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Trapping and desorption of hydrogen isotopes under irradiation of zirconium by deuterium atoms of thermal energies

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The results on trapping and desorption of hydrogen isotopes under irradiation of zirconium by deuterium atoms of thermal energies are presented. It is shown that the addition of oxygen to the operating gas during the irradiation causes the increase of the oxide layer thickness, the amount of hydroxyl groups in it and deuterium trapping in zirconium. Accelerated transport of deuterium atoms through the oxide layer saturated by hydroxyl groups is observed. Mechanisms of trapping and desorption of hydrogen isotopes and the role of oxygen in these processes are discussed.

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1. Introduction

Hydrogen behavior in metals is a very important aspect in many applications. Therefore, this subject has been actively investigated for a long time. It is known that oxide layers on the surfaces of some metals (e.g. zirconium, titanium, yttrium, etc.) and their hydrides act as a surface barrier that mitigates both hydrogen penetration into the metal and hydrogen desorption from the metal or from the hydride [1—6]. Authors of Ref. [7] and our previous papers [8—11] demonstrated that irradiation of the oxidized metal surface by low-energy ions, or by thermal-energy atoms, alters barrier properties of the oxide and influences trapping and desorption of hydrogen isotopes. A full picture of the processes which determine hydrogen transport through the surface oxide layer and include the participation of atomic particles irradiation is still absent. This work is dedicated to the investigation of the mechanisms and regularities of trapping and desorption of hydrogen isotopes under irradiation of zirconium by deuterium atoms of thermal energies, and was carried out by means of thermal desorption spectroscopy (TDS) and

X-ray photoelectron spectroscopy (XPS).

2. Experimental

The investigated samples were segments ~7 mm × 7 mm × 1 mm of tubes made of zirconium alloy E110 (Zr—1%Nb) preliminarily rinsed in the ultrasonic ethanol bath.

Irradiation of the samples by D-atoms of thermal energies was performed in "MIKMA" device that allows irradiation of a sample by atoms, ion beams, ions and electrons of a gas discharge, and then to transfer it to another chamber for TDS analysis without breaking vacuum [12]. Atomic flux onto the surface of the sample was produced by a device [13], where deuterium atoms were generated by means of heating of the tungsten spiral up to ≈ 1800 К in gaseous deuterium. The design of this device provides atomic flux directed perpendicular to the surface of the sample. Deuterium atoms emitted in other directions recombine into molecules by multiple collisions with the structural elements of the device.

Parameters of the experiments were as follows. The operating gas was the mixture $D_2 + (0-30)\%O_2$ with the deuterium pressure of 1.2×10^{-1} Pa measured by a vacuum capacitance manometer (Baratron). The atomic flux onto the surface was estimated as

~10^{15} cm^{-2} s^{-1}. Molecular flux onto the surface of a tungsten spiral, dissociation probability of deuterium molecules on the surface of tungsten at a given temperature and solid angle at which each section of the spiral "sees" the sample were taken into account in the calculation of atomic flux. The samples were irradiated by various doses in the range of ~(1–2) × 10^{19} cm^{-2}. The sample temperature in all of the experiments was equal to 600 K. A preliminary exposure of the samples to the gaseous ambient at the same parameters was conducted.

Residual gas pressure in the TDS chamber during analysis was ≤7 × 10^{-6} Pa, the sample was heated at a linear rate of 5 K/s. Desorption of H_2, HD, D_2, H_2O, HDO and D_2O was measured during the analysis. Desorption of other hydrogen-containing, or deuterium-containing molecules, was negligible. The flux of desorbed molecules (ordinate of TDS spectrum) was calculated based on the signals of a quadrupole mass-spectrometer (QMS) using two calibration coefficients (k_1, k_2).

Coefficient k_1 was calculated as the proportionality factor between the QMS signals and the readings of the vacuum gauge (gas pressure in TDS chamber). The procedure of k_1 determination was as follows. A constant gas flow was established into TDS chamber and, after that, both vacuum gauge reading and QMS signal were recorded. The operation was repeated for several values of gas pressure. Coefficient k_1 was specified after each experiment to exclude the influence of sensitivity change of mass-spectrometer.

