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HYDROGEN BEHAVIOR IN BIMETALLIC SYSTEMS: PERMEATION THROUGH THIN METAL FILMS

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The hydrogen permeation performances are presented for micron Mo, Ti, Nb, Zr, Cr, Ni, Cu, CuPd, TiN, and stainless steel films deposited on palladium from arc sputtered cathodes. Some physical mechanisms explaining anomalies behavior in above mentioned systems are suggested. In particular, it is shown that extreme high hydrogen permeability in the Mo-Pd system is caused by enhancing of diffusion coefficient in the system with a large number of connected pores. Also the possible use of such systems for an active control of recycling and erosion processes are considered. In the frame of non-ideal plasma theory the mechanism is suggested of hydrogen high content (clusters) formation as the result of hydrogen plasma phase transitions in metal. The small hydrogen clusters can be condensed in metal lattice. The arising of the large ones is more probably around defects and in submicro- and micro-pores appearing under, for example, plasma or energetic particle irradiation.

INTRODUCTION

Numerous investigations of hydrogen behavior in different materials and in plasma device volume were carried out in order to get possibility of active control of hydrogen isotope recycling process. The studies of materials, coated by thin films are very important part of such investigations due to high efficiency of such systems for hydrogen kinetics control. On the other hand, taking into account redeposition processes under plasma-materials interactions in plasma devices, knowledge of hydrogen behavior performances of thin metallic films, in particular, of hydrogen permeability at low pressure, is necessary for control of hydrogen isotope recycling and inventory, estimation of construction material state, etc. The bimetallic system, which consists of a rather thick (0.1-0.5 mm) Pd-substrate and a thin (1-10 μm) film, deposited on its surface is very convenient for measuring of hydrogen permeability characteristics of thin films. Really, the probability of hydrogen molecule penetration through a thin film to palladium membrane in a single collision is, in the most cases [1-3], essentially lower (usually in a few times) than that for bare palladium. Hence, a hydrogen permeability of such bimetallic system can be often considered as the hydrogen permeability of film only. Such bimetallic systems (thin metallic film - Pd substrate), placed inside a plasma device, could be used for an active control of a hydrogen isotope density near plasma facing surfaces, i.e. in order to perform some kind of the gas puffing for the surface protection. On the other hand, such systems could be used for high hydrogen concentration buildup in the plasma facing materials. As it was shown in recent work [4], the possibility exists to decrease carbon erosion by hydrogen shielding due to accumulation of high hydrogen content at nearest surface bulk during special regime of high-flux hydrogen ion bombardment. But it is not clear if the similar mechanism can be realized for metals. So, it was of a great interest also to consider the possible mechanism of high hydrogen content buildup in metallic (bimetallic) systems.

1. HYDROGEN PERMEABILITY PERFORMANCES OF BIMETALLIC SYSTEMS

A scheme of the experiments, experimental procedures and results on the hydrogen permeability of thin metallic films deposited from arc sputtered cathodes on palladium were described in details in previous paper [1-3]. Here are presented only some results about relative hydrogen permeability j/j_0 of films and the activation energy of hydrogen permeability E (Table) in order to discuss the possible use of such bimetallic system for control of erosion and recycling processes by high hydrogen content buildup in the nearest surface bulk of plasma facing components.

Table. Relative hydrogen permeability and activation energy of hydrogen permeability for metallic films (0.133Pa, 873K).

Metal	E, kJ/mole	E_m, kJ/mole	j/j_0, %
Ti	11	62.3	48
Zr	16.6	37.6	20
Nb	17.6	21.7	10
Ni	22.6	59.8	54
Stainless Steel	19.9	71.1	25
Cr	26		19
TiN	15		9
Cu	46	47.6	5
CuPd+ Cu_3Pd	9.2(<790K) 44 (>790K)		42
Mo	14.2	84.4	62

For comparison, the values of activation energy for bulky metals E_m [5] are presented in the Table, too.

As it is seen, the activation energies of permeability for most films are in a few times lower than the literature data for the bulky metals. This is due to a high porosity of films which caused by a big difference

