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HYDROGEN PUMPING AND RELEASE BY GRAPHITE UNDER HIGH FLUX PLASMA BOMBARDMENT

Y. Hirooka*, W.K. Leung*, R.W. Conn*, D.M. Goebel*,
B. LaBombard*, R. Nygren*, and K.L. Wilson**

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* Institute of Plasma and Fusion Research
Department of Mechanical, Aerospace and Nuclear Engineering
University of California, Los Angeles
Los Angeles, California 90024

** Physical Research Division
Sandia National Laboratories
Livermore, California 94550

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ABSTRACT

Inert gas (helium or argon) plasma bombardment has been found to increase the surface gas adsorptivity of isotropic graphite (POCO-graphite), which can then getter residual gases in a high vacuum system. The inert gas plasma bombardment was carried out at a flux $\approx 1 \times 10^{18}$ ions $\text{s}^{-1} \text{cm}^{-2}$ to a fluence of the order of 10^{21} ions/ cm^2 and at temperatures around 800 °C. The plasma bombarding energy was varied between 100 and 200 eV. The gettering speed of the activated graphite surface is estimated to be as large as 25 liters $\text{s}^{-1} \text{cm}^{-2}$ at total pressures between 10^{-6} and 10^{-7} torr. The gettering capacity estimated is 0.025 torr-liter/ cm^2 at room temperature. The gettering capability of graphite can be easily recovered by repeating inert gas plasma bombardment. The activated graphite surface exhibits a smooth, sponge-like morphology with significantly increased pore openings, which correlates with the observed increase in the surface gas adsorptivity.

The activated graphite surface has been observed to pump hydrogen plasma particles as well. From calibrated H-alpha measurements, the dynamic hydrogen retention capacity is evaluated to be as large as 2×10^{18} H/ cm^2 at temperatures below 100 °C and at a plasma bombarding energy of 300 eV. The graphite temperature was varied between 15 and 480 °C. Due to the plasma particle pumping capability, hydrogen recycling from the activated graphite surface is significantly reduced, relative to that from a pre-saturated surface. A pre-saturated surface was also observed to reproducibly pump a hydrogen plasma to a concentration of 9.5×10^{17} H/ cm^2 . The hydrogen retention capacity of graphite is found to decrease with increasing temperature. At temperatures between 450 and 480 °C, the hydrogen retention estimated for the activated surface and pre-saturated surface is 7.9×10^{17} H/ cm^2 and 2.7×10^{17} H/ cm^2 , respectively. A transient pumping mechanism associated with the sponge-like surface morphology is conjectured to explain the large hydrogen retention capacity. Hydrogen release behavior under helium and argon plasma bombardment was also investigated, and the result indicated the possibility of some in-pore retrapping effect. The effective plasma impact desorption cross sections are evaluated in the plasma bombarding energy range from 15 to 300 eV. A significant fraction (70-80%) of pre-implanted hydrogen was observed to release under inert gas plasma bombardment to a fluence of 6×10^{19} ions/ cm^2 . The graphite surface, once saturated, can be reactivated via plasma impact hydrogen desorption, regardless of the helium and argon bombardment energy examined here.

1. INTRODUCTION

Graphite is widely recognized as the most suitable material for plasma-facing components in existing and near-term magnetic fusion devices. Major tokamaks such as TFTR,¹ JET,² DIII-D³ and TEXTOR⁴ have been successfully operating with graphite limiters and protective armors. Also, the first D-T ignition tokamak, CIT, is currently designed to use graphite as the plasma-facing material for all key in-vessel components.⁵ These fusion applications of graphite were originally motivated by the physical properties including high heat resistance and low atomic number, which are obviously superior to those of existing metals and alloys. In addition, another encouraging property of graphite has been discovered in recent plasma confinement experiments in TFTR⁶ and JET.⁷

In TFTR, after helium plasma discharge conditioning, graphite used as the toroidal bumper limiter at room temperature pumps a large influx of hydrogen plasma particles during confinement discharges. As a consequence, the hydrogen recycling rate in the edge-plasma region is significantly reduced, which then results in a high temperature core plasma (often referred to as a 'Super Shot').⁶ The reduced local recycling is postulated to occur along with refilling of the near-surface hydrogen trapping sites in graphite that are emptied during the He-plasma discharge conditioning.^{8,9} In JET, however, graphite tiles on the inner toroidal wall are observed to reproducibly pump hydrogen plasma particles without particular discharge conditioning.⁷ This has led to an improvement of plasma parameters in confinement experiments. Currently proposed to explain the phenomenon observed in JET is a completely different pumping mechanism, based on the transient particle flux imbalance between fast implantation and relatively slow reemission from the graphite surface at temperatures around 300 °C.¹⁰

For these observations, the first noticeable difference can be found in the states of hydrogen in graphite. In the case of TFTR, most plasma-implanted hydrogen particles are bound to the trapping sites and few remain mobile in graphite whereas the opposite is true for JET. The surface temperature appears to play an important role in determining the state of hydrogen in graphite and hence the behavior of hydrogen reemission. On the other hand, it is in common for these tokamaks that graphite components have been extensively bombarded with high flux hydrogen plasmas since installation. High fluence hydrogen plasma bombardment often leads to a significant surface modification due to physical and chemical sputtering. Recent studies¹¹⁻¹³ have shown that such surface modification appreciably alters the effective surface porosity and roughness of graphite materials. The plasma-modified surface porosity will directly affect the behavior of gas adsorption, retention and desorption in a yet-to-be explored manner. This effect is particularly

important for porous graphite materials. Yet the graphite materials, POCO AXF-5Q in TFTR and CL 5890 PT in JET have relatively high porosities of 20 to 30%. These arguments naturally lead to a conjecture that the modified surface characteristics of graphite limiters might in part contribute to the plasma pumping effects observed in these tokamaks. Nevertheless, further investigation is necessary to understand the nature of pumping of plasma particles by graphite materials.

In the present work, the behavior of graphite under high flux, high fluence plasma bombardment has been studied using the PISCES-A facility.¹⁴ For completeness of investigation, several series of experiments are conducted here, namely: (1) plasma activation of a graphite surface; (2) hydrogen recycling from an activated graphite surface; and (3) hydrogen release from a saturated graphite associated with reactivation. Also, important implications from the results to fusion experiments are discussed.

II. EXPERIMENTAL

A. General experimental arrangement and procedure

A schematic diagram of the experimental setup is shown in Fig.1. After ultrasonic cleaning in acetone, a disk specimen of POCO-graphite (grade: HPD-1, the porosity = 25%) with a typical diameter of 4.5 cm and with a thickness of 5 mm was placed in steady-state plasmas of H, He and Ar in the PISCES-A facility. The plasma diameter was set around 6 cm. The magnetic field is perpendicular to the target surface and is 250 Gauss. The typical neutral pressure during plasma operation is 1×10^{-4} torr. The plasma bombardment flux, plasma density and electron temperature were measured by a Langmuir probe. Also, an optical spectrometer was aligned in such a way that plasma particle radiations (e.g. H-alpha) could be monitored in-situ, particularly near the specimen surface. Details of plasma characteristics and materials experiments in this facility can be found in our previous papers.^{11,14-16}

In order to simulate plasma discharges in existing magnetic fusion devices, the plasma bombardment was conducted for a relatively short period, typically 20-60 seconds although the PISCES-A facility can generate continuous plasmas. The general plasma bombardment conditions during these experiments were: flux in the range from 5×10^{17} to 2×10^{18} ions $s^{-1} cm^{-2}$; total fluence in the range from 10^{19} to 10^{21} ions/cm²; plasma bombarding energy in the range from 15 to 300 eV; plasma density of the order of 10^{12} cm⁻³; and electron temperature in the range from 5 to 20 eV. The temperature of the

specimen was varied between 15 °C and 800 °C. More specific experimental conditions will be described in each section.

