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Effect of irradiation by argon ions on hydrogen transport through the surface oxide layer of zirconium

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Abstract. Effect of zirconium irradiation by 1 keV Ar⁺ ions on hydrogen transport through the surface oxide layer is studied. It is shown that deuterium trapping under subsequent irradiation of the Ar-treated sample by deuterium atoms of thermal energies in D₂ + 30at.% O₂ gas mixture is 2 times less than trapping in the untreated sample. Besides, irradiation of the untreated sample by D-atoms provokes desorption of ≈25% of hydrogen contained therein, whereas hydrogen desorption from the ion-treated zirconium surface does not occur. It is proposed that oxygen depletion of the surface oxide layer, caused by ion bombardment, is a reason of mitigation of the hydrogen transport through this layer in both directions.

1. Introduction

Zirconium components of the active core of light-water reactors absorb hydrogen due to their interaction with water coolant and because of irradiation by hydrogen atoms and ions produced at radiolysis of water [1, 2]. Ion and atomic irradiation intensifies hydrogen transport through the surface oxide layer of zirconium in both directions causing desorption of part of the hydrogen atoms from zirconium, but, at the same time, accelerating hydrogen absorption [3-5]. Accumulation of hydrogen in zirconium components leads to embrittlement and subsequent degradation of zirconium. These processes limit reactor lifetime and fuel burn up. Thereby, methods of surface passivation against hydrogen penetration into zirconium are actively developed. Some authors [6, 7] observed deceleration of the ion-irradiated zirconium hydrogenation during exposure to overheated steam and ambient water. However, a mechanism of mitigation of the hydrogen penetration is not enough studied. In this work, the effect of Ar⁺ irradiation of zirconium on hydrogen transport through the surface oxide layer under irradiation by deuterium atoms of thermal energies was investigated employing thermal desorption spectroscopy (TDS) and X-ray photoelectron spectroscopy (XPS).

2. Experimental

The investigated samples were the tube sections with a size of ≈7×7×1 mm³ made of zirconium alloy E110 (Zr-1%Nb) preliminarily rinsed in ultrasonic ethanol bath. Some of the samples were further irradiated by ions of argon plasma. After that, both ion-treated and untreated samples were irradiated by deuterium atoms of thermal energies in deuterium-oxygen gas mixture. All the experiments and TDS analysis were performed in MIKMA device [8].



The argon plasma irradiation parameters were as follows: the ions with the energy of 1 keV were delivered at the flux of $1.1 \times 10^{20} \text{ m}^{-2} \text{ s}^{-1}$ to the fluence of $1.3 \times 10^{23} \text{ m}^{-2}$. Residual gas pressure in the plasma chamber did not exceed $1.3 \times 10^{-3} \text{ Pa}$, the main component of the residual gas was water molecules (>90%). The argon pressure before ignition of the discharge was set at $1.3 \times 10^{-1} \text{ Pa}$. The sample temperature during irradiation was maintained at 550 K.

Irradiation by deuterium atoms of thermal energies was carried out by the device [9], where deuterium atoms were generated by means of heating the tungsten spiral up to $\approx 1800 \text{ K}$ in gaseous deuterium. Parameters of the experiments were as follows: the operating gas – a mixture $\text{D}_2 + 30\% \text{O}_2$ with the deuterium pressure of $1.2 \times 10^{-1} \text{ Pa}$. Molecular flux onto the surface of the tungsten spiral, dissociation probability of deuterium molecule on the surface of tungsten at given temperature and solid angle, at which each section of the spiral “sees” the sample, were taken into account in the calculation of the atomic flux. The latter was estimated as $\sim 10^{19} \text{ m}^{-2} \text{ s}^{-1}$, and the fluence $\sim 10^{23} \text{ m}^{-2}$. The sample temperature during atomic irradiation was maintained at 600 K.

The residual gas pressure in the TDS chamber during analysis did not exceed $7 \times 10^{-6} \text{ Pa}$, while the sample was heated linearly at a rate of 5 K/s in the temperature range of 300-1500 K. Desorption of H_2 , HD, D_2 , H_2O , HDO, D_2O was registered during the analysis. Desorption of other molecules, containing hydrogen isotopes, was negligible. The amounts of hydrogen and deuterium in zirconium were obtained by integration of the TDS spectra of H-containing and D-containing molecules.

XPS depth profiling was performed in SPECS facility [10]. All the measurements were carried out at room temperature. The energy and current of etching ions were set to 3 keV and $10 \mu\text{A}$, respectively. Zr3d and O1s photoemission spectra were studied.

3. Results and discussion

Results of the XPS measurements have shown that irradiation of zirconium by ions of argon plasma leads to the growth of contribution of oxide components in the XPS Zr3d spectra throughout the investigated depth (figure 1, a). It should be interpreted as a growth of the oxide layer. At the same time, the ratio of ZrO_2 to all zirconium oxide components ZrO_x ($x \leq 2$) in the Zr3d spectrum near the surface of the ion-treated sample decreases (figure 1, b). This alteration indicates the appearance of the oxygen defects (anion vacancies or others) in the surface layer under the ion bombardment.

