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Chemistry of excited states: Its impact on plasma wall interactions in fusion devices [1]

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Abstract

Differently from molecular hydrogen, energetic hydrogen escaping from plasma is directly implanted into plasma facing materials depositing its energy to excite electrons, to displace lattice atoms and to excite phonons and finally thermalized in the target. This makes subsequent migration of the thermalized hydrogen in the target very complex. Electrons and photons escaping from plasmas are superposed to influence the hydrogen migration, too. Simultaneously, various particles are emitted from the surface, including reflected, sputtered, and re-emitted particles, secondary electrons and photons. Those emitted particles are not necessarily equilibrated thermodynamically with the temperature of the target surface but are often in higher excited states and some are even ionized. Hence the surface exhibits various chemical reactions with impurities and/or chemical change. Enhanced erosion of carbon materials by implanted hydrogen producing methane, the chemical sputtering of carbon, is one of the most well-known examples. Even atomic hydrogen emission from carbon is observed at such a low temperature as 1000°C. The super permeation of hydrogen in metals is also caused by impinging of energetic hydrogen. Re-emitted hydrogen molecules are not necessarily in thermal equilibrium at the surface and bring hyperthermal energy released upon recombination. Then the recombination model based on the surface equilibrium should be modified. And the hydrogen recombination process may not be the rate limiting process for hydrogen re-emission. Taking into account the present knowledge of surface physics and chemistry, the kinetics and mechanisms of those phenomena given by energetic hydrogen injection which are important in fusion devices are discussed. © 1997 Elsevier Science B.V.

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1. Introduction

Since the first wall of thermonuclear fusion devices is subjected to significantly high heat load and particle fluxes, the reduction of the heat load as well as heat removal is, now, one of the main concerns for construction of burning fusion devices like ITER (international thermonuclear experimental reactor) [1]. Sophisticated ideas or systems like gaseous divertor and impurity cooling are proposed but are not well established yet. In any case, the heat load must be below some tens MW/m^2 to avoid the surface melting [2]. Even so the surface must be heavily eroded and induced thermal stress would result in materials fracture.

Under such conditions, hydrogen (fuel) particles escaping from plasma impinge into the subsurface layer and subsequently are re-emitted from, retained in and permeated through the first wall. These are one of the key issues for fusion reactor development not only for the fuel recycling at the first wall but also for the safety concerns of tritium release to the surrounding. Differently from molecular hydrogen, energetic hydrogen escaping from plasma is directly implanted into the target materials depositing its energy to excite electrons, to displace lattice atoms and to excite phonons and finally thermalized. Subsequent migration of the thermalized hydrogen in the target is very much influenced by these phenomena caused by previously injected particles. Simultaneously, various particles are emitted from the surface which include reflected, sputtered and re-emitted particles, secondary electrons and photons. These emitted particles are not necessarily equilibrated thermodynamically with the temperature of the target surface but are often in higher excited states and some are even ionized. The energy distribution of both re-emitted

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and reflected hydrogen is very important because it directly correlates to their penetration length or ionization length in the boundary plasma.

Thus energetic hydrogen injection exhibits various chemical reactions with impurities and/or chemical change. Enhanced erosion of carbon materials by implanted hydrogen producing methane, i.e., chemical sputtering of carbon, is one of the most well known examples [3]. Recently atomic hydrogen re-emission from carbon was observed at such a low temperature as 1000°C [4]. Super permeation of hydrogen in metals is also caused by impinging of energetic hydrogen [5,6]. Electrons and photons escaping from plasmas are superposed to influence such anomalous phenomena.

In the present work, various anomalies caused by energetic hydrogen impinging to the materials such as super permeation of hydrogen, chemical sputtering or enhanced chemical reactions, radiation enhanced sublimations and so on are reviewed. Taking into account the present knowledge of surface physics and chemistry, the kinetics and mechanisms of these phenomena that are important in fusion devices are discussed.

2. Heat and particle load to plasma facing materials

Fig. 1 compares heat load or heat flux to the surface subjected to various heat sources. In the present large tokamaks the heat load often exceeds 10 MW/m^2 which is near the critical heat load for the melting of refractory metals [7]. Accordingly particle flux at the highest region would exceed $10^{22}/m^2$ s. Forthcoming burning machine like ITER the loading power to the divertor is expected to be as high as that of the sun surface if a sophisticated heat removal system (function) is not established. We have never experienced such a high heat load nor high flux of energetic particles simply because we did not have the heat source. Thus, the research on material performance under such conditions becomes one of the most urgent task.

It is important to note that the heat load or deposited energy shows a profile in depth which is quite different depending on the kind of the heat source, i.e., radiation (photon), charged particles or neutrons. In a fusion reactor the heat load is given by either or all of radiation, energetic hydrogen and helium particles, electrons and neutrons. Among all hydrogen and helium particles deposit their energy at very shallow range, whereas neutrons give homogeneous energy deposition for very thick range. Fig. 2 shows depth profiles of deposited energy by electron excitation and lattice displacement along with implanted profiles calculated by TRIM code. At very high energy, electron excitation or ionization (electron stopping) is the dominant process, whereas the displacement of lattice atoms (nuclear stopping) becomes dominant below several keV.