B. Vacuum characteristics of the PISCES-A facility

The main vacuum chamber of the PISCES-A facility is pumped by four turbo molecular pumps with the total nominal pumping speed of 6000 liters/s for nitrogen. The effective total pumping speed after conductance calibration is estimated to be 1700 liters/s by which the base pressure of the order of 10^{-6} - 10^{-7} torr is routinely attained. A residual gas analyzer was used to characterize vacuum conditions in the main chamber before plasma operation. Since the main vacuum chamber is not bakable, water vapor is the predominant residual gas identified the residual gas analyzer. The partial pressures are typically: $P(\text{H}_2\text{O}) : P(\text{H}_2) : P(\text{CO}+\text{N}_2) \approx 10 : 3 : 2$.

III. RESULTS AND DISCUSSION

A. Plasma Activation of Graphite Surface

1. General observations

In the first series of experiments, the effects of high fluence plasma bombardment on the gas adsorptivity and on the surface morphology of graphite are investigated. The graphite disk target with a diameter of 10 cm was first bombarded by continuous He or Ar plasmas at a flux of 1×10^{18} ions $\text{s}^{-1} \text{cm}^{-2}$ to a fluence of the order of 10^{21} ions/ cm^2 and at ion bombarding energies between 100 and 200 eV. The plasma bombardment was carried out under the erosion-dominated condition, which was defined in our previous work,¹⁵ for physically sputtered carbon atoms. During plasma operation, the total pressure in the PISCES-facility was typically 1×10^{-4} torr and the graphite temperature was around 800 °C. After a specified time, the plasma bombardment was turned off by closing the gas feed valve, and the total pressure in the vacuum system was monitored by a Bayard Alpert gauge as a function of time. Following shut down of the plasma, the graphite temperature dropped rapidly to room temperature.

One typical example of the total pressure change observed in this procedure is shown in Fig. 2. When the graphite target is not initially subjected to He plasma

bombardment, the total pressure rapidly decreases down to the base pressure of the vacuum chamber, which is $\approx 2 \times 10^{-6}$ torr in this particular case (see curve-a). However, after He-plasma bombardment at an energy of 100 eV for 10 minutes, the total pressure drops below the initial base pressure and remains there temporarily (see curve-b). Further He-plasma bombardment appears to elongate the duration of the temporary reduction of the total pressure (see curves-c and d). After exposure to He-plasma bombardment for 90 minutes, the total pressure falls to a level about a factor of 2.5 below the base pressure (see curve-e). It can be seen that in this case, the total pressure remains below the base pressure, while gradually increasing, as long as 30 minutes. Also, the total pressure fluctuates for a few minutes, which is referred as 'breathing' in Fig.2. (The breathing phenomenon will be discussed later.) Essentially the same behavior of the total pressure as that described above has been observed in the case when Ar-plasma bombardment at an energy of 200 eV is used.

2. Gettering speed and capacity of activated graphite

Observations described above clearly indicate that inert gas plasma bombardment 'activates' the graphite surface, which can then provide an additional pumping speed of about 2500 liters/s. This process immediately reminds us of 'activated charcoal', one of the typical adsorbent materials.¹⁷ In the remainder of this paper, the inert gas plasma bombardment to activate the graphite surface will be referred as the plasma-activation process (PA²). Since the geometrical plasma-facing surface area of the graphite target is 100 cm², the initial gettering speed of the activated graphite surface evaluated to be 25 liters s⁻¹ cm⁻², which is equivalent or superior to a typical value of a titanium-gettered surface at liquid nitrogen temperature.¹⁷

The volumetric arrival rate of a molecule, V_a , can be calculated, using the relation from the kinetic theory of gases:¹⁷

$$V_a = \sqrt{(2kT/\pi m)} \quad (1)$$

where k is the Boltzman constant, T is the temperature of the gas and m is the weight of the gas molecule. The volumetric arrival rates for H₂O-vapor, H₂ and N₂ + CO are estimated to be 15, 44 and 12 liters s⁻¹ cm⁻², respectively, at 15 °C. In general, the initial gettering speed due to multi-component gas adsorption, S_g , can be approximated by

$$S_g = \sum V_a v \quad (2)$$

where V_a and v are the volumetric arrival rate and the sticking coefficient of each gas, respectively. Unfortunately, to the best of our knowledge, the sticking coefficients for these residual gases are not well established for graphite with a strongly plasma-modified surface morphology which will be shown later. It is not possible to obtain the theoretical value of the gettering speed. However, one may conjecture from a vapor pressure viewpoint that the sticking coefficient for H_2O -vapor far exceeds those of other gases. The initial gettering speed evaluated for the activated graphite surface is thus considered to be within a reasonable range.

The total amount of pumped gas, Q , over a certain period can be calculated from the relation:¹⁷

$$Q = \int q dt. \quad (3)$$

Here, q is the gas throughput given by

$$q = P(t) S_{eff} \quad (4)$$

where $P(t)$ is the pressure as a function of time and S_{eff} is the effective pumping speed of the vacuum system. From the curve-e shown in Fig.2, the total gas gettering capacity of the activated gettering surface is estimated to be 0.025 torr-liter/cm² (i.e. 8.3×10^{17} molecules/cm²). It is important to note here that the graphite surface, once saturated, can be reactivated for gettering by inert gas plasma bombardment to a relatively low fluence. Assuming monolayer adsorption on graphite with a nominal surface density of 2.4×10^{15} atoms/cm², the estimated gettering capacity leads to a surface roughness factor of 345. This crude estimate of the roughness factor is not significantly different from reported values.¹³

3. Surface modification associated with plasma activation

Due to high fluence plasma bombardment, a significant surface modification is expected to be seen on the graphite target. Surface morphologies of graphite before and after PAP are shown in Fig.3. Intrinsic pores on the graphite surface even after ultra-sonic cleaning are still blocked by small machining dust particles with an average size of a few

microns (see picture-a). After PAP, the pore opening is significantly increased and the surface appears to be rather smooth (see pictures-b and c). The observed increase in pore opening is obviously due to surface modification via physical sputtering. In fact, He-plasma bombardment conditions during PAP lead to an erosion rate of typically $6.5 \mu\text{m}/\text{hour}$. This makes it possible to completely erode the dust particles blocking the pores. For these sponge-like surface morphologies, the large roughness factor evaluated in section III-A-2 is not surprising.

4. Possible mechanisms for gettering by activated graphite

Gettering by activated graphite may be explained by the following mechanisms:

(1) High flux inert gas plasma bombardment at elevated temperatures induces significant thermal and kinematical desorption of previously dissolved and adsorbed impurities from graphite. As a result, the surface adsorption sites will be unoccupied. Moreover, an appreciable number of radiation damages, which are likely to have unsaturated valences, will be generated on the surface during PAP. Therefore, the plasma-activated graphite surface is expected to have an increased gas adsorptivity. (2) More importantly, one can expect enhancement of the gas retention capability from the capillary effect¹⁷ due to the sponge-like surface morphology (see Fig.3). It follows that the gettering speed depends on the degree of surface pore opening. This is quite consistent with the observed fact that the gettering period was prolonged by increasing He-plasma bombardment fluence (see Fig. 2). Also, open pores on the surface will provide a better conductance for molecular flow into pores, which also contributes to the large initial gettering speed. (3) As mentioned earlier, the typical plasma bombardment flux (of the order of $10^{18} \text{ ions s}^{-1} \text{ cm}^{-2}$) during PAP is appreciably higher than the total arrival rate of residual gases (of the order of $10^{15} \text{ molecules s}^{-1} \text{ cm}^{-2}$ at total pressures around 10^{-6} torr). Therefore, high flux inert gas plasma bombardment will prevent the activated surface sites from being adsorbed with residual gases. After PAP, the adsorptive surface is exposed to residual gases and will then exhibit the gettering effect.

