

Features of hydrogen trapping and desorption during deposition of yttrium coating on zirconium in a gas discharge

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Abstract. Transport of hydrogen isotopes during the various regimes of deposition of yttrium coating on zirconium in argon plasma with addition of deuterium is studied. The influence of oxygen contamination in plasma-generating gas on the processes of trapping and desorption of hydrogen isotopes is also investigated. It is shown that deposition of yttrium coating on zirconium in Ar+5%D₂ plasma enhances both hydrogen desorption from zirconium and deuterium trapping into zirconium in comparison to those under plasma exposure without deposition. Yttrium deposition in Ar+25%O₂+5%D₂ plasma, conversely, mitigates both hydrogen desorption and deuterium trapping. Hydrogen desorption from zirconium increases with the increase of energy of ions, bombarding the sample during deposition of the coating in oxygen-free plasma, but it, on the contrary, decreases in oxygen-containing plasma.

1. Introduction

Protective coatings preventing hydrogen penetration into metal are widely used in many applications. Particularly, the coatings, protecting zirconium components of active core of light-water reactors from oxygen and hydrogen corrosion, are actively developed. Encouraging results of reactor-simulation tests of yttrium-based protective coatings deposited on zirconium in a gas discharge [1] demonstrate the prospects of development of these coatings. An important step of protective coatings creation is investigation of hydrogen behavior in multicomponent system consisting of materials of the coating and the substrate. The understanding of these regularities is also needed at the stage of deposition of the coating in a gas discharge, when the sample undergoes plasma irradiation. Features of trapping and desorption of hydrogen isotopes during the various regimes of yttrium deposition on zirconium in a gas discharge were investigated by thermal desorption spectroscopy (TDS) in a present work.

2. Experimental

Coatings were deposited in experimental device for thin films deposition in a gas discharge with a hot tungsten cathode. The experiments were carried out in two plasma-generating gas compositions – 95%Ar+5%D₂ and 70%Ar+25%O₂+5%D₂. Samples of zirconium alloy E110 (Zr–1%Nb) in the form of tube sections with a size of ~7×7×1 mm preliminarily rinsed in ultrasonic ethanol bath were used as substrates. According to the results of previous experiments the substrate should be irradiated by argon ions before the deposition of the coating to demonstrate the proper coating adhesion.

There were several types of the investigated coatings: yttrium coating and zirconium coating deposited on zirconium separately and two-component layer consisting of zirconium and yttrium as



well. Coatings were formed by yttrium or zirconium atoms sputtered by ions of plasma from targets made of corresponding metals. Joint deposition of zirconium and yttrium was performed by simultaneous gradual decrease of zirconium deposition rate and increase of yttrium deposition rate. Separate deposition of zirconium and yttrium coatings was carried out at floating potential (≈ 12 V) on the substrate. Two-component layers were deposited at two values of potential on the substrate: floating potential and 200 V. Deposition rate of all of the coatings in oxygen-free plasma at floating potential on the substrate was ≈ 800 nm per hour.

Pressure of plasma-generating gas in all the experiments was equal to 1.3×10^{-1} Pa, residual gas pressure did not exceed 2.6×10^{-3} Pa, the experiments lasted 80 min.

Trapping and desorption of hydrogen isotopes under deposition of coatings were investigated via thermal desorption spectroscopy in MIKMA device [2]. The results were compared with those of plasma exposure of the samples under the same conditions, but without deposition of any coating. Residual gas pressure in TDS chamber did not exceed 1.3×10^{-5} Pa. Samples were heated up linearly at a rate of 5 K/s. Molecules of H_2 , HD, D_2 , H_2O , HDO, D_2O were measured. Desorption of other molecules, containing hydrogen isotopes, was negligible.

3. Separate deposition of zirconium and yttrium at floating potential on the substrate

The amount of hydrogen atoms in the samples after preliminary ion bombardment before deposition was determined as $\approx 6 \times 10^{18} \text{ cm}^{-2}$. Figure 1 illustrates that exposure of zirconium to $Ar+5\%D_2$ plasma as well as to $Ar+25\%O_2+5\%D_2$ plasma at floating potential causes desorption of $\approx 60\%$ of hydrogen atoms from zirconium and trapping of a much lesser amount of deuterium atoms. In our previous work [3] it was shown that ion irradiation of a metal sample with oxidized surface initiates hydrogen exchange between the sample and the gas ambience of the experimental stand. The mechanism of this process is based on surface reactions occurring between hydrogen-containing and oxygen-containing particles of gaseous phase, from one side, and those of oxidized surface layer, from the other side.