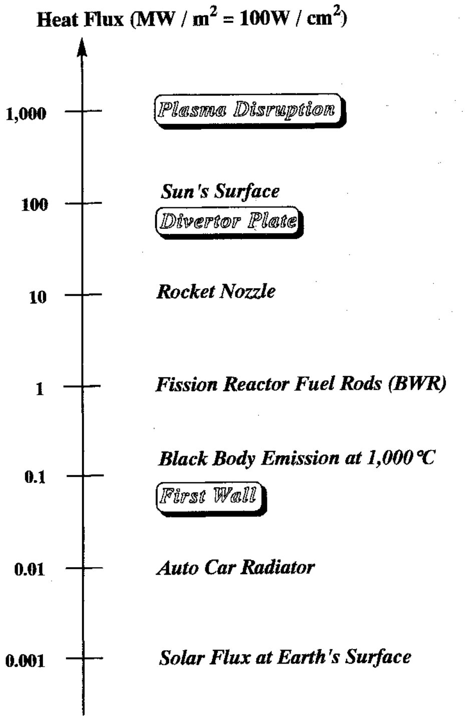

Fig. 1. Comparison of heat load or heat flux to the surface subjected to various heat source.

The lattice displacement produces interstitials and vacancies whose subsequent thermal motion result in various radiation damages such as interstitial loops, cavities and so on. The maximum yield of hydrogen physical sputtering appears at the energy of several keV where the displacement dominates at the surface [8]. When its energy is

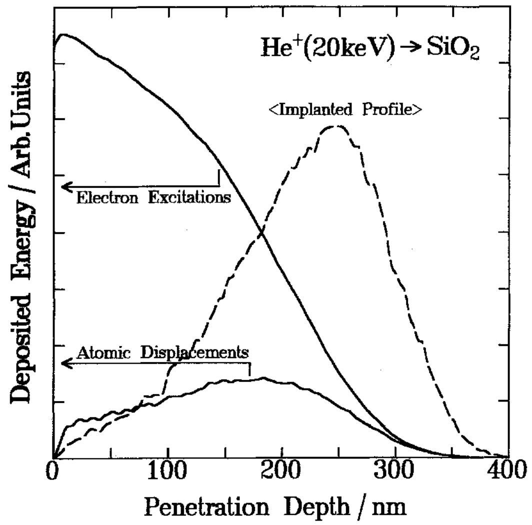

Fig. 2. Depth profiles of deposited energy by electron excitation and lattice displacement along with implanted profiles calculated by TRIM code for 20 keV He^+ injected in SiO_2.

below the threshold for the displacement, only possible loss mechanism is phonon excitation and implanted hydrogen is thermalized giving the implanted profile (or projected range) shown in Fig. 2. Therefore migration of previously implanted hydrogen is very much influenced by the excited electrons and radiation damages produced by subsequently implanted ones. The gradient in the deposited energy turns out to be that of the temperature gradient and also has a large influence on the migration process of implanted hydrogen as well as component elements of the material, resulting in radiation enhanced sublimation, migration and diffusion, surface precipitation and so on.

3. Release kinetics of implanted hydrogen

3.1. Re-emission, retention and permeation

Different from molecular hydrogen, energetic hydrogen escaping from plasma directly implanted into the projected range. Hence, hydrogen concentration near the projected range exceeds the solution limit given by residual hydrogen pressure (P) at the surface and hydrogen solubility (S) of the material, usually given by $C = SP^{1/2}$, until a saturation level attains which is determined by a balance between implanted hydrogen flux, and permeated and re-emitted fluxes. The re-emission and permeation are motivated by the concentration gradient of the hydrogen in solution sites. For the re-emission and permeation of the implanted hydrogen, the rate controlling process is generally believed to be the recombination process at the front and back surfaces, respectively, and a number of work has been done to obtain the recombination coefficient for various materials [9].

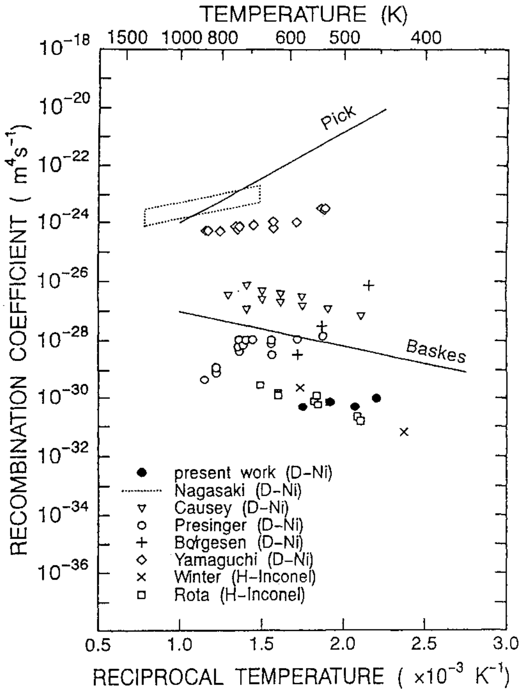

Fig. 3. An Arrhenius plot of recombination coefficients determined experimentally and estimated theoretically for hydrogen isotopes on nickel and its alloys (after Takagi et al. [10]).