During the breathing period shown in Fig. 2, the residual gas analyzer indicated a fluctuation of the partial pressure of water vapor, the predominant residual gas in the vacuum system. This implies that the breathing phenomenon may be caused by in-pore capillary condensation of water vapor (i.e. inhalation) followed by immediate sublimation (i.e. exhalation). However, further investigation is necessary to support this speculation.

The graphite target is eroded via physical sputtering during PAP. Consequently, sputtered carbon will be deposited on the chamber wall at room temperature. One question which can be raised here is whether or not the deposited carbon on the vacuum chamber wall contributes to the observed gettering effect. The answer is negative for the following reasons: (1) The geometrical surface area of the vacuum wall to be deposited with sputtered carbon is about two orders of magnitude larger than that of the graphite target. It follows that the carbon deposit is not thick enough to provide capillary effects. (2) It is true that the carbon deposition can provide a fresh surface on the vacuum wall at an average rate of the order of 10^{14} atoms $s^{-1} cm^{-2}$. However, the carbon-deposited wall is constantly exposed to residual gas molecules during PAP. The total arrival rate of residual molecules is of the order of 10^{15} molecules $s^{-1} cm^{-2}$ at total pressures around 10^{-6} torr. Unlike the graphite target, the carbon-deposited wall is not bombarded with the inert gas plasma during PAP. These arguments indicate that the carbon-deposited wall surface is saturated with adsorbed gases before PAP is finished. (3) Generally, carbon is not considered to retain its volatile compounds such as oxide (e.g. CO) and hydride (e.g. CH_4) on its surface at room temperature without capillary effect.

For completeness of investigation, plasma activation of graphite was attempted using H-plasma bombardment at an energy of 100 eV. However, no gettering effect was observed. This can be explained as follows. High flux, high fluence H-plasma bombardment induces surface radiation damages, physical sputtering and then provides a sponge-like surface morphology to graphite.¹¹ However, it is also true that H-plasma bombardment causes chemical sputtering of graphite. Due to chemical sputtering, active radiation damage sites will be likely consumed to produce hydrocarbons (e.g. CH_4). Also, refreshed surface adsorption sites, if exist, will be immediately occupied by reactive atomic hydrogen. Hence, when the H-plasma bombardment is finished, there is no longer enough surface gas-adsorptivity to provide observable gettering effects in the PISCES-A facility.

It should be emphasized here again that gettering by activated graphite is governed by physical adsorption of molecules on the surface. It follows that the gettering effect strongly depends on vacuum characteristics of the system. The fact that the base pressure of the PISCES-A facility is of the order of 10^{-6} - 10^{-7} torr brought about the present findings. In another word, it is probably difficult to observe the gettering effect in well-baked ultra high vacuum systems such as those employed for TFE or JET where the base pressure is of the order of 10^{-8} - 10^{-9} torr. Nevertheless, the present result is important from a vacuum science viewpoint in that porous graphite is observed to be a recoverable getter in high vacuum systems.

B. Hydrogen Recycling under Plasma Bombardment

The observations described in section III-A has led to a hypothesis that the gettering graphite surface will somehow retain a hydrogen plasma particle influx until it saturates and that this effect will be reflected in hydrogen recycling behavior. To verify the hypothesis, the graphite target was bombarded by H-plasmas with fluxes between 5×10^{17} and 2×10^{18} ions $\text{s}^{-1} \text{cm}^{-2}$. The H-plasma bombarding energy was set at 300 eV. These conditions are believed to be relevant to the plasma-surface interactions in tokamaks such as TFTR.^{8,18} Hydrogen recycling behavior was measured with H-alpha spectroscopy calibrated in the manner to be described in the next section. The exposure time to H-plasma bombardment for recycling measurements was limited to a relatively short period of 20 seconds to simulate discharge conditions in existing magnetic fusion devices. The plasma in the PISCES-A facility reproducibly reaches the steady state condition within a short time constant (0.1-0.2 second), compared with the characteristic recycling time constant to be discussed later.

1. H-alpha spectroscopy for hydrogen recycling measurements

To review briefly, the important atomic physics processes associated with hydrogen recycling from a material surface under H-plasma bombardment include:

- (1) dissociation reactions of reemitted molecular hydrogen (e.g. $\text{H}_2 + \text{e}^- \Rightarrow \text{H} + \text{H} + \text{e}^-$);
- (2) excitation reactions of atomic hydrogen (e.g. $\text{H} + \text{e}^- \Rightarrow \text{H}^*$);
- (3) relaxation reactions of excited atomic hydrogen (e.g. $\text{H}^* \Rightarrow \text{H} + \text{h}\nu$);
- (4) ionization reactions of atomic hydrogen (e.g. $\text{H} + \text{e}^- \Rightarrow \text{H}^+ + 2\text{e}^-$).

As a whole, one can understand the significance of these consecutive processes as follows. Reemitted hydrogen molecules with thermal energies will be most likely dissociated very near the surface. Consequently, the major component in the local recycling region is atomic hydrogen, the excited neutral of which emits H-alpha light. In the present work, the brightness of H-alpha radiation is approximated as an indirect measure of the density of reemitted hydrogen molecules although there are elaborate theories, e.g. the Monte Carlo neutral transport program, DEGAS,¹⁹ which treats more details of the atomic physics of hydrogen recycling.

For hydrogen recycling measurements, H-plasma bombardment conditions for hydrogen recycling measurements were reproduced within an accuracy of 2.5 % with

respect to plasma density and electron temperature. Within the accuracy of reproducibility, if necessary, the H-alpha brightness was corrected using the following relation:²⁰

$$B \propto n_H n_e \langle \sigma v \rangle, \quad (5)$$

where B is the brightness of H-alpha, n_H is the neutral atomic hydrogen density, n_e is the electron density, and $\langle \sigma v \rangle$ is the rate coefficient for the reaction: $H + e^- \rightarrow H^+ + 2e^-$ which is a function of electron temperature. Therefore, the corrected H-alpha brightness can be used as a semi-quantitative measure to represent hydrogen recycling behavior.

2. Hydrogen recycling at low temperatures

First, the graphite surface was activated by He-plasma bombardment in the manner described in section III-A-1. Immediately after PAP, H-plasma bombardment was initiated for hydrogen recycling measurement so that the activated graphite surface would not significantly getter residual gases in the vacuum system. The H-plasma bombardment was then continued 5 minutes to ensure surface saturation with hydrogen. The pre-saturated surface was again subjected to H-plasma bombardment for hydrogen recycling measurement.

In this experiment, the net H-plasma bombardment influx was set at 1×10^{18} ions $s^{-1} cm^{-2}$, corrected by the kinematical particle reflection coefficient of 0.15 from the TRIM code.²¹ The plasma density and electron temperature were $5.7 \times 10^{11} cm^{-3}$ and 20 eV, respectively. Under these conditions, the graphite surface is roughly estimated to be eroded by 5400 Å after 5 minutes. This means that the surface layer implanted and damaged with energetic helium ions during the initial PAP was completely removed before hydrogen recycling measurement was resumed.

Typical behavior of hydrogen recycling from the activated and pre-saturated graphite surfaces is shown in Fig. 4. Notice that hydrogen reemission from the activated surface is significantly retarded, relative to that from the pre-saturated surface, in the time to approach the steady state (100% reemission). This clearly shows that the activated surface can 'pump' H-plasma particles. The plasma pumping capability can be easily recovered, via plasma impact desorption of hydrogen, by He-plasma bombardment at 100 eV for 1 minute. The plasma impact desorption process associated with surface reactivation will be described later in detail.