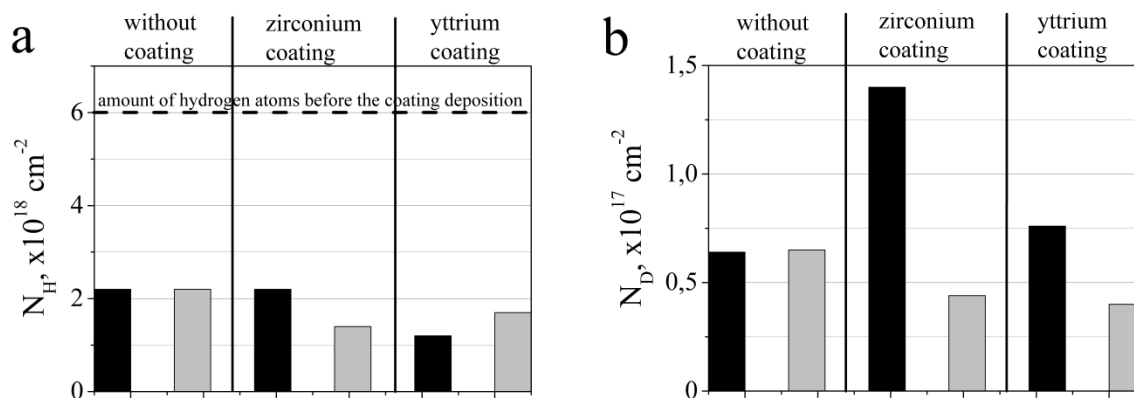


Figure 1. The amount of hydrogen (a) and deuterium (b) atoms in zirconium samples after exposure to plasma without deposition of any coating and after deposition of zirconium and yttrium (black – $Ar+5\%D_2$ plasma, gray - $Ar+25\%O_2+5\%D_2$ plasma).

Deposition of yttrium coating in $Ar+5\%D_2$ plasma enlarges hydrogen desorption by more than 25% in comparison to that under exposure to plasma without deposition. Besides, deuterium trapping increases by $\approx 17\%$. Hydrogen desorption under deposition of zirconium coating in $Ar+5\%D_2$ plasma is almost the same as that under plasma exposure. Deuterium trapping under zirconium deposition increases by more than 2 times.

Deposition of yttrium coating in $Ar+25\%O_2+5\%D_2$ plasma retards hydrogen desorption in comparison to that under the similar deposition in $Ar+5\%D_2$ plasma. Deposition of zirconium coating in oxygen-containing plasma, conversely, leads to the increase of hydrogen desorption. Deuterium trapping under deposition of any of the investigated coatings in $Ar+25\%O_2+5\%D_2$ plasma is 2-3 times less than that under its deposition in oxygen-free plasma.

4. Joint deposition of zirconium and yttrium at floating potential on the substrate

Hydrogen exchange under deposition of two-component layer, containing zirconium and yttrium, at floating potential on the substrate is similar to that observed during the deposition of yttrium coating (figure 2). Both hydrogen desorption and deuterium trapping decreases when oxygen content in plasma-generating gas increases. It should be also mentioned that the values of hydrogen desorption from zirconium under deposition of two-component layer in Ar+5%D₂ plasma are close to those under deposition of the components separately. At the same time, deuterium trapping under the joint deposition of zirconium and yttrium in oxygen-free plasma increases many times over the corresponding values obtained after deposition of zirconium or yttrium singly.

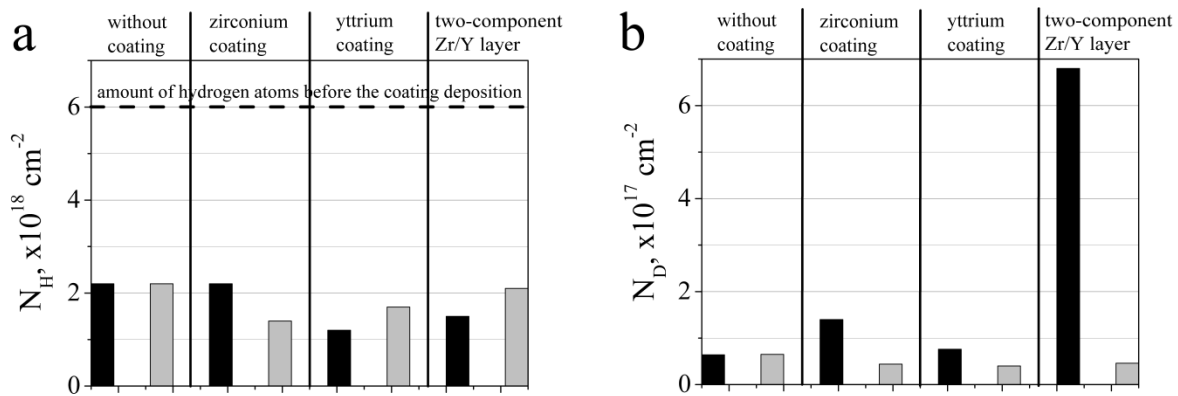


Figure 2. The amount of hydrogen (a) and deuterium (b) atoms in zirconium samples after exposure to plasma without deposition of any coating and after deposition of zirconium, yttrium and two-component layer Zr/Y (black – Ar+5%D₂ plasma, gray - Ar+25%O₂+5%D₂ plasma).