In spite of the extensive effort, both experimental and theoretical, to determine the recombination coefficients, there appears to be a large discrepancy among not only the experimental data but also the theoretical estimations (see Fig. 3). The migration process, in addition, is influenced by various defects (radiation damages) produced in the bulk and the surface process by sputter-cleaning and -roughening as well. Consequently, not only various anomaly appears in ion driven permeation (IDP) and plasma driven permeation (PDP) [10–15] but also theoretical investigation on them becomes very difficult. In Sections 3.2, 3.3 and 3.4 the release kinetics of implanted hydrogen are discussed in detail.

3.2. Experimental determination of recombination coefficient

There is no doubt that the release of hydrogen atoms dissolved in the material occurs through surface recombination except at elevated temperatures where the release of atomic hydrogen occurs [4]. However, there is some concern on the reliability of the recombination coefficients so far determined by IDP and PDP methods.

Experimentally, the recombination coefficient (K_r) is determined from a flux balance at a steady state among the implanted flux (Φ), re-emission rate (R) at the front surface and permeation rate (P) at the back surface,

$$\Phi = R + P, \tag{1}$$

and the concentration of interstitially movable hydrogen (C) at the surface, including surface geometrical and contamination factor α,

$$R = \alpha_1 K_{r1} C_1^2, \tag{2}$$

and

$$P = \alpha_2 K_{r2} C_2^2. \tag{3}$$

Unfortunately all physical parameters included in Eqs. (1)–(3) can not be determined simultaneously. Since Φ, R, P, C_1 and C_2 are observed experimentally, there remain six physical parameters to be determined, α_1, α_2, K_{r1}, K_{r2}, S (solubility) and D (diffusivity), though S could be related to C_1 and C_2 as $C = SP^{1/2}$. In most experiments, K_{r1} and K_{r2} were determined from Eqs. (1)–(3), simply assuming that S and D were not influenced by the injection. Permeation anomalies such as the permeation spike in IDP and PDP [9] were attributed to the changes in K_{r1}, K_{r2}, α_1 and α_2 by the energetic hydrogen bombardment. However, it should be pointed out that an alternative interpretation of the permeation anomaly by the modification of S and D is also possible [11,12]. Unfortunately most K_r values reported so far have been determined without examining whether the release process is truly the recombination limited or not.

Depending on the relative magnitude of K_r and D, four different regimes are distinguished [13,16], those are, RR (both re-emission and permeation are controlled by recombination), RD (re-emission is controlled by the recombination whereas permeation by diffusion, DR and RD as shown Brice and Doyle [16]. In exothermic hydrogen occluders like Nb and Ta the appearance of the RR regime is confirmed by a very high permeated flux, $P/\Phi = 0.1$ or above (super permeation). However their K_r values reported are widely scattered and clearly influenced by surface impurities [17]. In endothermic hydrogen occluders like Ni and SS, P/Φ is not large enough and only the square root dependence of the permeated flux on the incident flux has been used for the evidence of the recombination limited process. Nevertheless it should be point out that the second order desorption kinetics is not necessary the evidence of the recombination limiting process.

Even if the recombination coefficients were correctly determined at the steady state, the values were usually not checked for the description for dynamic process or transient state and hence hydrogen retention. At the steady state, the re-emission rate is simply equivalent to the incoming flux subtracted by a very tiny amount of the permeated flux. At the transient state, on the other hand, the re-emission rate is so small compared to the total hydrogen retention. Hence even very small change in the retention influences the re-emission very much. This is the reason why tokamak needs conditioning of the first wall and plasma physicist prefer wall pumping regime, i.e., very small recycling for easy density control of their plasma. Thus K_r experimentally determined at the steady state should be applicable even for transient state re-emission as well as retention.

Recombination coefficients would not be applicable to hydrogen recycling analysis in tokamak operation, too. Considering the hydrogen recycling in tokamak at a steady state, the recycling or re-emission coefficient is very near to one except exothermic hydrogen occluders in which hydrogen retention is very large. In addition, under such a high hydrogen flux as 10^{24} particles/m^2, the surface concentration becomes high enough to deviate from the surface recombination limited process. Therefore high flux measurement is an urgent task.