Coefficient k_2 links desorption flux with the readings of the vacuum gauge. The procedure for k_2 determination for hydrogen isotopes was as follows. Constant gas flow was established into TDS chamber from the graduated tube immersed in a container of oil and filled partly by oil and partly by the investigated gas. The flux of gas molecules was calculated based on the initial oil level in the tube and the rate of its growth during the gas inlet. Coefficient k_2 was derived as a proportionality factor between the flux of gas molecules and the difference in the vacuum gauge readings before and after the gas inlet.

The amounts of hydrogen and deuterium in zirconium were obtained by integration of TDS spectra of hydrogen-containing and deuterium-containing molecules. Hydrogen desorption from the sample during the experiment was calculated as a difference between the amounts of hydrogen atoms in the sample before and after the experiment.

A new sample was used for each experiment. Special measurements conducted prior the experiments showed that the variation of the hydrogen concentration in the samples was not higher than 8%, that is less than accuracy of TDS measurements (≈11%).

XPS depth profiling was performed in the SPECS facility described in Ref. [14]. All the measurements were carried out at room temperature. Energy and current of etching ions were 3 keV and 10 μA, respectively. Zr3d and O1s photoemission spectra were studied. Traces of tungsten were also detected on the surface of the irradiated samples.

3. Results

3.1. Gas exposure

Deuterium trapping during the exposure of the sample to gaseous D_2 and D_2 + 30%O_2 gas mixture did not exceed 2 × 10^{16} cm^{-2}. Hydrogen desorption from the sample during the exposure both to the mixture D_2 + 30%O_2 and to gaseous deuterium was within the measurement error.

At the same time, as shown in Fig. 1, the shape of TDS spectrum of hydrogen-containing molecules (mainly H_2) after the exposure of zirconium to the deuterium–oxygen gas mixture changed. The
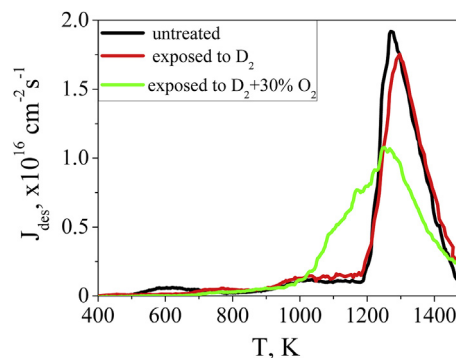

Fig. 1. TDS spectra of hydrogen-containing molecules after exposure (T = 600 K, t = 3 h) of the E110 sample to gaseous deuterium and to the deuterium–oxygen gas mixture.

height of the maximum at 1300 K decreased while the shoulder at lower temperatures increased.

3.2. Atomic irradiation

Irradiation of zirconium by deuterium atoms of thermal energies enhanced deuterium trapping in comparison with that of gas exposure at the same parameters. In addition, deuterium trapping in the sample irradiated in the deuterium–oxygen gas mixture exceeded that for the sample irradiated in pure deuterium (Fig. 2a). Irradiation of zirconium at first in D_2 + 30%O_2 and then in D_2 intensified the accumulation of deuterium even more. Moreover, the higher the dose of irradiation in the deuterium–oxygen gas mixture was, the larger was the deuterium trapping coefficient during the subsequent irradiation without oxygen.

The atomic irradiation by the dose of 10^{19} cm^{-2} caused 20–25% desorption of hydrogen atoms from zirconium (Fig. 2b). Unlike deuterium trapping, hydrogen desorption was not dependent on the presence of oxygen in the operating gas up to the dose of 10^{19} cm^{-2}. However, under the irradiation of zirconium in the oxygen-free ambient hydrogen desorption stopped in excess of 10^{19} cm^{-2} dose, whereas under the irradiation in the deuterium–oxygen gas mixture hydrogen continued to be released up to the dose of 2 × 10^{19} cm^{-2}. It should be also noted that upon deuterium accumulation in zirconium, the desorption of hydrogen decreased.

With the increase of the dose of irradiation in pure deuterium the peak at 1300 K in TDS spectrum of deuterium-containing molecules (mainly HD and D_2) grew faster than another maxima up to the dose of 2 × 10^{19} cm^{-2} (Fig. 3a). During irradiation in the deuterium–oxygen gas mixture by the dose of 10^{19} cm^{-2} deuterium was trapped in the same way (Fig. 3b). However, during the subsequent irradiation, the growth of the peak at 1300 K slowed down and all the peaks grew equally. Thereby total deuterium trapping decreased.