Because of the significant heat flux due to the H-plasma bombardment (≈ 55 W/cm²), the temperature of the graphite target on a water-cooled holder rises to 100 °C towards the end of the plasma exposure time. However, the rise of temperature is not so drastic as to cause significant excess reemission.²² Rather, it is important to point out here that the temperature of the activated surface under H-plasma bombardment is generally lower than that of the pre-saturated surface. The temperature measurement is done using a thermocouple attached to the specimen surface that is not exposed to the hydrogen plasma. Thus, the measured temperature is not directly related to the surface phenomena. Yet the observation described above is indicative of several possibilities: a reduced thermal conductivity from the activated surface to the bulk and/or some endothermic effect associated with hydrogen implantation.

3. Kinetic considerations of hydrogen recycling

Hydrogen recycling measurements have conventionally been conducted using ion beam facilities which are typically capable of producing hydrogen ion fluxes of the order of 10^{15} ions s⁻¹ cm⁻². It is observed in these ion beam experiments that unlike metallic materials, hydrogen reemission from graphite does not apparently initiate until the surface layer is saturated with implanted hydrogen to the implantation depth. The saturation concentration is normally 0.4 in terms of the H/C atomic ratio²³ and does not seem to depend strongly upon the implantation energy. The hydrogen saturation capacity is generally attributed to trapping sites existing in the graphite structure. However, one should always bear in mind that there is a hidden uncertainty as large as 50-100 % in the reported data because nominal properties of isotropic graphite materials are far more 'statistical'²³ than those of metals and alloys.

After surface saturation, hydrogen reemission from graphite rapidly approaches the steady state. Therefore, one may consider that the total hydrogen concentration at the steady state is not significantly different from the initial saturation concentration. In parallel, hydrogen accumulation (i.e. retention) proceeds in such a way that a limited number of trapping sites are competitively occupied with mobile hydrogen atoms in the implantation range, as described by the Local Mixing Model.²⁵ These characteristics of hydrogen retention in graphite, which can be compared to an 'overflowing bathtub', have recently been reviewed by Wilson and Hsu.²⁶ To date, however, the nature of the trapping sites in graphite materials is still controversial with issues such as trapping energies, behavior of formation and annihilation of trapping sites, etc.

In the present experiments, the typical H-plasma bombardment flux is about 3 orders of magnitude higher than the ordinary ion beam flux. This means that a 'bathtub' is expected to overflow soon after H-plasma bombardment starts in the PISCES-A facility. In fact, virtually no incubation period associated with the surface saturation is seen in the observed hydrogen reemission behavior shown in Fig. 4.

The hydrogen transport theory developed by Doyle²⁷ is applied here to determine the rate-limiting step in hydrogen reemission. From the theory, one can use the relation:

$$W_0 = (R_d/D)\sqrt{(K_0/J_0)}, \quad (6-a)$$

where W_0 is the dimensionless transport parameter for the upstream surface, R_d is the implantation depth, L is the thickness of the target, D is the hydrogen diffusivity, K_0 is the recombination constant, and J_0 the net incoming hydrogen flux corrected by the kinematical particle reflection coefficient. The dimensionless parameter, W_0 , is calculated to be above unity, using reported values²⁸ for the constituent parameters and R_d calculated from the TRIM code. In this case, hydrogen reemission kinetics is categorized in the DD-regime (diffusion-limited) under the present experimental conditions. From the same theory,²⁷ the recycle time is defined by the relation:

$$\tau_{1/2} = R_d^2/D \text{ (for } W_0 > 1). \quad (6-b)$$

The calculated recycle time is 5×10^{-2} s, too short to interpret the data shown in Fig. 4.

Based on the result from the dimensionless parameter analysis, the DIFFUSE code²⁹ was executed with a Sieverts' law boundary condition to simulate the hydrogen recycling behavior. The parameters for Sieverts' constant are tabulated elsewhere.²⁸ For this calculation, the hydrogen implantation profile is computed using the TRIM code (see Fig.6). The trapping site concentration (in terms of the $n_{\text{trap}}/n_{\text{carbon}}$ ratio, where n is the density) is set at 0.4 over the implantation depth. The hydrogen trapping energy is assumed to be 2.5 eV.²³ For simplicity, the rise of the temperature is approximated by a linear ramp from 15 to 95 °C at a constant rate of 4 degrees/s. In Fig.5, the computed hydrogen recycling behavior with the DIFFUSE code is compared with the experimental data for the activated graphite. The calculated hydrogen reemission shows considerably rapid rise to the steady state, compared with the experimental observation. Generally, the dimensionless transport parameter theory and the DIFFUSE code have been successful in analyzing hydrogen recycling from various materials. However, graphite seems to be exceptional in

this regard. This is probably due to the complicated surface characteristics of the graphite material used in this work.

As a fitting procedure to evaluate the characteristic time constant, the observed reemission curve is approximated by an exponential increase followed by a saturation in the manner:

$$J_r(t) = J_0\{1 - \exp(-t/\tau)\}, \quad (7)$$

where J_r and J_0 are the reemitting and net incoming fluxes of hydrogen, respectively, and τ is the characteristic time constant. The calculated reemission curves from eq.(7) are superimposed on the experimental data points shown in Figs 4 and 5. The fitted time constants for hydrogen reemission from the activated and pre-saturated surfaces are 1.7 and 0.8 s, respectively.

Similarly, the following relation defines the 'dynamic' retention of hydrogen, C_r , during H-plasma bombardment:

$$C_r(t) \equiv \int (J_0 - J_r) dt = \tau J_0\{1 - \exp(-t/\tau)\}. \quad (8)$$

The 'dynamic' retention is the total non-reemitted hydrogen fluence including hydrogen trapped in graphite and hydrogen lost due to surface erosion. The final dynamic retention of hydrogen, given as $C_r(\infty)$, is calculated to be 1.7×10^{18} ions/cm² and 7.9×10^{17} ions/cm² for the activated and pre-saturated surfaces, respectively. Considering the typical composition of hydrogen plasma species in the PISCES-A facility:¹¹ 75% H⁺, 20% H₂⁺ and 10% H₃⁺, the hydrogen retention values above correspond to 2×10^{18} H/cm² and 9.5×10^{17} H/cm², respectively.

4. Possible mechanisms for high hydrogen retention

High hydrogen retention data for graphite materials have been recently reported.^{30,31} Using a glow discharge technique, Langley³⁰ obtained a hydrogen retention of 2×10^{18} H/cm² in POCO-graphite at an ion bombarding energy of 400 eV for the graphite target at room temperature. The hydrogen retention value was calculated from the pressure drop in the isolated discharge system. The high hydrogen retention was attributed mainly to chemisorption of atomic hydrogen at active carbon sites, probably with a low binding energy. However, the origin and concentration of these chemisorption sites

were not well defined or correlated with the observations. Hsu and Causey³¹ observed an apparently high hydrogen retention of 1.1×10^{19} D/cm², using a Penning discharge system with graphite cathodes, at implantation voltages between 300 and 500 eV. This high retention value was, however, found to be due to formation of a hydrogen-rich (7.2×10^{17} D/cm²) carbonaceous film, via co-deposition, on the discharge vessel wall components. The nature of the co-deposited film might be similar to that of the carbonized wall in TEXTOR 4 although details are still unclear. These arguments are not directly applicable to the present experiments nor do they appear to explain the present findings. Therefore, several possible mechanisms are proposed here.

The activated surface is found here to have about a factor of two larger dynamic retention of hydrogen than the pre-saturated surface. The net effect of He-plasma activation, i.e. the difference in the dynamic hydrogen retention for activated and pre-saturated surfaces, appears to be equivalent to the gettering capacity of the activated surface. This leads to a conjecture that the extra hydrogen might reside at activated surface adsorption sites, both on the 'flat' and in-pore surfaces, perhaps in the form of surface radicals such as C-H and H-C-H although details of the surface chemistry are still unknown. Recently, Causey et.al.³² have also found out that at temperatures below ≈ 130 °C, surface chemisorption sites in the internal pores can increase the effective retention of deuterium and tritium implanted at an energy of 100 eV to the level significantly exceeding the one that the bathtub concept predicts.

