Hydrogen transport through oxide metal surface under atom and ion irradiation

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Abstract. Both the latest and earlier achieved results on gas exchange processes on metal surfaces (including stainless steel, titanium, zirconium, tungsten with deposited aluminum oxide coating) under hydrogen atom or plasma irradiation with occasional oxygen impurity are presented in the paper. Mechanisms and regularities of these processes are discussed. It is demonstrated that surface oxide layer properties as a diffusion barrier strongly depend on external influence on the surface. In particular, it is revealed that low energy hydrogen ion irradiation could slow down hydrogen desorption from metals. Hydrogen atom or ion irradiation combined with simultaneous oxygen admixture accelerates hydrogen desorption from metals.

1. Introduction
Hydrogen content in metals and coatings is usually an unwanted feature that decreases their operational parameters. The negative effects can be worse if an oxide layer is present on the surface that acts as a diffusion barrier for hydrogen atoms. As it has been shown [1], surface oxide layers alter their properties under hydrogen atom or ion irradiation especially when this irradiation is performed with oxygen addition.

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2. Gas exchange processes between hydrogen plasma and stainless steel surface.
Multifunctional research apparatus for mass-spectrometry analysis (MIKMA) [1] was used for these and all other experiments presented in the paper. This device allows performing of sample irradiation with hydrogen atoms or plasma ions and gas composition analysis as well as thermal desorption analysis (TDS) of the samples. TDS ramp rate was 5 K/s in all experiments. During irradiation vacuum chamber wall were air-cooled so that their temperature did not exceed 40 C. Residual gas (H₂O ~ 95 at. %, H₂ ~ 5 at. %) pressure was less than 1x10⁻⁴ Pa. Working gas pressure was 6.6×10⁻⁵ Pa.

At the first stage of experiments the vacuum chamber wall was irradiated with deuterium atoms from D₂+O₂ working gas that were generated by D₂ dissociation at a heated tungsten wire. Then, plasma
discharge was initiated in the same gas mixture thus irradiating chamber walls with deuterium ions as well as atoms. At the second stage of experiments deuterium was substituted for hydrogen and vacuum chamber wall was irradiated with hydrogen atoms and ion from H$_2$+O$_2$ gas mixture. These series of experiments was performed with various oxygen concentrations: 2, 5, 10, 20 and 30 at%. Working gas composition change for D$_2$+10%O$_2$ gas mixture after cathode heating and plasma initiation are presented at figure 1a. Hydrogen atom irradiation of the chamber walls led to rapid oxygen content decrease in the working gas. It fell below mass spectrometer sensitivity level. At the same time molecules of HD, HDO D$_2$O appeared in the working gas with simultaneous H$_2$ and H$_2$O content increase. When plasma discharge was initiated no further radical changes in gas composition were observed. These results show that hydrogen atom and ion irradiation initiated formation of hydrogen containing molecules on the stainless steel surface. These molecules contained hydrogen from working gas as well as hydrogen from the sorption layer that had diffused from the bulk of the wall.

Figure 1. Working gas composition change during: a) D$_2$+10% O$_2$ gas mixture, vacuum chamber wall irradiated with atoms and subsequent plasma irradiation, b) H$_2$+10% O$_2$ gas mixture with atom irradiation after the wall was irradiated in deuterium plasma.
The processes described above can be supported by a series of exothermic reactions that took place on the surface (Figure 2). Hydrogen atoms and ions initiated these reactions by interacting with chromium oxide (Cr₂O₃) and also participated in subsequent reactions. Oxygen atoms reduced chromium oxide and took part in all “water” molecules generation. At the second stage of experiments hydrogen atom irradiation stimulated deuterium release from the wall which had been trapped during the first stage (Figure 1b).

3. Hydrogen transport through the surface under ion irradiation.

Ion irradiation influence on hydrogen transport through 1 μm titanium layer saturated with deuterium at Ti:D=1,7 concentration deposited on molybdenum substrate was studied. The samples were heated to 350 C both with and without hydrogen plasma with oxygen content (0, 2, 4, 10% oxygen) irradiation for the same time. Ion energies were 650 and 3500 eV, ion flux $7\times10^{15}$ at/cm²s.

Deuterium concentrations in the titanium layer before and after the experiments are presented at table 1. It is shown that without any irradiation about half of deuterium is released from the target when it is heated. Deuterium is also released under 3500 eV ion irradiation but no release was registered under 650 eV ion irradiation. In both these cases hydrogen was trapped in the sample. The conclusion can be made that a kind of barrier layer is formed when hydrogen atoms are stopped in the near surface layer. When oxygen is added to the working gas at first hydrogen trapping increases but after the oxygen concentration reaches 4% it decreases. Deuterium desorption from titanium increased with oxygen content and almost half of deuterium was released when oxygen content was 10%. This shows that after certain amount of oxygen in plasma, surface irradiation stimulates not only deuterium but also hydrogen desorption. Thus, similar processes to those on stainless steel surface are likely to take place.