Shape modification of TDS spectrum of hydrogen-containing molecules caused by the atomic irradiation (Fig. 4) was similar to that observed after exposure of the sample to the deuterium–oxygen gas mixture (Fig. 1). But contrary to the gas exposure, the atomic irradiation led to change of the shape of TDS spectrum even in the absence of oxygen in operating gas, albeit to a lesser extent (Fig. 4a).

After the irradiation in D_2 + 30%O_2 mixture by the dose of 10^{19} cm^{-2} the height of the peak at 1300 K was the same as after the gas exposure at the same parameters (Fig. 4b). The other maxima became lower due to desorption of hydrogen. With the increase of the dose the height of the peak at 1300 K decreased whereas the
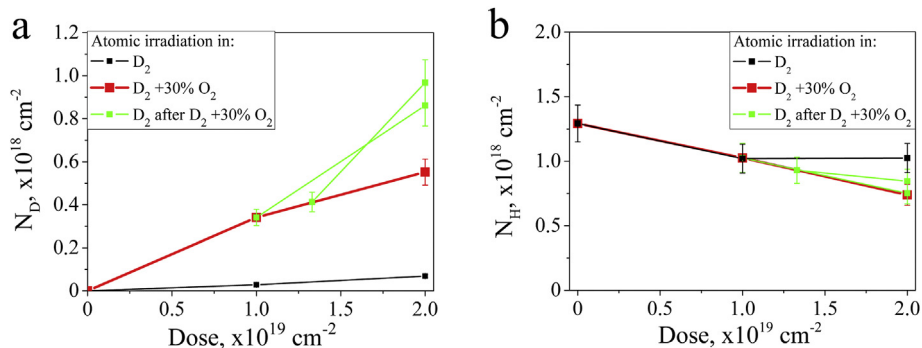
Fig. 2. Deuterium (a) and hydrogen (b) content in the E110 sample versus the irradiation dose.
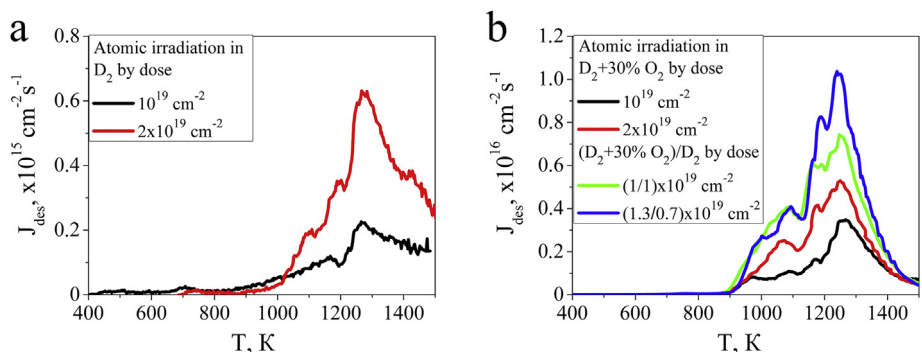

Fig. 3. TDS spectra of deuterium-containing molecules after atomic irradiation of the E110 sample in gaseous deuterium (a) and in the deuterium−oxygen gas mixture (b).
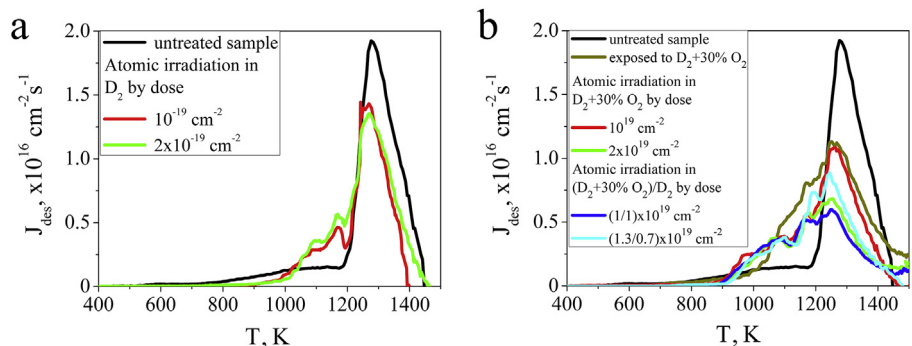