between substrate temperature (570K) and melting of most deposited metals. In such situation the hydrogen permeability of Mo-film can be more higher than that for Ti or Ni, in spite of the fact, that in the hydrogen permeability row of metals, Mo stay far behind Ti and Ni (on the literature data base one can suggest such row from high to low hydrogen permeation - Ti, V, Zr, Nb, Ta, Fe, Ni, steel, stainless steel, Co, Cr, Al, Cu, Mo, Ag, Pt, W). This fact can be easily explained in the frame of model of anomalies diffusion in the system with the net of connected pores [6], when hydrogen diffusion coefficient increases in two orders of value. Such phenomenon could be useful for creation of erosion high resistible component with the use of diffusion membrane coated by erosion high resistance material. The possible model of such component is given in Fig. 1. The palladium (Ag-Pd alloys) is the unique material, which can provide high hydrogen isotope concentration and high hydrogen flows to protective layer. A potential barrier on the boundary between film and Pd-substrate might be easily overcome because hydrogen in palladium is in atomized or partially ionized state, similar to plasma state [7]. So, even films with the high–energy hydrogen coupling (Ti, Nb, Zr) are not resistible for hydrogen penetration from Pd. It must be noted that not only metal films could be applied in such scheme but nonmetal material too, e.g., carbon, carbides, nitrides, etc. In the case of hydrogen recycling control such scheme can provide different regimes: with high recycling coefficient (gas puffing through membrane) and with low recycling coefficient (hydrogen pumping by membrane). In the latter air or oxygen must be inputted instead of hydrogen.

So, the simple method exists to provide high hydrogen flows to protective layer. But a physical

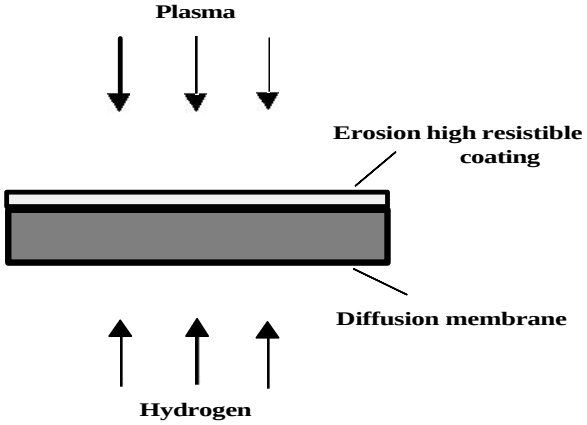

Fig. 1. The possible scheme of the high erosion resistance plasma facing component.

mechanism of the attractive forces between hydrogen atoms (ions) in metals providing the high concentration phase (clusters) formation is not clear . In this paper we make attempt to explain the process of the hydrogen-cluster formation from point of view of hypothesis of hydrogen plasma state in metals [7] ("metals" means in our case, mainly, palladium , as the PdH -system is the most studied). Such point of view permits the hydrogen-cluster formation not only in the grain-boundaries, pores, but in metal lattice, too.

2. THE POSSIBLE MECHANISM OF THE HYDROGEN-CLUSTERS FORMATION

The hydrogen (below it means all hydrogen isotopes - protium, deuterium, tritium, if there are no special reservations) concentration in metal $n \sim p^{0.5}$, where p-hydrogen pressure over metal surface. It means, that hydrogen in metal volume is, at least, in atomic state. What is more, the hydrogen gas in lattice can be ionized, so the state similar to plasma state is possible. The arguments in favor of such state are: the anomalous high hydrogen diffusion coefficient in many metals, what one can explain by small size of proton, the disappearance of paramagnetism (when hydrogen concentration increases to H/Pd ~ 0.65 the palladium converts into the poor diamagnetic), the results of the researches of positive muons in Pd, superconductivity of PdH and electro-diffusion experiments /8/. So, we suppose that the palladium lattice plays the role of original ionizer and trap and then we consider the hydrogen plasma performances without account of plasma-lattice interaction.

In a general case the hydrogen plasma in metal contains different particles, such as H^+(proton), e^- (electron), H(atom), H^-, H_2^+, H_2. For the concentrations $n > 10^{18}$ cm^3 and temperature more than ≈1K there will be only protons (or D^+, T^+) and electrons in plasma, i.e. the hydrogen plasma in metal is fully ionized. Really, as it is seen in hydrogen phase diagram in Fig. 1, the Mott criterion /9 / ($n_p = 1.2\text{x}10^{18}$ xT(K); $r_D = (kT/4\pi e^2 n_p)^{1/2} = 0.84 r_B$, where n_p and n_c - proton concentration and critical density, accordingly; r_D and r_B - Debye and Bor radiuses, accordingly), which

