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Discharge in Hydrogen-Noble Gas Mixture as the Method to Increase Efficiency of Conditioning of the In-Vessel Components of Large-Scale Fusion Devices

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Abstract

Fusion devices are needed very long wall conditioning time for preparation to experiments with hot plasma. The conditioning procedure is based on chemical reactions when hydrogen atoms and ions of low temperature plasma interact with contaminants coating the walls. With that, the efficiency of removal of carbon atoms is quite small, $\sim 2-3\,\%$. The possible way to enhance the efficiency of C film cleaning is to use the plasma produced by discharge in mixture of hydrogen with one of heavy rare gases, as was suggested and demonstrated in [1]. This approach is acceptable in fusion reactor projects, where the addition of a rare gas (heavier than helium) is considered as the method to control the periphery plasma parameters.

In the present paper we analyze the published data on the most important reactions in a low-temperature plasma produced in mixture of hydrogen with gases: Ne, Ar, Xe, Kr. The peculiarity of such plasma is the appearance of a group of hydride ions, NeH^+, ArH^+, XeH^+, KrH^+, which probably are important factor increasing the rate of C film removal compare to pure hydrogen plasma. The comparison of data on cross sections of different reactions demonstrates clearly that among all rare gases the highest concentrations of hydride ions would be in the Ar-H_2 mixture plasma.

Keywords:

conditioning, discharge, hydrogen-noble gas mixture, noble-gas-hydride ion, carbon-carbon bond, chemical erosion

1. Introduction

In fusion devices, to exclude an influx of metallic impurities into the confined plasma, the protective tiles from carbon-based materials are widely used (*e.g.*, [2]). As a result, carbon is the main component in the erosion product. It is transported inside the vacuum vessel and deposits on surfaces remote from locations of the strongest plasma impact. Due to co-deposition of hydrogen isotopes and other impurity atoms that are in a background atmosphere or are the part of composition of in-vessel components, the deposit can have a complicated composition with carbon predominance. The methods of surface cleaning from a carbon film are based on high chemical activity of hydrogen (deuterium) atoms and ions when volatile molecules containing carbon (mainly CH_4) and oxygen (H_2O) are created, which can be evacuated out by standard pumping equipment. However, the efficiency of hydrocarbon molecules production is quite small, $\sim 2-3\,\%$ [3] that is why the regular provided conditioning procedures take the time orders of magnitude exceeding the time of experiments with hot plasma.

One possible way to increase the efficiency of cleaning surfaces from carbon-containing films is to use for conditioning a discharge in a mixture of hydrogen (deuterium) with one of heavy noble gases as was shown for the first time by authors of [1]. This approach is acceptable for a fusion reactor, where the use of a noble gas addition is suggested to control the parameters of the periphery plasma [4]. The effect in [1] was different for different noble gases added to hydrogen, Ne, Kr, or Xe. The partial pressures of impurity-containing molecules in plasma, as well as the rate of conditioning, depended on the composition of mixture (i.e., on ratio of densities of noble gas atoms to hydrogen molecules). Table 1 shows the ratios of partial pressure of indicated masses

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Table 1 Rise of partial pressure for indicated mass numbers of impurity-containing molecules [1].

Mixture	Ratios of partial pressure values of some impurities with and without noble gas addition				
	15*	16*	17*	18*	28*
H_2 + Ne	1.9	1.4	1.9	1.3	1.6
H_2 + Xe	2.8	2.6	1.5	1.8	2.6
H_2 + Kr	2.6	4.8	7.7	3.1	3.1

* Mass of impurity-containing molecules.

during discharges with rare gas addition to values without rare gas, i.e., when discharge was provided in pure hydrogen (the data are taken from Fig. 7 of [1]). It is seen that the highest conditioning efficiency was with Kr added.

However, the physical principle of increasing the conditioning efficiency with noble gas addition was not clearly explained in [1]. Besides, the experiments with Ar-H_2 mixture were not provided. Therefore, from [1] impossible to make a conclusion on the optimal choice of the rare gas-H_2 mixture. Meanwhile, the analysis of published experimental and theoretical data on processes in plasma of the mixture of hydrogen with a rare gas, shows that the most promising for conditioning efficiency increase should be addition of argon to hydrogen (or to deuterium). Below a detailed analysis is presented.