5. Joint deposition of zirconium and yttrium at 200 V on the substrate

Dependence of hydrogen desorption from zirconium under irradiation by ions of ≈ 200 eV (without deposition of any coating) on oxygen content in plasma differs from that observed when zirconium was exposed to plasma at floating potential. Addition of oxygen to plasma-generating gas leads to sufficient increase of hydrogen desorption from the sample (figure 3).

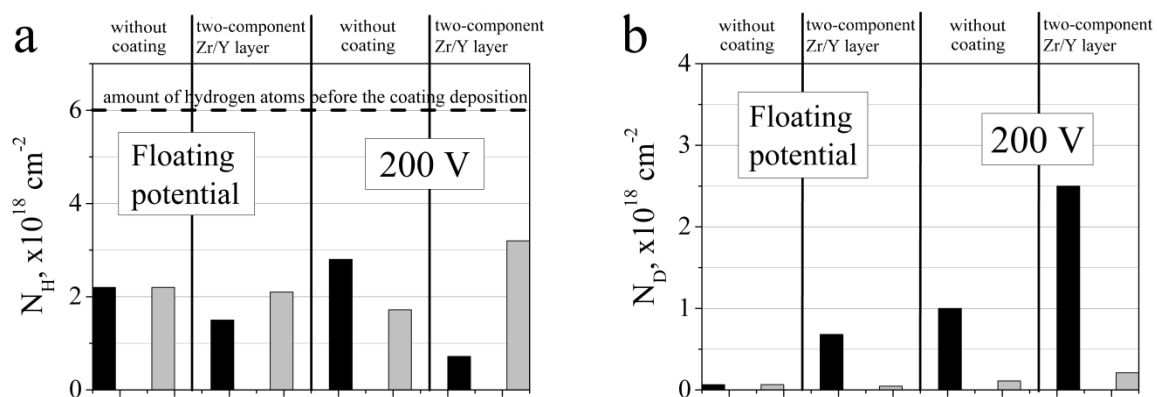


Figure 3. The amount of hydrogen (a) and deuterium (b) atoms in zirconium samples after exposure to plasma without deposition of any coating and after deposition of two-component layer Zr/Y (black – Ar+5%D₂ plasma, gray - Ar+25%O₂+5%D₂ plasma).

At the same time, regularities of hydrogen desorption under deposition of two-component layer at biasing potential of 200 V on the substrate are similar to that observed during the deposition of this coating at floating potential. Namely, joint deposition of zirconium and yttrium in Ar+5%D₂ plasma

causes the increase of both hydrogen desorption from the sample and deuterium trapping into the sample in comparison to those under exposure to plasma without deposition of any coating. Deposition of two-component layer in oxygen-containing plasma, conversely, decreases both hydrogen desorption and deuterium trapping. Besides, when the biasing potential on the sample increases from floating potential to 200 V, discrepancy in hydrogen desorption under deposition of the coating in Ar+5%D₂ plasma and in Ar+25%O₂+5%D₂ plasma reveals to a greater extent.

6. Conclusion

The experiments have shown that deposition of yttrium coating on zirconium sample in a gas discharge significantly affects the regularities of hydrogen exchange between the plasma irradiated sample and the gaseous ambience of the experimental stand.

In particular, it was observed that under deposition of yttrium coating in Ar+5%D₂ plasma hydrogen atoms desorb from zirconium more intensively than under plasma exposure without deposition of any coating. At the same time, deposition of zirconium coating at the same parameters does not affect the rate of this process. Deposition of yttrium in Ar+25%O₂+5%D₂ plasma mitigates hydrogen desorption in comparison to that under plasma exposure without deposition of the coating, whereas zirconium deposition under the same conditions, conversely, intensifies it.

Deuterium trapping under deposition of any of the investigated coatings in Ar+5%D₂ plasma is 2-3 times larger than that under exposure to plasma without deposition. Besides, under the joint deposition of zirconium and yttrium deuterium atoms trap at a significantly greater extent than under deposition of zirconium or yttrium separately. Under deposition of any of the investigated coatings in oxygen-containing plasma deuterium trapping decreases, apparently, due to enhancement of deuterium desorption from the surface as a part of water molecules.

The increase of energy of ions irradiating the sample enlarges the difference in the amounts of hydrogen atoms desorbing during the joint deposition of zirconium and yttrium in oxygen-containing plasma and in oxygen-free plasma.

One could propose that the main reasons of alteration of hydrogen behavior during yttrium deposition (in comparison to that during zirconium deposition or plasma exposure without deposition) are different values of enthalpy of hydrogen solution in these metals ($\Delta H_s = -0.66$ eV/at.H for Zr and $\Delta H_s = -0.85$ eV/at.H for Y [4]) as well as different values of standard Gibbs energy of formation of their oxides ($\Delta G = -1042.8$ kJ/mol for ZrO₂ and $\Delta G = -1816.6$ kJ/mol for Y₂O₃ [5]). These parameters are supposed to determine thermodynamic conditions of hydrogen transport in systems “zirconium-yttrium” and “zirconia-yttria” as well as surface reactions, regulating hydrogen exchange [3].

Acknowledgments

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