One may apply the bathtub concept to a highly porous surface. The existing hydrogen saturation concentration data are mostly taken from isotropic graphite materials, pores of which may not be fully opened to the surface. It is not easy to determine whether the BET surface area of an isotropic graphite material increases due to removal of dust particles along with high fluence plasma bombardment. However, increasing open pores on the graphite surface will certainly increase the effective plasma-facing surface area. It follows that the sponge-like surface morphology, shown in Fig. 3, can topographically increase the effective hydrogen retention capacity in terms of H/cm². Unfortunately, the surface roughness factor evaluated here does not quantitatively support this argument.

As observed for stainless steel,³³ pre-damage sites due to He-plasma bombardment associated with PAP might lead to an increase in the number of internal trapping sites for hydrogen. As shown in Fig. 6, the radiation damages generated by He-PAP at 100 eV distribute to a depth of 20 Å or less. However, implanted hydrogen during recycling measurement at 300 eV significantly exceeds the depth of PAP induced damages. This means that the observed high hydrogen retention cannot be totally explained by the pre-damaged site concept.

5. *Dynamic hydrogen retention by pre-saturated graphite*

It is important to point out here that the *pre-saturated* surface also appears to pump H-plasma particles to a significant amount. This effect has been found to be reproducible, meaning that the surface is virtually non-saturable with hydrogen. The definition of the '*pre-saturated*' surface is not consistent with this finding. Therefore, one should attribute the observed plasma pumping by the pre-saturated surface to a dynamic hydrogen retention capability. From the sponge-like surface morphology, a transient pumping mechanism is conjectured here that hydrogen might be stored temporally in pores under plasma bombardment and then be released later on. This will cause a particle imbalance between the fast implantation and slow release of hydrogen during plasma bombardment.

Generally, behavior of gas release from a surface can be influenced by stagnation of released gas. This is particularly true when the gas-surface system is not well ventilated. Thus, the slow release of hydrogen in this case is probably due to the narrow, deep pore channels. This may be one of reasons for the fact that the kinetic analysis of the present data using the DIFFUSE code has been unsuccessful.

This transient plasma pumping behavior is phenomenologically similar to that observed in JET⁷ in that the graphite surface can reproducibly pump H-plasmas without He-plasma discharge conditioning. In JET, the delayed hydrogen reemission peak is observed with H-alpha spectroscopy when the H-plasma is moved from the inner graphite wall. However, this delayed H-alpha peak observed in JET has not been clearly attributed to a surface structural effect. In order to experimentally verify the transient pumping mechanism conjectured here, we attempted to observe the delayed reemission of hydrogen from the pre-saturated graphite surface, using a residual gas analyzer, immediately after H-plasma bombardment. Because the hydrogen partial pressure is high (typically, 1×10^{-4} torr) during plasma operation in the PISCES-facility, no clear evidence of the delayed reemission of hydrogen was obtained. However, a delayed emission of CH_4 was observed in such a way that the intensity of CH_4 signal peaks before it fades out (shown schematically in Fig. 9). This is indicative of transient storage of molecules in the pores. Unfortunately, no further experimental evidence is available to date.

6. Effect of reactivation procedure on hydrogen recycling

The activated surface, once saturated, can be reactivated by He-plasma bombardment at an energy of 100 eV. During reactivation, graphite is subject to surface erosion at a physical sputtering yield of 3×10^{-2} atoms/ion.³⁴ The graphite surface is eroded by 1600 Å after exposure to He-plasma bombardment at a flux of 1×10^{18} ions $\text{s}^{-1} \text{cm}^{-2}$ for 1 minute. As shown in Fig. 6, the implantation depth of hydrogen at 300 eV in graphite is 150 Å or less. These calculations indicate that pre-implanted hydrogen will be completely removed along with carbon erosion during reactivation. As a result, graphite is given a fresh activated surface.

One question here is whether or not the graphite surface can be reactivated even if He-plasma bombardment is not energetic enough to remove pre-implanted hydrogen completely. To investigate this possibility, a pre-saturated graphite surface was bombarded by a He-plasma at 15 eV, an energy below the theoretical physical sputtering threshold for carbon (≈ 28.5 eV³⁴). Subsequent hydrogen recycling measurements indicated that the graphite surface is reactivated even by non-sputtering He-plasma bombardment. In fact, the characteristic time constant for hydrogen recycling is evaluated to be 1.8 s, which is essentially the same as that of graphite reactivated by He-plasma bombardment at 100 eV. The pre-saturated graphite surface was also bombarded by Ar-plasmas at 50 and 100 eV, energies below the theoretical physical sputtering threshold for carbon (≈ 112.7 eV³⁴). The resultant graphite surfaces clearly exhibited plasma pumping capabilities. The important implication of these non-sputtering reactivation processes will be described later in detail.

7. Effect of air-exposure of activated graphite on hydrogen recycling

In this section, the effect of air-exposure of an activated surface on hydrogen recycling behavior is discussed. The graphite target was first activated and immediately exposed to the air for 5 min. The air-exposed surface was then subjected to H-plasma bombardment for recycling measurement. The plasma bombardment flux in this experiment was 5.2×10^{17} ions $\text{s}^{-1} \text{cm}^{-2}$ and the bombarding energy was set at 300 eV. The surface temperature was controlled below 100 °C. The result is shown in Fig. 7. The measured intensity of H alpha from the air-exposed surface is normalized to that from the pre-saturated surface at the steady state. Notice that the H-alpha intensity from the air-exposed surface is significantly higher than that for the pumping and pre-saturated sur-

faces. This is obviously due to adsorption of molecules, e.g. H_2O , during air exposure. It follows from this that the activated surface is very air-sensitive, consistent with the gettering nature described in section III-A.

The H-alpha intensity, once increased after air-exposure, gradually decreased and reached the level similar to that for the pre-saturated surface after extensive H-plasma bombardment to a fluence of the order of 10^{21} ions/cm². This reminds us of tokamak wall conditioning using hundreds of hydrogen plasma discharges. As shown in Fig. 7, the air-exposed surface was found to be reactivated by He-plasma bombardment at an energy of 100 eV for only 1 minute, corresponding to a fluence of 6×10^{19} ions/cm². It follows directly from these findings that PAP will be quite useful in conditioning graphite surface components in a large toroidal fusion device, particularly after vacuum openings.

The dynamic hydrogen retention estimated in this case is 1.9×10^{18} and 6.2×10^{17} H/cm² for the activated and pre-saturated surfaces, respectively. These well agree with the corresponding values obtained when the H-plasma bombardment flux is set at 1×10^{18} ions s⁻¹ cm⁻². This indicates that the activated and pre-saturated surface have respective constant plasma-pumping capacities, regardless of plasma bombardment flux. Therefore, it can be expected that if the plasma particle load is smaller, a activated graphite limiter will provide reduced local recycling for more confinement discharges.

8. Hydrogen recycling at elevated temperatures

To investigate hydrogen reemission behavior when surface recombination plays an important role (i.e. in the RD-regime for $W_0 \ll 1$ ²⁷), the graphite temperature was controlled between 450 and 480 °C. In this experiment, the H-plasma bombardment flux and energy were 6×10^{17} ions s⁻¹ cm⁻² and 300 eV, respectively. The result is shown in Fig. 8. Again, hydrogen reemission from the activated surface is retarded, relative to that from the pre-saturated surface. However, no steady state reemission is attained within the specified plasma exposure time. Only a short transient plateau is observed for the pre-saturated surface, around 3-4 seconds after H-plasma bombardment starts. For convenience, the H-alpha intensity is normalized to that at the initial plateau region for the pre-saturated surface. The increase in H-alpha intensity beyond 100% is most likely due to thermal degassing of hydrogen in the elevated temperature range. The initial plateau is probably due to a transient particle balance between plasma implantation and thermal release of hydrogen. On the other hand, the computed hydrogen recycling behavior with the DIFFUSE code clearly shows saturation behavior. In this calculation, the trapping energy

is assumed to be 2.5 eV. These results suggest that there might be other trapping sites with lower binding energies which lead to a thermal desorption at lower temperatures. Further experiments at elevated temperatures are under way.