2. Reactions in the plasma of H_2-noble gas mixture

The rate coefficient of reactions in cold plasma with low ionization degree produced by glow or ECR (Electron Cyclotron Resonance) discharge in the mixture of noble gas with hydrogen are shown in Table 2 by the example of Ar-H_2 mixture. The data on the most important reactions for other rare gases are compared in Table 3. These data were taken from different published papers which are referenced in [5].

As seen, the distinctive feature of such plasma is that it contains a group of noble gas hydride ions, XH^+, which are a quite long-lived plasma component, but disintegrate quickly after the ion becomes neutral, as show data of Table 4 [6]. A priori, we may suppose that just existence of noble gas ions, X^+, and XH^+ ions, does determine, to a considerable degree, the increase of conditioning efficiency in comparison with the case when during conditioning the discharge in a monocomponent gas (H_2 or D_2) is in use. If so, to increase the efficiency of conditioning (i.e., the rate of cleaning the walls from carbon films) one has to reach the maximal concentration in the discharge just of these ions.

Table 2 Rate coefficients, *k*, for reactions in the low temperature plasma of a discharge in the argon - hydrogen mixture taken from references in [5].

No	Reaction	k at ~room temperature, 10^{-9} cm^{3}molecule^{-1}s^{-1}
1	$Ar^+ + H_2 \rightarrow ArH^+ + H$	0.62; 0.68; 1.6; 1.6; 1.7; 0.98; 0.54; 1.1; 1.0; 1.3; 0.82; 0.95; 1.7; 2.0; **1.2**
2	$H_2^+ + Ar \rightarrow ArH^+ + H$	2.3; 1.24; 2.0; 2.2; 1.8; 2.2; **2.0**
3	$ArH^+ + H_2 \rightarrow H_3^+ + Ar$	0.5; 0.32; 0.8; 0.34; 0.35; **0.5**
4	$Ar^+ + H_2 \rightarrow H_2^+ + Ar$	0.27; 0.1 **0.15**
5	$H_2^+ + Ar \rightarrow Ar^+ + H_2$	~0.27; ≤ 0.1; 0.27 **0.25**
6	$H_2^+ + H_2 \rightarrow H_3^+ + H$	2.05; 2.4; 2.0 **2.2**
7	$H_3^+ + Ar \rightarrow ArH^+ + H_2$	0.37; 0.06; 0.5 **0.2**
8	$e + ArH^+ \rightarrow Ar + H$	~**100**

Table 3 Rate coefficients, *k*, for most important reactions in the low temperature plasma of a discharge in a rare gas-hydrogen mixture taken from references listed in [5].

Reaction	k at ~room temperature, 10^{-9} cm^{3}molecule^{-1}s^{-1}				
	He	Ne	Ar	Kr	Xe
$H_2^+ + X \rightarrow XH^+ + H$	0.12 0.16 0.1	1.1 2.3	2.3 1.2 2.0 2.2 1.8	2.9 2.3	2.4 2.1
$X^+ + H_2 \rightarrow XH^+ + H$	~0[a] ~0[a]	~0[a] ~0[b]	0.7 1.6 1.6 1.0 1.1 0.9	0.15 0.6 0.17 0.2 0.17 0.28	< 0.02
$XH^+ + H_2 \rightarrow H_3^+ + X$	1.4	0.9	0.3		

a : < 0.0035, b :< 0.008

From Table 3 one can see that the probability for XH^+ ions to be produced is lowest for He-H_2 plasma.

Table 4 Measured and calculated energy of dissociation of rare gas hydride ions and molecules [6].

Hydrides	Dissociation energies, Δ_{dis}, eV	
	Experimental	Calculated
NeH^+	2.15	
NeH		0.26
ArH^+	$\geq 2.65; \geq 2.14$	3.03
ArH		0.17
KrH^+	$3.42 \leq \Delta_{dis} \leq 4.09$	3.46
KrH		0.12
XeH^+	$1.2 \leq \Delta_{dis} \leq 3.19$	2.66
XeH		0.15

Much higher reaction rates are in the Ne-H_2 and Xe-H_2 mixtures. For these gases, practically only one reaction (2) leads to a positive result, i.e., to production of XH^+ ions. For Kr-H_2 mixture both reactions give the desired products, but asymmetry is still very high between both brunches, ~one order in magnitude. And only for Ar-H_2 mixture the ArH^+ ions are formed by both reactions, (1) and (2), with rate coefficients which are not too much different.