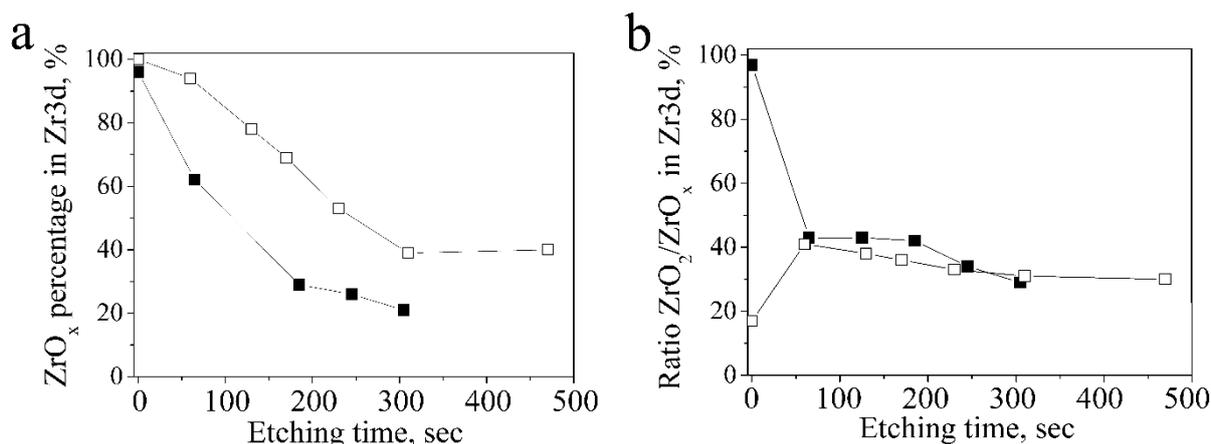


Figure 1. a) ZrO_x ($x \leq 2$) percentage in the XPS spectrum Zr3d versus etching time of the ion-treated sample (\square) and the untreated one (\blacksquare); b) Ratio of ZrO_2 to all zirconium oxide components ZrO_x ($x \leq 2$) in the XPS spectrum Zr3d versus etching time of the ion-treated sample (\square) and the untreated one (\blacksquare).

Irradiation of the both ion-treated and untreated samples by deuterium atoms of thermal energies in deuterium-oxygen gas mixture leads to growth of the oxide layer to approximately equal thickness. At the same time, percentage of oxide components in XPS spectrum Zr3d (figure 2, a) and the ratio of ZrO_2 to all zirconium oxide components ZrO_x ($x \leq 2$) (figure 2, b) near the surface of the ion-treated

sample is less than that of the untreated one. Thus, it could be proposed that defects, generated by the ion bombardment of zirconium, remain in the oxide layer after subsequent irradiation by deuterium atoms of thermal energies in the gas mixture $D_2+30\%O_2$.

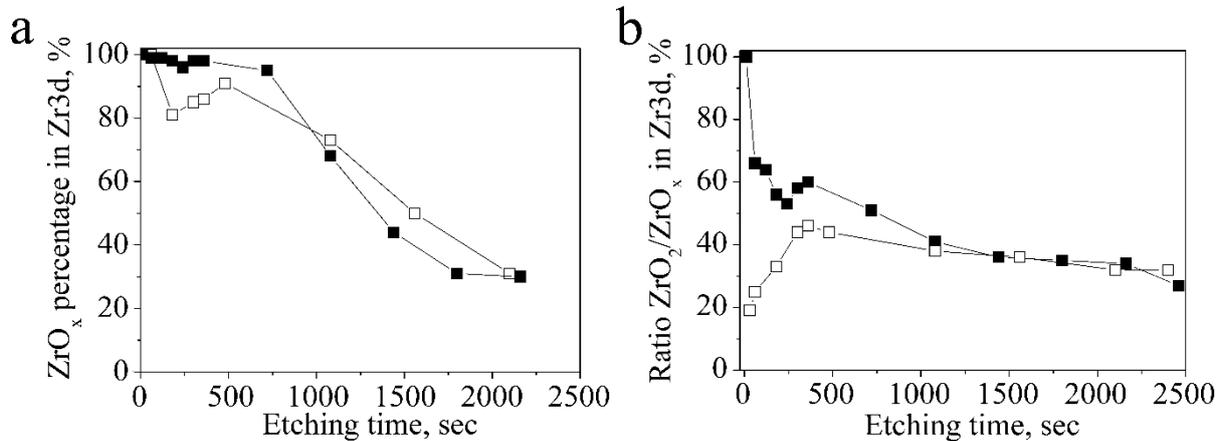


Figure 2. a) ZrO_x ($x \leq 2$) percentage in the XPS spectrum Zr3d versus etching time of the ion-treated sample (\square) and the untreated one (\blacksquare) after irradiation by D-atoms in $D_2+30\%O_2$; b) Ratio of ZrO₂ to all zirconium oxide components ZrO_x ($x \leq 2$) in the XPS spectrum Zr3d versus etching time of the ion-treated sample (\square) and the untreated one (\blacksquare) after irradiation by D-atoms in $D_2+30\%O_2$.