Because of the non-saturation nature, eq.(7) cannot be applied to estimate the dynamic hydrogen retention. Instead, the dynamic hydrogen retention to the initial plateau level is graphically evaluated to be 7.9×10^{17} and 2.7×10^{17} H/cm² for the activated and pre-saturated surfaces, respectively. The dynamic hydrogen retention is appreciably reduced, relative to that estimated at temperatures below 100 °C. However, this is not surprising since the surface adsorptivity is generally lower at elevated temperatures. Also, it is well known that hydrogen trapping sites are largely (70-80%) disabled at temperatures around 500 °C.²⁶ Nevertheless, the dynamic hydrogen retention evaluated here is still significantly larger than that one would expect from the bathtub concept based on the temperature dependent hydrogen trapping capacity.

C. Hydrocarbon Formation during Hydrogen Recycling

As can be seen in earlier sections, H-alpha spectroscopy measurements provide the key information to analyze hydrogen recycling behavior. For a given amount of incoming H-plasma flux, however, the brightness of H-alpha radiation may be reduced due to chemical sputtering of the graphite surface since hydrogen is consumed for hydrocarbon formation as well as reemission. In this section, the behavior of chemical sputtering of an activated graphite surface and its effect on H-alpha measurements are briefly discussed.

For this purpose, the intensity of CH₄ radiation band at a wave length of 5430 Å was monitored during H-plasma bombardment. The H-plasma bombardment was carried out at a flux of 5×10^{17} ions s⁻¹ cm⁻² at an energy of 300 eV. The surface temperature was controlled below 100 °C. (These conditions are essentially the same as those used for hydrogen recycling measurements described in section III-B-6.) A typical result is shown in Fig. 9. The intensity of CH₄ radiation band shows an exponential increase followed by a steady state, time dependent behavior similar to hydrogen reemission. This clearly indicates that the steady state chemical sputtering requires surface saturation with hydrogen, which is consistent with earlier measurements.^{35,36} As a consequence, the chemical sputtering yield of the activated surface is noticeably lower than that of the pre-saturated surface, particularly before the steady state erosion is established.

It follows from these results that the H-alpha brightness from the activated surface is less affected by chemical sputtering than that from the pre-saturated surface. In addition,

no significant hydrocarbon formation is expected from chemical sputtering at temperatures below 100 °C. There are some atomic physics processes to decompose hydrocarbons into atomic hydrogen, which then emits H-alpha light. This effect can virtually increase the intensity of H-alpha brightness. However, these processes are not likely to occur near the graphite surface for the plasma densities and electron temperatures generated in the PISCES-A facility. Details of atomic physics processes including hydrocarbons can be found elsewhere.³⁷ As a whole, there is no significant effect due to chemical sputtering on H-alpha measurements.

D. Hydrogen Release by Plasma Impact Desorption

In many fusion devices, plasma discharge cleaning has been used for conditioning plasma-facing components so as to minimize impurity emission during confinement experiments. In this regard, it is important to understand the mechanism of particle release from the surface under plasma bombardment. To date, considerable effort has been made to establish a data base, particularly for ion impact desorption cross sections.³⁸ These measurements have never been conducted using high flux plasmas. In the present work, inert gas plasma bombardment has been found to remove saturated hydrogen and reactivate the graphite surface. It is of great interest to investigate behavior of hydrogen release along with the reactivation process. It is also true that if inert gas plasma bombardment is used for wall conditioning in fusion devices, these inert gases will be released and behave as impurities in the subsequent H-plasma discharges. For these reasons, plasma impact desorption of hydrogen, helium and argon is discussed in detail in this section.

1. Basic theoretical considerations

To describe the plasma impact desorption process, the recycling effect on the net removal rate must be considered unlike the ordinary ion impact desorption process. Let n be denoted as the number of particles retained on the surface. The following desorption rate equation is obtained:

$$\frac{dn}{dt} = \sigma_{ij} I_{p,n} - R \left(\frac{dn}{dt} \right) \quad (9)$$

where σ_d is the cross section for plasma impact desorption, J_0 is the plasma flux, t is the time and R is the particle recycling coefficient. The solution of eq.(9) is expressed as

$$\ln\{(n - n_\infty)/(n_0 - n_\infty)\} = -\sigma_d^* J_0 t \quad (10-a)$$

where n_0 and n_∞ are the values of n at $t = 0$ and $t = \infty$, respectively, and

$$\sigma_d^* \equiv \sigma_d/(1-R). \quad (10-b)$$

Here, σ_d^* is defined as the 'effective' cross section for plasma impact desorption. At the early stages of plasma impact desorption where $n_\infty \ll n$ and $n_\infty \ll n_0$, the solution of eq.(10-a) can be simplified to the form:

$$\ln(n/n_0) = -\sigma_d^* J_0 t. \quad (10-c)$$

The particle recycling coefficient, R , in the PISCES-A facility is equivalent to the probability of redeposition defined in our previous work.¹⁵ This means that R is a function of the mean free path for electron impact ionization of the particle released from the surface. Generally, the mean free path for electron impact ionization, λ , can be calculated from the relation:

$$\lambda = V_{av}/(n_e \langle \sigma v \rangle), \quad (11)$$

where V_{av} is the averaged velocity over the energy distribution of the desorbing particles, n_e is the plasma density and $\langle \sigma v \rangle$ is the rate coefficient for electron impact ionization. Assuming a planer surface potential, the energy distribution needed to determine V_{av} is given by the relation:

$$N(E) = E/(E+E_b)^3, \quad (12)$$

where E is the energy and E_b is the binding energy of the element to the surface.

2. Experimental observations of plasma-impact desorption

The effective plasma impact desorption cross sections have been measured in the following cases: (1) H-desorption by He-plasma bombardment; (2) H-desorption by Ar-plasma bombardment; (3) He-desorption by H-plasma bombardment; and (4) Ar-desorption by H-plasma bombardment. For cases; (1) and (2), pre-saturated graphite was used after H-plasma bombardment at an energy of 300 eV. Helium and argon pre-implantation for cases; (3) and (4) was conducted at an energy of 100 eV to a fluence of 3×10^{20} ions/cm². Plasma bombardment for desorption measurements was done at a flux of $\approx 1 \times 10^{18}$ ions s⁻¹ cm⁻² at energies between 15 and 300 eV. Plasma parameters were controlled such that the recycling coefficient described in the previous section can be minimized. Thus, little recycling and redeposition occur. The graphite target temperature was held below 60 °C so as to avoid any significant thermal outgassing during plasma-impact desorption. The plasma-impact desorption process was monitored in-situ by spectroscopic measurements of H-alpha, He-I and Ar-I radiation lines at a wave length of 6562.8, 3888.6 and 6965 Å, respectively. The spectroscopic technique used here is based on the relation:

$$\ln(I/I_0) = \ln(n/n_0) = -\sigma_d^* J t \quad (13)$$

where I and I_0 are the intensity of the radiation line of interest at $t=t$ and $t=0$, respectively.