The following two points should also be mentioned: (1) the re-emitted molecules after the recombination are not

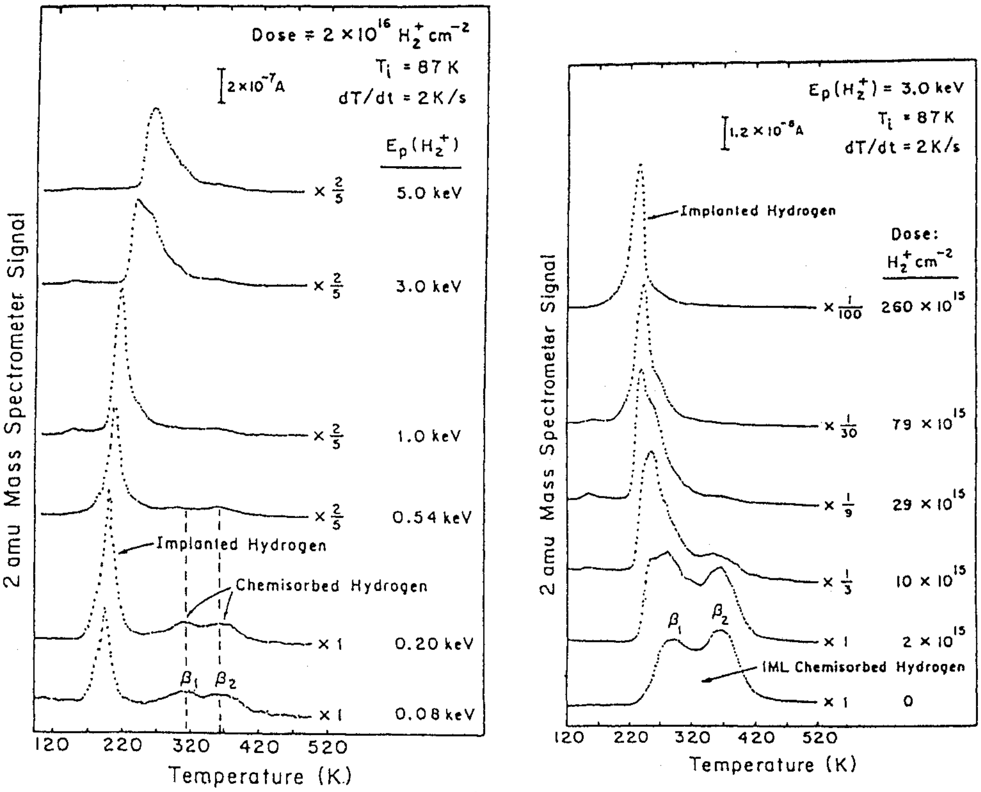

Fig. 4. Temperature programmed desorption spectra of hydrogen implanted in Ni(111) as function of (a) implanted energy and (b) dose (after Chrokendorf et al. [21]).

necessarily thermalized to the surface temperature of the target and (2) some fraction of the injected hydrogen is directly reflected without being thermalized. Both are discussed later.

3.3. Theoretical estimation of K_r

Several authors including Baskes [18], Pick and Sonnenberg [19] and Richards [20], have independently made theoretical estimations of K_r by employing the literature data of diffusivity (D) and solubility (S) for hydrogen molecules in equilibrium with the material. Depending upon their model not only the absolute values but also the temperature dependence of theoretical estimations are quite different from each other. The experimentally determined values often differ from the theoretical ones by several orders of magnitude (see Fig. 3 [10]) and the difference was in most cases attributed to the roughness factor or cleanness of the surface (α_1, α_2) in Eqs. (2) and (3) [9].

Under energetic hydrogen injection, re-emitted or permeated hydrogen molecules are often not in equilibrium with gas phase, taking higher energy states than expected from the material temperature [2]. Fig. 4 is one clear example. One can see that implanted hydrogen in Ni is released at a much lower temperature than that for chemisorbed hydrogen on Ni surface. In such cases, hydrogen atoms recombine at the subsurface having an excess energy released upon recombination [22,23]. Depending on how large a fraction of the energy released by the recombination is brought to the recombined molecules, they are distributed in the energy range from the highest 4.7 eV (binding energy of H_2) to the lowest target temperature (here the energy state of hydrogen atom in the target is not considered). In Fig. 5 dimensional potential energy diagrams for D_2 and D desorption are compared with an endothermic hydrogen occluder of Cu and an exothermic one of Pd [22,23]. One can see that hydrogen atoms easily recombine at the subsurface and desorb without any influence on the surface barrier (Eb) in the endothermic occluders. Consequently, desorbing hydrogen molecules have a higher velocity than that expected from the material temperature. The excess energy might cause a synergistic effect enhancing migration or diffusion, recombination or chemical reaction with impurity. Sometimes hydrogen reacts with surface impurities producing H_2O, CH_4 and so on, which is one of the most important source of the impurity in plasma as discussed later.

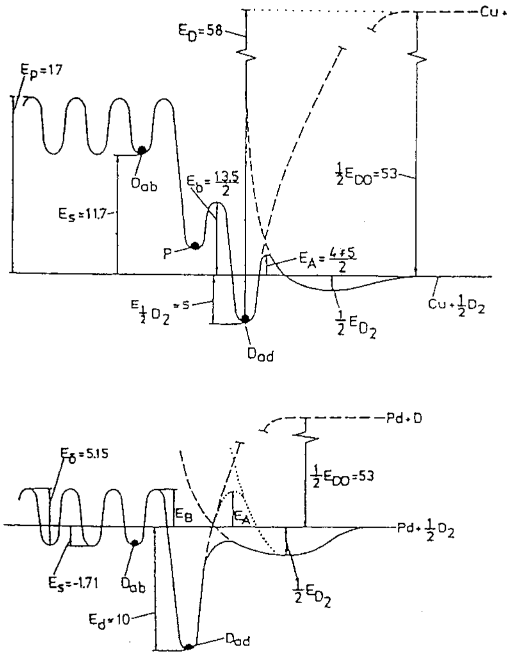

Fig. 5. (a) One dimensional potential energy diagram for D_2 and D for (a) Cu (an endothermic hydrogen occluder and (b) Pd (an exothermic hydrogen occluder). All energies are in kcal/mol per D atm (after Comsa and David [22,23]).