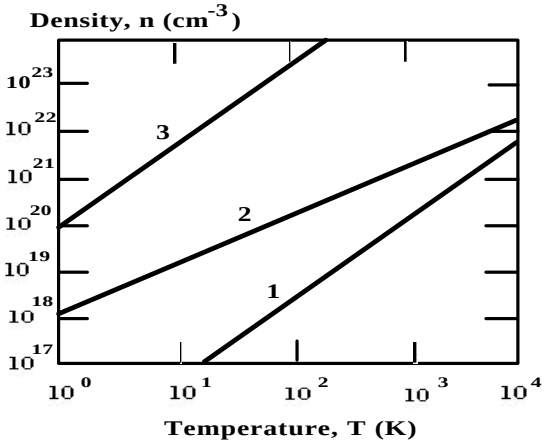

Fig. 2. The hydrogen plasma characteristics on density-temperature coordinate plane: 1- electron degeneracy line ($n_e L_e^3 = 1$); 1 - Mott line ($r_D = 0.84 r_B$); 3- proton degeneracy line ($n_p L_p^3$)

determines the hydrogen metal plasma transition to stripped plasma state, is released at above mentioned parameters (curve 2, fig.2). It was shown earlier [7] that at 1 at the hydrogen pressure over palladium surface the temperature of Mott transition is 520K that is near of

565K critical temperature of gas-liquid (also called α-β) type phase transition in palladium.

During the Mott transition the more dense hydrogen plasma "drops" (clusters) formation can begin in any unit cell. The small clusters with ion number N ~ 12-100 appears (fig.3). The driving force for such clusters formation can be the new phase additional chemical potential $\Delta\mu = \Delta\mu_e + \Delta\mu_H$, where $\Delta\mu_e$ -is the caused by electron Fermi-level change by plasma electrons and $\Delta\mu_H$ is caused by palladium lattice distension (it is known [8] that unit cell parameter for palladium α-phase is ≈3.89A, and for β-phase ≈ 4.025A), i.e. conditioned by the lattice elastic deformation energy. The attractive mechanism between protons, which is founded on ideas that the proton deforms crystal lattice and creates the observed another protons long-range deformation field, was given in [8]. The large hydrogen-clusters formation (N>100) is possible both in lattice volume, and in regions of defect accumulation (macro- and micro-pores, dislocations, grain-boundaries, micro-cracks, etc.). The former requires the certain conditions for point defect (vacancies and host interstitial atoms) generation. The irradiation by plasma and energetic particles can be, for example, as the mechanism, providing hydrogen-clusters formation conditions. In the latter the large clusters are generated when hydrogen plasma condensed in dense phase into

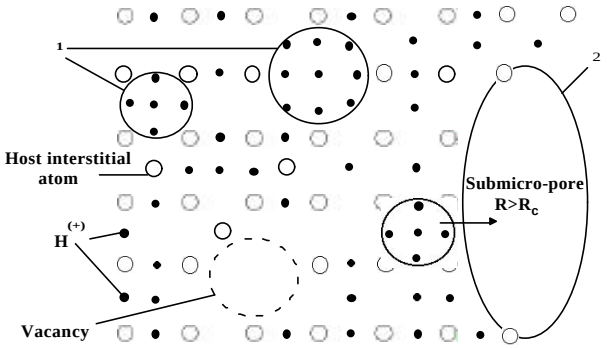

Fig.3. The small (1) and large (2) hydrogen-clusters formation in metal.

micro-pores, micro-cracks, dislocations and grain-boundaries. According to Lifshits-Sljozov-Wagner diffusion coalescence theory [10-12] there are only pores with sizes more than $R_c > ((n_v/\Delta n_v)/2\gamma(A/kT)$ in metals, where A is the atomic volume, γ is specific surface energy, n_v is vacancy concentration, Δn_v - vacancy supersaturation, R_c – the critical radius of pore. The pores with the sizes smaller than R_c dissolve and move to larger pores or micro-cracks, grain-boundaries and dislocations, forming the pores chains [8]. The condensation of the dense hydrogen plasma into such micro- and submicro-pores causes the large hydrogen-clusters formation. In very large pores hydrogen clusters may be destroyed, forming molecular gas. As the impurities segregation on pores boundaries is usually observed, the hydrogen back dissociation and sorption by metal is difficult, the conditions for hydrogen permeation into pores and back are asymmetric, so hydrogen pressure in pores can achieve high values (according to dates in /8/ it is about 1000-2000 at.), that leads to disruption of metal in some cases.

With further increasing of the hydrogen concentration in metal the amount of new phase (number of clusters) increases and the hydrogen shielding effect could be possible. When the plasma density keeps the increase, one more phase transition, which connected with proton degeneracy [7], is possible (curve 3, fig.2). For protium and tritium plasma this is Fermi-Dirac degeneracy. For deuterium plasma this phase transition means Bose-condensation.

CONCLUSION

The use of the diffusion membranes coated by erosion high resistible material could be as a perspective variant for plasma facing components providing both erosion and hydrogen recycling processes control.

In the frame of strongly non-ideal plasma theory it is possible to explain the high density phase (hydrogen-clusters) formation in metals, as the result of the phase transitions of hydrogen plasma in metal. The small clusters can be condensed in metal lattice. The large clusters formation is more probably in submicro- and micro-pores.

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