Unfortunately, there is no established data base for the binding energies of H, He and Ar to the graphite surface or bulk. A best guess is that E_b may be a few electron volts. To determine a benchmark value (possible maximum) of R in eq.(10-b), let us assume Ar to be released from graphite with $E_b = 2$ eV under He-plasma bombardment with $n_e = 2 \times 10^{12}$ cm⁻³ and $T_e = 10$ eV. Having $\langle \sigma v \rangle \approx 2 \times 10^{-8}$ cm²/s from Lotz's formula³⁹ and $V_{av} \approx 5 \times 10^5$ cm/s, one can estimate $\lambda \approx 12$ cm, leading to the conclusion that $R \leq 10\%$.¹⁵ This means that σ_d^* can be practically regarded as σ_d within an accuracy of 10%. Therefore, in the present paper, we would rather deal with σ_d^* as measured.

Typical desorption behavior of hydrogen under He-plasma bombardment at energies between 15 and 300 eV is shown in Fig.10-a. The spectroscopic data are plotted according to eq.(13) so that the effective plasma impact desorption cross section can be given as the slope of the linear part of the entire profile. Notice that the intensity of H-alpha decreases by 70.30% within a minute. Once He-plasma bombardment is done, the surface is reactivated.

The characteristic desorption curves exhibit a significant deviation from the prediction of eq.(13) in the plasma bombardment fluence range above $\approx 1 \times 10^{19}$ ions/cm². Similar deviations have been observed in earlier studies.⁴⁰⁻⁴² There are several possible causes for the deviation observed here. One simple possibility is that the assumption: $n_{\infty} \ll n$ to support eq.(10-c) might fail as desorption proceeds. However, the plasma bombardment fluence at which the deviation starts seems to be too small to cause the mathematical error. Another possibility is the retrapping effect on the desorption rate, as proposed by Wampler.⁴⁰ This retrapping model can be described as follows: As ion-impact desorption proceeds, the number of unoccupied trapping sites increases. Consequently, detrapped hydrogen becomes more likely to be retrapped before it leaves the surface. The net desorption rate decreases, relative to that when there is no retrapping. The retrapping effect might in part contribute to the present result. However, the depth of kinematic interaction between pre-implanted hydrogen and bombarding helium, which is 10-60 Å (see Fig. 6), is somewhat too shallow to yield a significant retrapping effect of this kind.

Topographical effects on hydrogen release behavior are conjectured here for the sponge-like surface structure (see Fig. 3). As mentioned earlier, a significant fraction of pre-implanted hydrogen is considered to reside in the pores. The in-pore hydrogen will undergo several collisions with the surface in the narrow pore channel before being ejected. This collisional process causes kinematical slow-down and eventually leads to an in-pore retrapping. Also, it follows from this postulation that there will be no strong in-pore retrapping effect at the early stages of plasma impact desorption since hydrogen on the 'flat' surface area will be released predominantly, consistent with the observation.

3. Evaluation of plasma-impact desorption cross sections

The effective plasma impact desorption cross sections are deduced from the initial linear part shown in Fig. 10-b and summarized in Fig. 11 as a function of plasma bombarding energy. In general, the ion impact desorption process is kinematically enhanced when implantation profiles for pre-implanted particles and for bombarding ions strongly overlap. In the energy range examined here, the implantation profiles for helium and argon ions are significantly shallow, as shown in Fig. 6, compared with that for pre-implanted hydrogen. It is also true that the plasma bombarding energies examined here are significantly lower than those in earlier studies.^{38,40-42} For these reasons, one can not expect high-rate desorption. In fact, the plasma impact desorption cross sections obtained

here are about one to two orders of magnitude below the existing data from ion beam experiment, conducted under high-energy, overlapping depth-profile conditions.^{38,40-42}

These arguments indicate that He and Ar-plasma bombardment, particularly at non-sputtering energies, will not kinematically affect pre-implanted hydrogen below a certain depth. However, it is found that the hydrogen-saturated graphite surface can be reactivated, via plasma impact desorption, regardless of the bombarding energy examined here. This means that reactivated graphite can pump hydrogen plasma particles even if internal trapping sites are occupied with pre-implanted hydrogen. It follows directly from this that the bathtub concept cannot totally explain the plasma-pumping capability of graphite. Rather, the activated sites on the sponge-like surface of graphite appear to play an important role in plasma-pumping phenomena observed in the present work.

IV. Summary

The effects of inert gas plasma bombardment on characteristics of isotropic graphite have been investigated with respect to: (1) modification of the surface morphology; (2) surface gas-adsorptivity; (3) hydrogen plasma recycling; (4) surface chemical erosion, and (5) hydrogen release behavior.

The inert gas (He and Ar) plasma bombardment at energies between 100 and 200 eV at temperatures around 800 °C strongly modifies the graphite surface via physical sputtering. Small graphite particles blocking intrinsic pores are removed and the resultant graphite surface exhibits a significantly porous, sponge-like surface morphology. The surface roughness factor is roughly estimated to be 345, not surprising for such sponge-like surfaces.

The activated graphite surface getters neutral residual gases in vacuum. The initial gettering speed is evaluated to be as large as 25 liters s⁻¹ cm⁻², and the total gettering capacity is 0.025 torr-liter/cm² (8.3×10^{17} molecules/cm²) at room temperature. After saturation, the graphite surface can be easily reactivated by inert gas plasma bombardment. The nature of a activated graphite surface is attributed in part to the capillary effect of the sponge-like surface and surface radiation damage sites.

The activated graphite surface is found to pump hydrogen plasma particles as well. This effect results in a significantly retarded hydrogen reemission. The dynamic hydrogen retention is estimated to be as large as 2×10^{18} H/cm² at a plasma bombarding energy of 300 eV at temperatures below 100 °C. A pre-saturated graphite surface reproducibly pumps hydrogen to a concentration of 9.5×10^{17} H/cm². This is attributed to a transient

pumping capability associated with the sponge-like surface morphology of graphite. The transient plasma pumping is due to a particle imbalance between fast implantation and slow release of hydrogen through pore channels. The net increase in hydrogen retention due to He-plasma activation appears to be close to the neutral gettering capacity, suggesting that the extra hydrogen is trapped on activated adsorptive surface sites. Also, the hydrogen retention capacity of graphite is found to decrease rapidly with increasing temperature. At temperatures between 450 and 480 °C, the hydrogen retention estimated for the activated surface and pre-saturated surface is 7.9×10^{17} H/cm² and 2.7×10^{17} H/cm², respectively.

The surface chemical erosion rate during hydrogen recycling is found to track with hydrogen saturation. Consistently, the activated surface exhibits a reduced hydrocarbon formation and release rate, relative to the pre-saturated surface.

Hydrogen release under inert gas plasma bombardment is controlled by the plasma impact desorption process which may be influenced by in-pore retrapping. Hydrogen release from pre-saturated graphite under He and Ar plasma bombardment has been observed in a wide energy range from 15 to 300 eV. This result allows us to utilize the plasma-impact desorption technique for wall conditioning in magnetic fusion devices. In fact, DC He-glow discharge without magnetic field has recently been used for surface conditioning in DIII-D tokamak, and has led to reduced local recycling ($R < 1$) at the graphite limiter area in several successive confinement experiments.⁴³