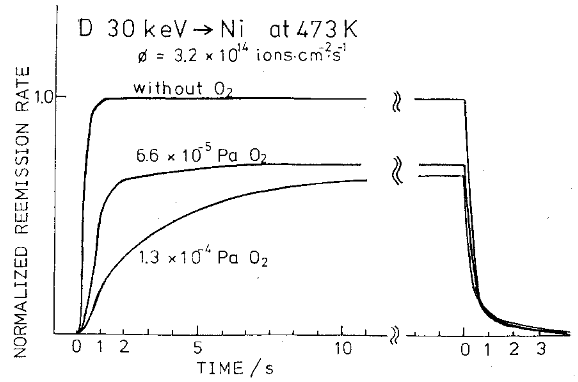

Fig. 6. Comparison of re-emission of implanted D with and without residual oxygen. The difference in the reemission is due to the release either in the form of D_2O or HDO (after Tanabe et al. [12]).

Surface blocking of hydrogen recombination by impurities has been clearly demonstrated by Comsa and David [23]. In this case sulfur atoms occupy all surface sites and hydrogen atoms are forced to recombine beneath the top surface. As a result the desorbed hydrogen molecules retain excess energy released at the recombination without being equilibrated with the surface absorption sites. If binding of surface oxygen to the matrix surface is not strong enough to keep the oxide stable, then hydrogen reacts with the surface oxygen and desorbs with as a form of H_2O as demonstrated in Fig. 6 [12]. In this particular case, because NiO is not stable under a hydrogen atmosphere, most of the deuterium once implanted in Ni is released as a form of D_2O until most of the oxygen is removed from the surface.

The excess energy released by the recombination or other chemical reactions enables the release of the molecules directly from the subsurface over the surface potential barrier. Even atomic hydrogen is re-emitted from metal surface under energetic hydrogen injection at elevated temperatures [4].

All of the proposed theories for the determination of the recombination coefficient are based on the surface equilibrium of dissolved hydrogen atom and hence could not be applicable to such cases. If the true recombination coefficient is much larger than the currently expected ones from the theory, the rate limiting process must not be the recombination but another process in the bulk or subsurface layers.

3.4. Remarks on experimental determination of K_r

It is significant to note that in most of the IDP and PDP studies the permeated flux P/Φ ranges from 10^{-4} to 10^{-1} irrespective of the material examined [9]. This is mainly due to the experimental limitation, i.e., incident flux is usually about an order of 10^{18} to 10^{19} ions/m^2 s and the detection limit of permeating flux is about 10^{14} to 10^{16} molecules/m^2 s. In other words, P/Φ of 10^{-4} to 10^{-1} is a reasonably measurable range in the laboratory experiments. On the other hand, differences of diffusion coefficients and solubilities among materials are much wider [9]. Accordingly, theoretical estimation of K_r, which uses D and S, scatters in a very wide range. This means that α_1, K_{r1} or C_1 should compensate with each other to keep P/Φ around 10^{-4} to 10^{-1} and, thus, the deviation of the experimental K_r from the theoretical one was attributed to the surface cleanness in most cases. Taking into account hydrogen flux as large as 10^{24} particles/m^2 s the divertor plate is not likely covered by the impurities. It should be noted that in the DD regime P/Φ depends only on the thickness and incident energy but not on the material. In this respect it seems more realistic to analyze P/Φ based on DD with a suitable modification. Although static hydrogen trapping in radiation damage like retention has been examined rather well [24], the dynamical trapping at the radiation damage or defect, i.e time transient behavior of implanted hydrogen migration, is still an open question especially for less hydrogen occluding bcc metals like Mo and W in which hydrogen trapping is known to be very large [25].

Livshitz et al. [5,6] have proposed the application of super-permeation membrane for hydrogen pumping in ITER utilizing exothermic hydrogen occluders like Nb and Ta covered with surface impurities like C, O and S which are strongly bonded to substrate and work as a permeation barrier. Applying Nb membrane, they have succeeded to demonstrate the super-permeation with a compression of 10^4 in hydrogen pressure. Here again arises a question on the stability of the surface impurities under high hydrogen potential, or high hydrogen flux. In Nb, a huge amount of hydrogen is dissolved exothermically. Even so the hydrogen potential increases with its concentration and at a very high concentration hydrogen may react with surface impurities to make H_2O, CH_4, H_2S, etc. This means there is a certain limit in hydrogen flux beyond which the super-permeation would disappear. In the exothermic hydrogen occluders, hydrogen concentration throughout the membrane should be very flat. Hence the cleaning would happen both at the front and back surfaces, simultaneously. However, energy deposition by the impinging hydrogen on the front surface would enhance the surface reaction at the front side as discussed later and reduce the permeation further.