Table 1. Hydrogen and deuterium concentration change after sample heating at 350 C and after irradiation in (H₂+n%O₂) plasma with 650 or 3500 eV ions at 350 C.

| Action                                      | Hydrogen concentration (at/cm³) | $H_{after}$ / $H_{before}$ | Deuterium concentration (at/cm³) | $D_{after}$ / $D_{before}$ |
|---------------------------------------------|---------------------------------|----------------------------|---------------------------------|----------------------------|
| Sample before heating                       | $0.6\times10^{22}$              | 9.6×10²²                   |                                 |                            |
| Sample heating without irradiation          | $0.25\times10^{22}$             | 4.2×10²²                   |                                  | 0.44                       |
| 650 eV ion irradiation in H₂ plasma         | $1.1\times10^{22}$              | 9.6×10²²                   |                                  | 1                          |
| 3500 eV ion irradiation in H₂ plasma        | $0.9\times10^{22}$              | 3.2×10²²                   |                                  | 0.35                       |
| 650 eV ion irradiation in H₂+2%O₂ plasma    | $1.2\times10^{22}$              | 9.5×10²²                   |                                  | 1                          |
| 650 eV ion irradiation in H₂+4%O₂ plasma    | $0.9\times10^{22}$              | 8.5×10²²                   |                                  | 0.88                       |
| 3500 eV ion irradiation in H₂+10%O₂ plasma  | $0.3\times10^{22}$              | 4.3×10²²                   |                                  | 0.45                       |
4. Hydrogen transport through zirconium surface under plasma irradiation.

Hydrogen transport in “Э-110” (Zr-1%Nb) zirconium alloy under argon ion irradiation was studied in relation to residual gas pressure. Samples of 7×7×1 mm size were irradiated by 250 eV argon ions with 7.5×10^{15} at/cm^{2} s flux. Total fluence was 9×10^{18} at/cm^{2}, sample temperature 550 K, residual gas pressure was varied between 0.13-4.0×10^{-2} Pa (H_{2}O ~ 92%, H_{2} ~ 5%).

It can be seen (Figure 3) that during irradiation at (1.3–30)x10^{-3} Pa residual pressure hydrogen trapping decreased contrary to irradiation at 3-4×10^{-2} Pa residual pressure at which hydrogen desorped from the sample. Preliminary experiments showed that hydrogen desorption from the surface oxide layer occurs at roughly 400 and 1000 K, whereas from the bulk of zirconium at 1300 K. This information allowed to judge on hydrogen trapping sites location based on TDS spectra shape before and after irradiation in argon plasma (Figure 4).

Figure 3. Hydrogen content in irradiated sample versus residual gas pressure. Dotted line marks hydrogen content in non-irradiated sample.

Figure 4. Zirconium alloy (“Э-110”) TDS spectra difference before and after irradiation in argon plasma at residual pressure of: 1.3×10^{-3} Pa (■), 1.1×10^{-2} Pa (○), 2×10^{-2} Pa (●), 4×10^{-2} Pa (□)
At \((1.3-30) \times 10^{-3}\) Pa residual pressure hydrogen is seen to be trapped both in the surface oxide layer and in the bulk of the material. At higher residual gas pressures less hydrogen is trapped in the bulk. One may suppose that oxygen atoms generated from water molecules in plasma stimulated similar to described above processes on the surface of zirconium.

5. Barrier properties of aluminum oxide layer on tungsten surface.

Behavior of hydrogen and deuterium atoms trapped in tungsten after depositing aluminum oxide coating layer was studied. 300 eV deuterium ions were irradiating the sample with \(7.3 \times 10^{15}\) at/cm\(^2\) flux, \(2.6 \times 10^{19}\) at/cm\(^2\) total fluence at 500 K sample temperature. After that, aluminum oxide coating was formed on both sides of the sample by sputtering an aluminum target in Ar+n\%O\(_2\) gas mixture (n=1-8). During deposition sample temperature was 450-500 K, resulting coating thickness was 200-700 nm, deposition duration 1 h per each side of the sample.

It is shown (Table 2), that during deposition in plasma with less 1% oxygen addition deuterium content in the sample decreased by roughly 50%. In 4 and 8% oxygen addition cases ~90% of deuterium was released. The behavior of “technological” hydrogen present in the sample was practically the same.

| Oxygen concentration in plasma | Hydrogen desorption (at/cm\(^2\)) | Deuterium desorption (at/cm\(^2\)) | \(\frac{(H_{\text{before}}-H_{\text{after}})}{H_{\text{before}}}\) | \(\frac{(D_{\text{before}}-D_{\text{after}})}{D_{\text{before}}}\) |
|-----------------------------|-------------------------------|-------------------------------|---------------------------------|---------------------------------|
| <1%                         | \(2.2 \times 10^{17}\)       | \(1.5 \times 10^{16}\)       | \~13%                           | \~21%                           |
| 4%                          | \(5.4 \times 10^{16}\)       | \(3.2 \times 10^{15}\)       | \~68%                           | \~82%                           |
| 8%                          | \(7.1 \times 10^{16}\)       | \(3.5 \times 10^{15}\)       | \~75%                           | \~83%                           |

Similarity of the results obtained in all these experiments could be connected with the similarity in experimental conditions. In all cases an oxide layer on the surface was irradiated by ion from plasma containing both hydrogen and oxygen atoms. Only the surface of the sample was affected, with no direct influence on hydrogen diffusion through the bulk of material or oxide layer.

6. Summary

Surface oxide layer properties as a diffusion barrier on metals strongly depend on external influence. Slow hydrogen atoms or ions that are stopped in the oxide layer or just beyond it slow down hydrogen diffusion to the surface. High energy ions that are stopped further in the bulk increase hydrogen concentration in irradiated material. Thus hydrogen diffusion to the surface and its desorption is accelerated.

When oxygen is added to the working gas slow hydrogen atoms and ions initiate a series of exothermic reactions involving surface oxide layer and hydrogen from the bulk of material. As a result of these reactions hydrogen atoms are associated in hydrogen-containing molecules that are released from the surface. Acceleration of hydrogen diffusion from the bulk of material as a result of these processes shows that hydrogen atom relaxation on the surface is the main factor defining barrier properties of surface oxide layers. Acceleration of relaxation activates hydrogen removal from metals.

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References

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