Fig. 4. TDS spectra of hydrogen-containing molecules after the atomic irradiation of the E110 sample in gaseous deuterium (a) and in the deuterium−oxygen gas mixture (b).

other maxima remained unchanged. The TDS spectra obtained after the irradiation of zirconium in regimes $D_2 + 30\%O_2$ (1019 cm^{-2})/D_2 (10^{19} cm^{-2}) and $D_2 + 30\%O_2$ (2×10^{19} cm^{-2}) were almost identical.

XPS analysis showed that irradiation of zirconium in deuterium−oxygen gas mixture causes the increase of thickness of the oxide layer as well as oxygen concentration in it (Fig. 5).

Apart from the main maximum close to 531 eV the XPS spectra O1s contained an additional peak at about 533 eV (Fig. 6a) which was associated with hydroxyl groups in Refs. [15−17]. Concentration of these groups at the surface was the highest, then rapidly decreased with the depth and further remained constant at the level of $\approx 15-20\%$ of total O1s signal (Fig. 6b).

Under the irradiation of zirconium in the deuterium−oxygen gas mixture the number of hydroxyl groups in the oxide grew with the increase of the oxygen concentration. The percentage of O−D(H) component in spectrum O1s near the surface also became larger.
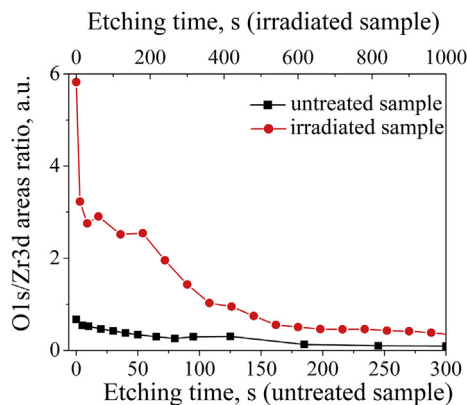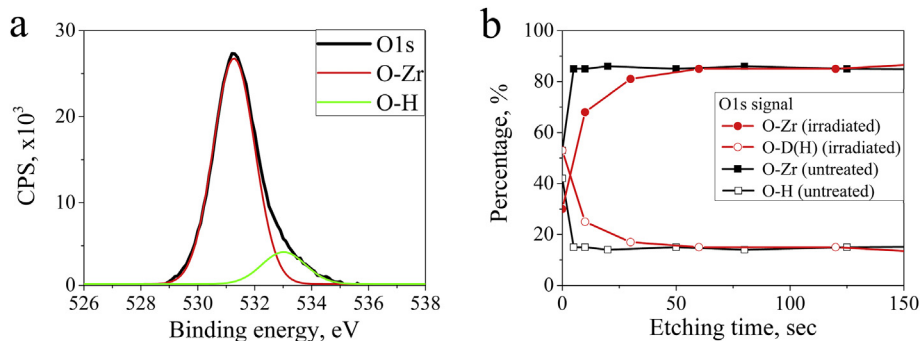

Fig. 5. Areas ratio of the peaks O1s and Zr3d versus etching time for the E110 sample irradiated in $D_2 + 30\%O_2$ (dose 10^{19} cm^{-2}) and for untreated one.

Fig. 6. (a) XPS spectrum O1s from the surface of the untreated E110 sample; (b) percentage of the components O−Zr and O−D(H) in O1s spectrum versus etching time for the E110 sample irradiated in $D_2 + 30\%O_2$ (dose 10^{19} cm^{-2}) and for the untreated one.

4. Discussion

According to TDS spectra interpretation given in our previous work [8,9], the peak at 1300 K testifies to the desorption of hydrogen retained in the bulk of zirconium, whereas the maxima at 1050 K and 1170 K correspond to desorption from trapping centres in the oxide layer. Based on this the modification of shapes of the TDS spectra given in Figs. 1 and 4 could be understood as follows. During both the exposure to deuterium−oxygen gas mixture and the irradiation in this ambient some of the hydrogen atoms transfer from the bulk of zirconium to the oxide layer. Simultaneously, the thickness of the oxide layer increases as shown by XPS analysis. Apparently, the transport of hydrogen from zirconium to the oxide layer accompanies the oxygen diffusion that occurs during oxide growth. It should be noted that hydrogen transfers to the oxide layer even in the absence of oxygen in the gas if the sample is irradiated by atoms, but this process stops after a dose of 10^{19} cm^{-2}.