Deuterium trapping under atomic irradiation of the untreated sample is equal to $3.4 \times 10^{21} \text{ m}^{-2}$, whereas the ion-treated sample absorbs ≈ 2 times fewer deuterium atoms. Maximum at 1050 K in the TDS spectrum of deuterium-containing molecules from the ion-treated sample is higher, and the peak at 1300 K is lower than the corresponding maxima in the TDS spectrum obtained from the untreated sample (figure 3, a). According to interpretation given in our previous works (e.g., [5]), the peak at 1300 K testifies to desorption of deuterium retained in the bulk of zirconium, whereas the maximum at 1050 K corresponds to desorption from trapping centers in the oxide layer. Thus, the amount of deuterium atoms accumulated in defects of the oxide layer of the ion-treated sample is larger, but penetration of deuterium into zirconium is retarded.

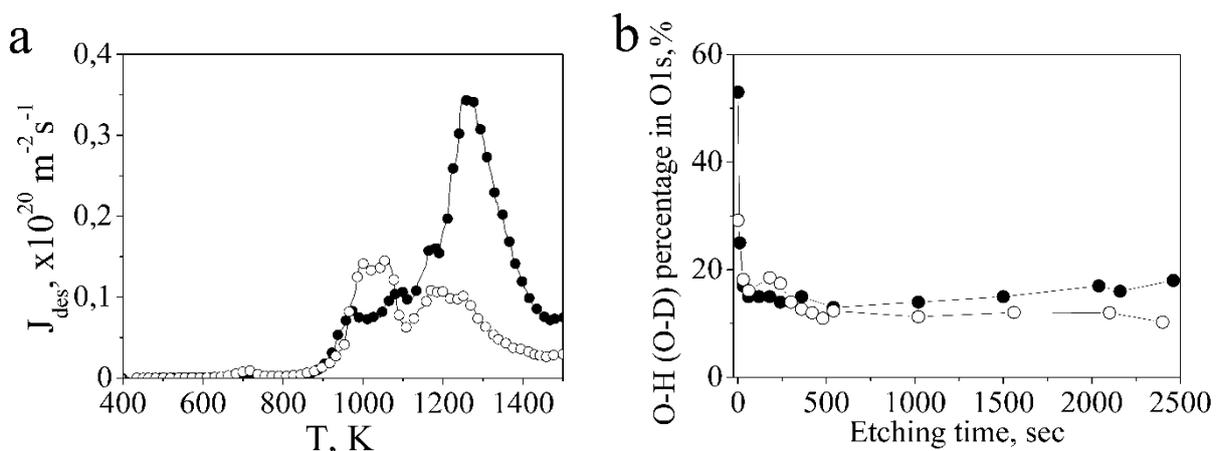


Figure 3. a) TDS spectra of deuterium-containing molecules from the ion-treated sample (\circ) and the untreated one (\bullet) after irradiation by D-atoms in $D_2+30\%O_2$; b) O-H (O-D) percentage in the XPS spectrum O1s versus etching time of the ion-treated sample (\circ) and the untreated one (\bullet) after irradiation by D-atoms in $D_2+30\%O_2$.

Irradiation of the untreated zirconium by D-atoms provokes desorption of $\approx 25\%$ of hydrogen atoms contained therein. In contrast, hydrogen desorption during irradiation of the ion-treated zirconium is not observed. It should be also mentioned that percentage of hydroxyl component (that may contain either H or D atoms) in the XPS spectrum O1s in the depth of the oxide layer of the ion-treated sample after irradiation by D-atoms is less than that of the untreated sample (figure 3, b).

Based on the described results, one could assume that retardation of the hydrogen transport through zirconium oxide layer irradiated by ions of argon plasma occurs due to the presence of oxygen defects produced by ion bombardment. Hydrogen in zirconia diffuses by hopping between adjacent oxygen ions [11], so the decrease of the oxygen concentration in the oxide layer caused by the ion bombardment leads to increase of the mean distance between adjacent oxygen ions. As a result, probability of the hopping decreases and hence, the hydrogen transport decelerates.

4. Conclusion

Experimental results have shown that irradiation of zirconium by argon ions with the energy of 1 keV leads to decrease of the oxygen concentration in the surface oxide layer, apparently, due to production of oxygen defects (anion vacancies or others). Defectiveness of the surface oxide layer remains after irradiation of the ion-treated zirconium by deuterium atoms with thermal energies in the deuterium-oxygen gas mixture. Deuterium trapping in the ion-treated zirconium under irradiation by D-atoms is 2 times less than that of the untreated sample. Hydrogen desorption from the ion-treated zirconium under atomic irradiation is not observed, and the oxide layer contains fewer amount of hydroxyl groups. One could propose that oxygen depletion of the surface layer, caused by ion bombardment, is the reason of retardation of the hydrogen transport through zirconium oxide layer in both, in and out, directions.

Acknowledgments

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