3. Reactions in argon-hydrogen mixture plasma

In the Ar-H_2 mixture the hydride ions can be produced by several reactions known for plasma of a rare gas - H_2 mixture, if the temperature of ions and neutrals (Ar atoms and H_2 molecules) is below 1 eV (what is frequently realized in discharges used for wall conditioning). The ArH^+ ions are formed as a result of exoteric reactions of Ar atoms with H_2^+ ions in all available vibrational states, by reaction of Ar^+ ions in ground ($^2P_{3/2}$) and excited ($^2P_{1/2}$) states with H_2, and in reaction with H_3^+ ions, which are frequently the most abundant ion component in low temperature H_2 plasma. Under the term "low temperature plasma" we imply everywhere below in the text the plasma with near room temperature of ion and atom components, with the electron temperature near two orders in magnitude higher.

It is seen from Table 2 that on the average the observed rates for the reaction $Ar^+ + H_2 \rightarrow H_2^+ + Ar$ are lower than for reaction $H_2^+ + Ar \rightarrow ArH^+ + H$. Roughly the value of $k(Ar^+ + H_2)/k(H_2^+ + Ar)$ ratio is close to 1/2 what is in a quite good agreement with results of calculations in [7] where this ratio was found to be ~ 0.7 for reactions in H_2-Ar and D_2-Ar mixtures. However, the energy dependence of theoretical and experimental cross sections of reactions (2) and (4) in Table 2 are very different, i.e., the experimental cross section decreases with energy much faster than theory predicts ($\sim E^{-1/2}$) [8]. For further analysis of reactions that occur in the Ar-H_2 mixture we will use some "average" values of rate coefficients, which are shown in Table 2 as the bold figures.

4. Conditioning by ECR discharge plasma

Taking into consideration the data of Table 2, the balance equation for the hydride ions (ArH^+) in low temperature hydrogen plasma is:

$$\begin{aligned}\partial n(ArH^+)/\partial t = & k_1 \cdot n(Ar^+)n(H_2) + k_2 \cdot n(H_2^+) \cdot n(Ar) \\ & + k_7 \cdot n(H_3^+) \cdot n(Ar) - k_3 \cdot n(ArH^+) \\ & \cdot n(H_2) - k_8 n_e \cdot n(ArH^+) \\ & - n(ArH^+)/\tau(ArH^+). \qquad \text{(a)}\end{aligned}$$

In this equation there is no term corresponding to ionization of metastable argon atoms; the term $\tau(ArH^+)$ designates the life time of ArH^+ ions.

For the mixture with identical initially both components, Ar50 % + $H_2$50 %, which relates to the experimental conditions described in [1] with $n(H_2) \approx n(Ar) \approx 1/2$ [$4 \cdot 10^{12}$ cm^{-3}], the approximate equality $n(H_2) \cong n(Ar)$ has to fulfill during all the discharge time as the relative concentration of every ion component satisfies inequalities: $n(Ar^+)/n(H_2) \ll 1$, $n(H^+)/n(H_2) \ll 1$, $n(ArH^+)/n(H_2) \ll 1$. Besides, at the stationary state of discharge the left part of this equation is zero, thus, after substitution of all numbers the equation (a) becomes:

$$10\{1.2 + 2 + 0.2 - 0.5 - 1.5\} = 10^{-2}/\tau(ArH^+),$$

and from this relation we see that for the given rate coefficients the degree of ionization near 1 % is close to a critical value, i.e., for better realization of the conditions that would provide the accumulation of ArH^+ ions in the discharge, the degree of ionization of the Ar-H_2 mixture has to be below 1 %.

Two indispensable conditions are necessary to provide the production and accumulation of ArH^+ ions in accordance with reactions (1)-(7) in Table 2 : (i) the long enough life time of hydride ions, what means that they have rather high dissociation energy, and (ii) the life time of ArH molecules is short, i.e., their dissociation energy is small. The data presented in Table 4 demonstrate that these conditions are really satisfy: $\Delta E_{dis}(ArH) \ll \Delta E_{dis}(ArH^+)$.