Fig. 4 demonstrates that under irradiation of zirconium in the deuterium−oxygen gas mixture hydrogen atoms located in the oxide layer undergo desorption. With the increase of the irradiation dose hydrogen transport from the bulk of zirconium to the oxide layer continues so that the number of hydrogen atoms in the oxide remains constant.

A plausible mechanism of hydrogen desorption from zirconium is formation of HDO molecules by D-atoms from the irradiation flux and OH-groups from the oxide layer. Lack of dependence of hydrogen desorption on the oxygen content in the operating gas up to a dose of 10^{19} cm^{-2} means that oxygen from the gas ambient does not participate in the formation of these molecules. During the irradiation of zirconium in the oxygen-free gas the oxygen depletion of the surface layer occurs due to HDO desorption. As a result, both hydrogen transport from zirconium to the oxide layer and hydrogen desorption from zirconium stop (Figs. 2b and 4a).

The irradiation of zirconium by D-atoms leads to formation of OD-groups on the surface because the O−D(H) bond is stronger than the Zr−D(H) bond [18]. However, as mentioned above, irradiation in the oxygen-free ambient reduces the number of oxygen-containing particles on the surface, causing desorption of hydroxyl groups within water molecules and thereby retarding deuterium accumulation. Oxide growth during the irradiation of zirconium in the oxygen-containing ambient points to the fact that the rate of surface oxidation exceeds the rate of desorption of water molecules from the surface. Therefore, in this case, the OD-groups content increases both on the surface and in the bulk of the oxide layer (Fig. 6b). Thus, the increase of deuterium trapping under irradiation in the deuterium−oxygen gas mixture in comparison with that under irradiation in pure deuterium is apparently caused by more intensive formation of OD-groups and their diffusion into the bulk.

Penetration of deuterium through the oxide layer, saturated by OD-groups under irradiation in D_2, occurs much more effectively than through the oxide on untreated samples in spite of the fact that the latter oxide is significantly thinner. This could be explained as follows. The OD-group in the oxide is accompanied by weakened Zr−O bonds. Since the O−D(H) bond is stronger than the Zr−D(H) bond, diffusion of deuterium atoms by their transition over Zr−D bonds is to faster than if these atoms were part of OD-groups. Thus, formation of a large amount of OD-groups in the oxide may lead to the appearance of "facilitative" ways for penetration of deuterium atoms through the oxide layer under irradiation in the oxygen-free ambient.

Deceleration of hydrogen desorption and deuterium trapping, occurring with the increase of irradiation dose, apparently means that as deuterium atoms accumulate in zirconium they take increasing part in the total desorption of hydrogen isotopes.

5. Conclusions

The following concluding remarks can be made:

- During the exposure or irradiation of zirconium in the deuterium−oxygen gas mixture hydrogen atoms from the bulk of zirconium transfer to the oxide layer. If the sample is irradiated by D-atoms the process takes place even in the absence of oxygen in the gas, but stops after the dose of 10^{19} cm^{-2}.
- Atomic irradiation leads to desorption of hydrogen from the oxide layer of zirconium by means of formation of HDO molecules by D-atoms from the irradiation flux and OH-groups from the oxide layer. With the oxygen depletion of the surface the hydrogen desorption stops.
- Deuterium trapping under D-atom irradiation grows with the increase of the oxygen concentration in the gas. Presumably, it is a result of more intensive OD-group formation and diffusion of these groups into the bulk during the oxide growth.
- Saturation of the oxide layer by OD-groups creates conditions for accelerated penetration of deuterium through the oxide during the irradiation in the oxygen-free ambient. It could be caused by appearance of an opportunity of deuterium transport over Zr−D bonds which are weaker than O−D ones.

Competitive Growth of Kazan Federal University. XPS measurements were carried out at the PCR Federal Center of Shared Facilities of KFU.

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