4. Reflection

As already mentioned, some part of the impinging hydrogen is directly reflected at the surface. The reflection coefficient increases with decreasing incident energy down to about a few tens eV [26]. Below this energy the reflection coefficient is not measured because of the difficulty of getting such a low energy ion source estimated theoretically due to the uncertainty in the potential employed for the calculation.

Depending on their velocities the reflected particles show various states in their electron configuration. At very high velocity, ionic states are preferred, whereas neutrals are dominant at lower energies. The neutral particles are, however, not necessary in the ground state but distributed in various excited sates, which is confirmed by Balmer series emission measurements from the reflected hydrogen [27]. Thus, a difference in the reflected hydrogen in their electron excited state would show different chemical effects at the surface from the re-emitted molecules. Even the re-emitted molecules are, as mentioned before, not necessarily in the ground state but sometimes hyperthermal. Unfortunately, however, there are no detailed data on the energy distribution of the released particles under energetic hydrogen injection and on the population of the excited states (distribution of electron configuration) in the reflected particles.

In a tokamak, hydrogen recycling is very important for the control of plasma density. Usually plasma operation is very easy under wall pumping conditions and a low hydrogen recycling regime assures good confinement. Hydrogen recycling from the wall is consisted of at least two components, reflected atoms and re-emitted molecules [28,29]. Because reflected hydrogen brings back its energy to the plasma, they are not a serious concern for the hydrogen recycling. The re-emitted molecules, because not only they are dominant but also they take energy from the plasma by the dissociation and ionization, should be reduced. This is a reason why the low recycling regime is preferred.

Generally a metallic wall is preferred compared to graphite from the aspect of hydrogen recycling [7] because hydrogen retention in the former is much small than the latter and the reflection is higher in the former. In this respect high Z metals such as Mo and W owing to their large reflection coefficients seem very good compared with carbon, though this must be confirmed in a tokamak [30]. Interestingly, recent gaseous divertor concepts need a high density of thermalized molecules for the edge plasma cooling. There seems to be some contradiction between hydrogen recycling and the gaseous divertor concept.

5. Enhanced chemical reaction: Chemical erosion and atomic hydrogen re-emission

When PFM is composed of those elements that react with hydrogen, like graphite, a chemical reaction occurs between re-emitted hydrogen and the materials. As a result, an apparent sputtering (erosion) yield is enhanced from that estimated by physical sputtering or a simple collision process. Methane formation on hydrogen injection to graphite is one of the most well known examples (see Fig. 7). Oxygen sputtering with Mo and W exhibits chemical sputtering, producing volatile oxides MoO_3 and WO_3 as shown in Fig. 8 [31–33]. It is previously mentioned in Fig. 6 that surface impurity oxygen on Ni is easily removed by a hydrogen injection producing H_2O and the re-emission rate of implanted hydrogen seems to be depressed.

All those energetic ion induced reactions, if compared with molecular reaction with equivalent particle flux, seem to have two different effects: a temperature increasing effect and enhancement of the reaction rate. As the surface temperature increases, chemical equilibrium in the following reactions:

$$CH_4 = C + 2H_2 \text{ (or 4H)}, \tag{4}$$

$$CO_2 = CO + O, \quad CO = C + O, \tag{5}$$

$$H_2O = O + H_2 \text{ (or 2H)}, \tag{6}$$

$$H_2 = 2H, \tag{7}$$

inclines to right hand side (except for CO = C + O). Accordingly the first increase of the methane formation with temperature is due to enhancement of the reaction rate whereas the turning off over 800 K is due to high temperature instability of methane (see Fig. 7) [8]. Owing to a very large binding energy between C and O, most of the implanted O in carbon reacts with C to produce CO and/or CO_2 [3]. As a result the chemical erosion yield of carbon by oxygen bombardment is nearly independent of the irradiation temperature. At higher temperatures CO_2 is not produced because of the smaller stability of CO_2 than CO.

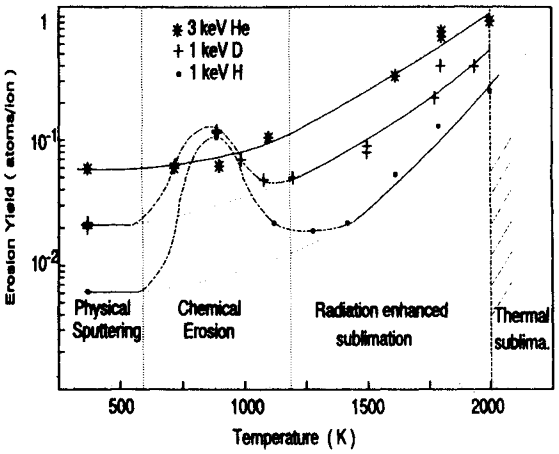

Fig. 7. Temperature dependence of graphite erosion yield by energetic hydrogen bombardment (after Eckstein and Philipps [8]).

