(a)}$	$R_I^{(a)}$	R_W
Units	H/cm^2s $\times 10^{15}$	H/cm^2s $\times 10^{15}$	Atoms/cm ² $\times 10^{15}$	H/cm^2s $\times 10^{15}$			
500°K	40	.2	2.8	13	.52	1.00	1.00
300°K	70	2	8.4	20	.13	.98	.97
80°K	55	17	17	—	.33	.80	.70

(a) Ion current is 1.8 A, an average of 2.7 hydrogen nuclei per ion times the hydrogen ion flux gives $83 \times 10^{15} H/cm^2s$.

Table 2. Relationship of Hydrogen Concentration in the Wall
at the End of a Pulse to Ion Current Density

	$I_{pw}^{(1)}$ (A)	$Q^{(2)}$ (3)	Q/I_{pw}	Q^2/I_{pw}
~15 at. % O 200 ms pulses	.5	6	12	72
	1.0	10	10	100
	1.5	15	10	150
	2.2	19	8.6	164
~35 at. % O 200 ms pulses	.45	2.5	5.6	13.9
	1.2	5.7	4.7	27.1
	1.6	6.8	4.2	28.9
	2.3	7.3	3.1	23.2
~45 at. % O 1.4 s pulses	.5	13	26	338
	.6	14	23	326
	.8	17	21	361
	1.2	20	17	333
	1.4	20	14	286

(1) $1.8 \text{ A} \approx 8 \times 10^{16} \text{ H/cm}^2\text{s}$.

(2) c is proportional to Q .

(3) Arbitrary units.

Figure Captions

Fig. 1. Data obtained with wall at 500, 300 and 80 K showing pressure changes and rate of change of hydrogen in the wall. (The 80 K pressure data is arbitrarily displaced downward 1 Pa to facilitate ΔP comparisons.

Fig. 2. Data from a series of plasma pulses in the simulator with the wall at 80 K. After each pulse hydrogen is admitted to the discharge chamber to bring the pressure to 3.3 Pa for the start of the next pulse. Pulses were separated by several minutes, but no significant adsorption or desorption occurred between pulses because of the low temperature. Note the increased recycling due to the increase in Q the series of shots progresses.

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