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REFERENCES

1. H.F.Dylla and TFTR Team, *J.Nucl.Mater.* **145-147**, 48 (1987).
2. L.De Kock, *J.Nucl.Mater.* **145-147**, 26 (1987).
3. N.H.Brooks, P.Petersen and the DIII-D group, *J.Nucl.Mater.* **145-147**, 770 (1987).
4. J.Winter, *J.Vac.Sci. & Technol.-A* **5**, 2286 (1987).
5. M.Ulickson, J.L.Cecchi, B.Lipschultz, *J.Vac.Sci.&Technol.-A* **5**, 2257 (1987).
6. J.D.Strachan, M.Bitter, A.T.Ramsey et.al., *Phys.Rev.Lett.* **58**, 1004 (1987).
7. K.J.Dietz, K.Sonnenberg, E.Deksnis and R.Shaw, 'Wall Protection in JET', *JET Rep. JET-P* (85) 16
8. K.W.Hill, V.Arunasalm, M.G.Bell et.al., *Proc.IAEA 11th Int.Conf.on Plasma Physics and Controlled Fusion Research*, Kyoto, p. 207 (1986).
9. H.F.Dylla, P.H.LaMarche, M.Ulickson et.al., 'Conditioning of the Graphite Bumper Limiter for Enhanced Confinement Discharges in TFTR', *PPPL Rep. PPPL-2448*.
10. S.A.Cohen, J.Ehrenberg, T.T.C.Jones et.al., to be published in *Plasma Physics & Controlled Fusion*.
11. D.M.Goebel, Y.Hirooka, R.W.Conn et.al., *J.Nucl.Mater.* **145-147**, 61 (1987).
12. A.E.Pontau, R.A.Causey and J.Bohdansky, *J.Nucl.Mater.* **145-147**, 775 (1987).
13. K.Nakayama, S.Fukuda, T.Hino and T.Yamashina, *J.Nucl.Mater.* **145-147**, 301 (1987).
14. D.M.Goebel, G.A.Campbell and R.W.Conn, *J.Nucl.Mater.* **111&112**, 457 (1982).
15. Y.Hirooka, D.M.Goebel, R.W.Conn et.al., *J.Nucl.Mater.* **141-143**, 193 (1986).
16. Y.Hirooka, D.M.Goebel, R.W.Conn et.al., *Nucl.Instr. & Methods-B* **23**, 458 (1987).
17. S.Dushman, 'Scientific Foundations of Vacuum Technique, 2nd ed.', John Wiley & Sons, (1962).
18. D.B.Herferetz, M.L.Baskes, H.F.Dylla and M.Ulickson, *J.Nucl.Mater.* **145-147**, 326 (1987).
19. D.B.Herferetz, D.Post, M.Petravic, J.Weisheit and G.Bateman, *J Comp Phys.* **46**, 309 (1982).
20. E.S.Mattar, *J.Nucl.Mater.* **76&77**, 59 (1987).
21. H.Vernickel, *J.Nucl.Mater.* **128&129**, 708 (1984).

22. R.A.Langley, J.Bohdansky, W.Eckstein et.al., 'Data Compendium for Plasma-Surface Interactions', Sepecial Issue of Nucl. Fusion (1984).
23. W.P.Eatherly, R.E.Clausing, R.A.Stehlow et.al., 'Graphite for Fusion Energy Applications', ORNL Rep. ORNL/TM-10280.
24. B.L.Doyle, W.R.Wampler, D.K.Brice and S.T.Picraux, J.Nucl.Mater. **93&94**, 551 (1980).
25. K.L.Wilson and W.L.Hsu, J.Nucl.Mater. **145-147**, 121 (1987).
26. B.L.Doyle, J.Nucl.Mater. **111&112**, 628 (1982).
27. Summarized in D.E.Post and R.Behrish (ed.), 'Physics of Plasma-Wall Interactions in Controlled Fusion', NATO ASI-series vol. 131, Plenum Press (1986).
28. M.I.Baskes, 'DIFFUSE 83', SNL Rep. SAND83-8231.
29. J.P.Biersack and L.G.Haggmark, Nucl.Instr.& Meth. **121**, 257 (1980).
30. R.A.Langley, J.Vac.Sci.&Technol.-A **5**, 2205 (1987).
31. W.L.Hsu and R.A.Causey, J.Vac.Sci.&Technol.-A **5**, 2768 (1987).
32. R.A.Causey, M.I.Baskes and K.L.Wilson, J.Vac. Sci. and Technol.-A **4**, 1189 (1986).
33. K.L.Wilson, A.E.Pontau, L.G.Haggmark et.al., J.Nucl.Mater. **103&104**, 493 (1981).
34. N.Matsunami, Y.Yamanaka, Y.Itikawa et.al., Atomic Data and Nucl.Data Tables **31**, 1 (1984).
35. C.M.Braganza, S.K.Erents and G.M.McCracken, J.Nucl.Mater.**75**, 220 (1978).
36. R.Yamada, K.Nakamura, K.Sone and M.Saidoh, J.Nucl.Mater. **95**, 278 (1980).
37. A.B.Ehrhardt and W.D.Langer, 'Collisional Processes of Hydrocarbons in Hydrogen Plasmas', PPPL Rep. PPPL-2477.
38. For example, A.Sagara and K.Kamada, J.Nucl.Mater. **111&112**, 812 (1982).
39. W.Lotz, Zeitschrift fur Physik **216**, 241 (1968).
40. W.R.Wampler and S.M.Myers, J.Nucl.Mater.**111&112**, 616 (1982).
41. J.Roth, B.M.U.Scerzer, R.S.Blewer et.al., J.Nucl.Mater. **93&94**, 601 (1980).
42. M.C.Underwood, S.K.Erents and E.S.Holston, J.Nucl.Mater. **93&94**, 575 (1980).
43. G.L.Jackson, T.E.Evance, M.Ali Mardavi et.al., APS Fall Meeting, San Diego, (1987).

FIGURE CAPTIONS

- Fig. 1 A schematic diagram of the experimental setup.
- Fig. 2 A typical example of observed behavior of change of the total pressure in the PISCES-A facility after shut-down of helium plasma operation for plasma activation of the graphite surface.
- Fig. 3 Surface morphologies of the graphite target: (a) after ultrasonic cleaning in acetone and vacuum degassing at about 800 °C; (b) after He-plasma activation; and (c) after extensive hydrogen recycling experiments.
- Fig. 4 Hydrogen recycling behavior from the activated and pre-saturated graphite surfaces under H-plasma bombardment at a flux of 1×10^{18} ions $\text{s}^{-1} \text{cm}^{-2}$ at an energy of 300 eV and at temperatures below 100 °C. Experimental data are interpolated by eq.(7) with the fitted characteristic time constants.
- Fig. 5 Comparison of hydrogen recycling behavior computed with the DIFFUSE code ²⁹ and that observed for an activated graphite under H-plasma bombardment at a flux of 1×10^{18} ions $\text{s}^{-1} \text{cm}^{-2}$, at an energy of 300 eV and at temperatures below 100 °C.
- Fig. 6 Trapping profiles for H, He and Ar in graphite computed with the TRIM code. ²¹ The darkened area represents a hydrogen-saturated surface layer.
- Fig. 7 Effect of air-exposure of the activated graphite surface on the subsequent hydrogen recycling behavior under H-plasma bombardment at a flux of 5.2×10^{18} ions $\text{s}^{-1} \text{cm}^{-2}$ at an energy of 300 eV and at temperatures below 100 °C.
- Fig. 8 Hydrogen recycling behavior from the activated and pre-saturated graphite surfaces under H-plasma bombardment at a flux of 6×10^{17} ions $\text{s}^{-1} \text{cm}^{-2}$ at an energy of 300 eV and at temperatures between 450 and 480 °C. The computed recycling behavior with the DIFFUSE code ²⁹ is compared with the experimental data.

Fig. 9 In-situ spectroscopic observation of chemical sputtering behavior during hydrogen recycling under H-plasma bombardment at a flux of 5×10^{17} ions $s^{-1} cm^{-2}$ at an energy of 300 eV and at temperatures below 100 °C.

Fig.10 Hydrogen release behavior from pre-saturated graphite under He-plasma bombardment at a constant flux of 1×10^{18} ions $s^{-1} cm^{-2}$ at energies between 15 and 250 eV to a fluence of 6×10^{19} ions/ cm^2 (a) and to a fluence of 1×10^{19} ions/ cm^2 (b).

Fig.11 Effective plasma impact desorption cross sections for H, He and Ar from graphite as a function of plasma bombarding energy.

FIG. 1

FIG. 2

a.

b.

c.

Fig. 3

FIG. 4

FIG. 5

FIG. 6

FIG. 7

FIG. 8

FIG. 9

FIG. 10

FIG. 11