Under conditions of the above cited example, due to acceleration by the sheath potential the ions will gain energy ~15 eV. When hitting the surface, the heavy Ar^+ and ArH^+ ions will give a much larger portion of their energy to absorbed impurity molecules than the light H_2^+ ions, what follows from the kinematic ratio:

$E = E_0 \cdot \{4M_1M_2/(M_1 + M_2)^2\}$, with M_1 and M_2 as masses of ion and impurity molecules and E_0 - the ion energy, E - the energy which the particle on the surface will get after collision with ion. If the surface is coated by a carbon film, the C atom will get $0.7E_0$ energy due to collision with ArH^+ ion and only $\sim 0.2E_0$ due to collision with H_2^+ ion. The energy $E_0 \approx 15\,eV$, that ions gain passing through the sheath potential when $T_e = 5\,eV$, is not enough for sputtering of absorbed molecules, but is sufficient to break their bonds. Thus, we can suppose that the effect of increasing efficiency of conditioning in [1] is based on the following mechanism. The heavy ArH^+ ions after acceleration by the sheath potential hit the adsorbed impurity molecules and break some intermolecular bonds. At this process they become neutral and quickly dissociate to Ar and H atoms (see Table 4). The free Ar atoms go into plasma, but the free H atoms occupy the released bonds and form new molecules, part of which are volatile and can be pumped out. The Ar^+ ions do also break bonds of contaminants and thus facilitate formation of volatile molecules by those H atoms which are produced in the plasma by dissociation of H_2^+ ions and H_2 molecules and hit surface as single atoms. Without heavy Ar^+ and ArH^+ ions, in pure hydrogen plasma with identical ion flux density to the contaminated surface, similar process would have significantly lower efficiency.

5. Conditioning by glow discharge plasma

In glow discharge the plasma characteristics are not much different as compare to the ECR plasma. The only important difference is a quite high sheath potential ($\sim 150 - 300$ volts) exceeding strongly that for the ECR plasma. Thus, all ions hitting the wall will gain the high energy, and the processes of sputtering and desorption can occur. To avoid an uncontrolled sputtering of the walls by Ar^+ and ArH^+ ions in such conditions, the relative Ar concentration has to be maintained at lower level than was supposed above. For example, in [9] was shown that sputtering of stainless steel walls of the vacuum chamber by ions of glow discharge plasma (anode potential 300 V at pressure of $Ar+H_2$ mixture 10^{-2} Torr) was at the low level right up to the Ar^+/H_2^+ flux ratio ~ 2. With increasing the argon to H_2 ratio above ~ 2 the sputtering rate was observed to rise significantly.

Authors of [10] showed that addition of Ar^+ flux with energy 200 eV consisting only of 0.25 % to flux of H atoms resulted in significant rise of the erosion rate of the carbon film. The absolute erosion rate of C film became about one order in magnitude higher than due to physical sputtering by Ar^+ alone. The increase of C film cleaning efficiency occurs because the Ar ions break the C-C-bonds which are passivated by hydrogen atoms.

6. Conclusion

As follows from above shown data, in the low temperature plasma of an $Ar-H_2$ mixture, the ArH^+ ions can be formed due to several reactions. The process of ArH^+ ion production in conditions that can be realized during conditioning procedure in fusion devices is more effective in the $Ar-H_2$ mixture compare to mixture of H_2 with other rare gases. The heavy ions, present in plasma, can gain energies corresponding to the sheath potential, and highly increase the probability of sputtering and desorption of impurities from the surfaces subjected to plasma containing hydrogen ions. Furthermore, the H atoms liberated due to disintegration of ArH molecule on the surface, would facilitate the generation of volatile molecules of light impurities which can be pumped out.

We suppose that such a process has resulted in an increase of desorption rate of impurity-containing molecules in the HL-1 tokamak [1] when the rare gas - H_2 mixture was used as a working gas.

The use of noble gases for wall conditioning is compatible with requirements in fusion devices, *e.g.*, full exclusion of oxygen.

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