It is important to note that implanted hydrogen does not necessarily release all the energy or become thermalized as already mentioned. Quite recently atomic hydrogen re-emission was observed in the re-emission experiments of implanted hydrogen from graphite at higher temperatures but far below the thermodynamically expected temperature for atomic hydrogen production [4]. This is something like the temperature increasing effect in Eq. (7). From a time of flight measurement the re-emitted hydrogen atoms have more energy than expected from the target temperature and deviates from Boltzman distribution [34].

6. Radiation enhanced sublimation

If displaced interstitial atoms migrate to the top surface without completely losing their energy or momentum, they are released from the materials surface with excess energy compared with thermalized particles at the surface. Such an example is seen in radiation enhanced sublimation (RES) [8] of graphite and carbon based materials irradiated with energetic ions irrespective of the injected species (see Fig. 7). RES erosion dominates above 1200 K where all erosion yield an increase monotonously until they exceed, at 2000 K, the physical sputtering yields by more than a factor of 10. The composition of carbon species emitted by RES differs significantly from those of physical sputtering and normal sublimation. The main features of RES can be reasonably well examined with an interstitial model in which RES is due to the desorption of interstitials produced by the irradiation [8]. In this particular case the flux dependence is examined well as shown in Fig. 9 [35]. At a lower flux the erosion yield shows nearly $\Phi^{-0.1}$ dependence, whereas the erosion yield decreases more steeply compared to the extrapolation from the low flux data, probably owing to the collision (or cascade) overlap.

The RES is believed to appear only in carbon based materials but not in metals, which has not yet been confirmed experimentally with sputtering measurements for metals at elevated temperatures. It is very important to understand the mechanism of RES.

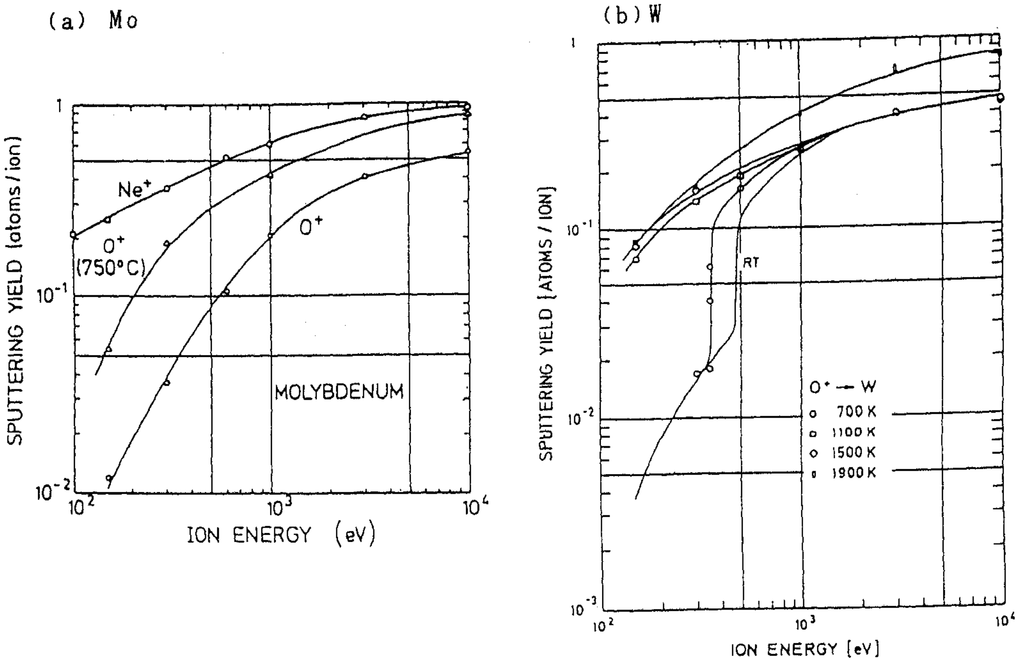

Fig. 8. Temperature dependence of oxygen sputtering yield of (a) Mo and (b) W (after Hechtel et al. [31–33]).

Radiation induced segregation and/or diffusion of the constituent element of the target are related to the vacancies produced by the lattice displacement [36]. Here one should take into account two component transport equation, i.e., migration of vacancies and atoms. Since there is no way to detect the migrating element in the solid directly, it is not easy to make a dynamic measurement. Although the electron excitation effect is known to play a very important role in the defect formation in ionic crystals, that on the radiation induced diffusion in metals has not been investigated.

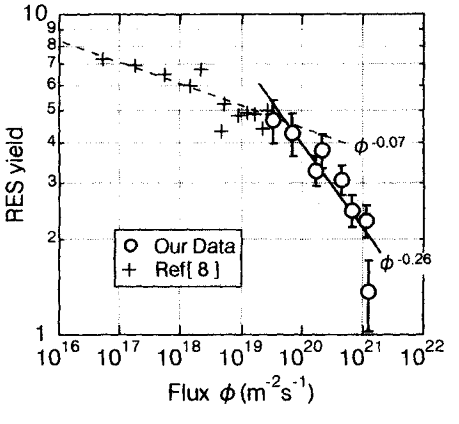

Fig. 9. Flux dependence of RES of graphite at 2000 K by 5 keV Ar beam (after Ueda et al. [35]).

7. Synergistic effect

As described above, the energetic particles impinging into the solid deposit their energy by electron excitation, atomic displacement and phonon excitation. All these deposited energies cooperatively influence the migration of the implanted particles through, for example, producing excited or ionized atoms, defect trapping and enhanced diffusion, respectively.

In the fusion environment, other energetic particles like electrons and neutrons and various radiation are loaded simultaneously.

If one would concentrate only on the migration of implanted species, we could make a transport equation employing diffusion, trapping and surface release kinetics like recombination of Eqs. (1)–(3). However the implanted species could still have a certain momentum at the projected range where the species are believed to be thermalized, or could get additional momentum from the excited electrons by simultaneously implanted projectiles. Such momentum transfer or energy transfer is not included in the transport equation and may the origin for the synergistic effect. In a similar way, the displaced interstitials could get additional momentum. This may be the reason for the radiation enhanced diffusion and RES as well.

Haasz et al. have tried [37] to observe the effect of simultaneous electron irradiation on the chemical erosion of carbon and found a very small effect, probably because the flux density of the electron was so small compared with the number of excited electrons in the target by impinging hydrogen ions. The effect of electron excitation by the impinging ions is clearly demonstrated by ion induced luminescence studies of Al_2O_3 and SiO_2 by Tanabe et al. [38]. In the metals, unfortunately, it is not possible to detect the electron excitation through photon emission, which makes examination of the electron excitation effect in the metals difficult.

The reduction of the RES at a very high flux seen in Fig. 9 is another example of the appearance of the synergistic effect, not enhancement but depression. With such high flux irradiation, the excited electron density may be saturated and/or cascade overlap occurs. Surface dynamics like recombination of implanted hydrogen is also more likely affected by the excited electrons and the surface damage, though the effect is not examined nor discussed well.

One should take into account that excited electrons lose their energy within a certain lifetime, fs to ns, and lattice displacement occurs around ps to μs and diffusion (particle and heat) needs more than μs. Thus we have to distinguish spontaneous effects of ion impact, i.e., the effects of excited electrons and atomic displacement and subsequent phenomena during thermalizing process and simple thermal process. To do this time-resolved measurement using a pulsed beam (either photon, electron or ion) must be very useful. And the energy distribution of the released hydrogen, both reflected atoms and re-emitted molecules, is very important in investigating the surface kinetics occurring under energetic hydrogen injection.

8. Conclusion

Differently from molecular hydrogen, energetic hydrogen particles escaping from plasma directly impinge into the solid, deposit their energy by electron excitation, atomic displacement and phonon excitation, and finally become thermal. All these deposited energies cooperatively influence the subsequent migration of the thermalized hydrogen in the target through, for example, producing excited or ionized atoms, defect trapping and vibrational diffusion enhancement, respectively. As a result various anomalies are observed in re-emission, diffusion and permeation of implanted hydrogen. In a fusion environment, other energetic particles like electrons and neutrons and various radiation are loaded simultaneously, which makes the behavior more complex. Thus hydrogen molecules re-emitted and/or permeated after the energetic hydrogen injection are often not in equilibrium with the gas phase, taking higher energy states than expected from the material temperature. And the hydrogen recombination process may not be the rate limiting process.

In addition to the re-emitted hydrogen molecules, various particles are emitted from the surface, which include reflected, sputtered particles, secondary electrons and photons as well. Those emitted particles are not necessarily equilibrated thermodynamically with the surface temperature of the target but are often in higher excited states and some are even ionized.

If displaced interstitial atoms migrate to the top surface without completely losing their energy or momentum, they are released from the material surface with excess energy compared with thermalized particles. Such an example is seen in radiation enhanced sublimation (RES) of graphite and carbon based materials irradiated with energetic ion irrespective injected species. Chemical erosion of carbon materials by implanted hydrogen producing methane is one of the most well known phenomena. Recently even atomic hydrogen re-emission from carbon is observed at such a low temperature of 1000°C. Super permeation of hydrogen in metals is also caused by impinging of energetic hydrogen.

Some part of impinging hydrogen is directly reflected at the surface. Depending on their velocities the reflected particles show various states in their electron configuration which could result in a different chemical effect at the surface.

The energy distribution of both re-emitted and reflected hydrogen is very important not only to investigate the surface kinetics occurring under energetic hydrogen injection but also to understand the role of the re-emitted hydrogen and impurities on the plasma materials interactions because it directly correlates to their penetration length or ionization length in the boundary plasma.

All these energetic hydrogen induced effects could originate from the super position of electron excitation, atomic displacement, phonon excitation and thermal motion, all of which have their own characteristic time. This indicates that time-resolved measurement using a pulsed beam (either photon, electron or ion) could be very useful to examine the dynamic transport process of the implanted hydrogen.

Finally, it should be pointed out that strong electric and magnetic fields in fusion environment may have some influence on these phenomena. But it has not been examined yet.

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