Protective coatings preventing hydrogen desorption from titanium during ion irradiation

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Abstract. Effect of yttria and titanium nitride coatings on features of deuterium desorption from titanium layer is investigated. It is shown that both coatings significantly raise the temperature of maximum of deuterium thermal desorption from titanium under linear heating and prevent desorption under prolonged keeping at the operating temperature of a neutron tube target. However, under irradiation with ions of H$_2$+O$_2$ plasma the barrier properties of titanium nitride appear to degrade.

1. Introduction
Hydride-forming metals (Ti, Zr, Y, Sc, V, La, etc.) can accumulate significant concentrations of hydrogen isotopes. Thereby, some of these metals are used as hydrogen sorbents in various devices, e.g. in the targets of neutron tubes. The target of the neutron tube consists of a sorbent layer (generally Ti, sometimes Zr or Sc) intended for the accumulation of hydrogen isotopes and a molybdenum substrate. The decrease of hydrogen concentration in the sorbent layer during the operation of the neutron tube leads to the decline in the efficiency of this device and to the reduction of its service lifetime. One of the possible ways for mitigating hydrogen losses from the neutron tube target is the deposition of protective coating on the sorbent layer’s surface [1, 2]. Choosing the material for this coating, one should take into account that the coating must act as a hydrogen desorption barrier and its barrier properties must not degrade under ion bombardment during the operation of the neutron tube. However, the features of alteration of barrier properties of protective coatings by ion irradiation are not enough studied yet.

In this work, the effect of yttria and titanium nitride coatings on deuterium desorption from titanium layer on molybdenum substrate under heating and ion irradiation is investigated employing thermal desorption spectrometry (TDS).

2. Experimental
All of the coatings were deposited in the electron-induced gas discharge with a hot cathode. The residual gas pressure in the deposition chamber in all of the experiments was <$10^{-3}$ Pa, operating gas pressure – $1.3\cdot10^{-3}$ Pa. Argon was used as a main component of the operating gas. The energy of ions irradiating the surface of emerging coating did not exceed 20 eV, sample temperature – 450 K.

Titanium layer (sorbent layer) of 1 µm was deposited in Ar + 5 % D$_2$ plasma on molybdenum substrate of 7×7×0.5 mm$^3$. Thus, the saturation of the sorbent layer by deuterium occurred during the
deposition of this layer. After deposition of the sorbent layer some of the samples were covered by yttria (in Ar + 20 % O₂ plasma) or titanium nitride (in Ar + 25 % N₂ plasma) coatings of 50 nm.

Investigation of the hydrogen barrier properties of the coatings under heating and ion irradiation, as well as thermal desorption analysis (TDS analysis) of the samples, were conducted in MIKMA facility [3]. TDS analysis consisted of the linear heating of a sample from ≈300 to 1500 K with the rate of 5 K/s and simultaneous measuring of desorption flux from this sample by the quadrupole mass-spectrometer QMG220 (Pfeiffer).

For testing of the ability of a coating to prevent the deuterium desorption at the operating temperature of the neutron tube target a coated sample was heated at the temperature 623 K in vacuum ambient for 4 h. Desorption flux from the sample was measured during this procedure. After that, the sample was cooled down to ≈300 K and then underwent TDS analysis in order to measure the amount of deuterium atoms remaining after the heating.

For testing of the resistance of a coating to deuterium desorption under ion irradiation, a coated sample was irradiated with 650 eV/at. ions (mainly H₂⁺) of H₂ + 2% O₂ and H₂ + 30 % O₂ plasma delivered by the flux of 5·10¹⁰ m⁻² s⁻¹ to the fluence of 1.8·10¹⁸ m⁻² for 1 h. The sample temperature during the irradiation was equal to 623 K. After that procedure, TDS analysis of the sample was performed.

Hydrogen barrier properties of the genuine oxide films on the uncoated sorbent layers were tested the same way as those of the investigated coatings. Before and after the irradiation the content of the sample’s surface layer were analyzed by the energy-dispersive X-ray spectrometry (EDX) module INCA-xAct (Oxford Instruments).

3. Results and discussion

The results of TDS analysis showed that the deposition of either yttria or titanium nitride on the sorbent layer’s surface led to the increase of the temperature of deuterium desorption from this layer under linear heating (figure 1). Shift of the maximum of thermal desorption of deuterium from the yttria-coated sample was ≈180 K, from the one coated by titanium nitride – ≈240 K.

![Figure 1. TDS spectra of deuterium from the samples: □ – Mo + sorbent layer (Ti); ▲ – Mo + sorbent layer (Ti) + yttria; ● – Mo + sorbent layer (Ti) + titanium nitride.](image)

Keeping of the uncoated sample (Mo + sorbent layer) at the constant temperature of 623 K for 4 h resulted in the release of 67 % of deuterium atoms contained in the sorbent layer, with 18 % of deuterium atoms desorbed during the first hour of the heating (table 1). Desorption of deuterium from the sorbent layer coated by either yttria or titanium nitride remained negligible (<5 %) during the 4 h of the similar tests. The increase of the temperature of deuterium desorption under linear heating and significant decrease of deuterium losses from the sorbent layer under the prolonged keeping at the constant temperature are the evidence that both yttria and titanium nitride coatings have better (in comparison to genuine titanium oxide film) barrier properties for the thermal desorption of deuterium contained in the sorbent layer.

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Table 1. The results of tests of the coatings on ability to prevent deuterium desorption from the sorbent layer under heating and ion irradiation.

|                                      | Mo + sorbent layer (Ti) | Mo + sorbent layer (Ti) + titanium nitride | Mo + sorbent layer (Ti) + yttria |
|--------------------------------------|-------------------------|--------------------------------------------|---------------------------------|
| Deuterium concentration in the sorbent layer before the tests | 1.2·10^{18} cm\(^{-3}\) | 1.1·10^{18} cm\(^{-3}\)                   | 1.1·10^{18} cm\(^{-3}\)        |
| Deuterium desorption during keeping at 623 K for 1 h (4 h) | 18 % (67 %)             | – (<5 %)                                   | – (<5 %)                       |
| Deuterium desorption during irradiation with ions of H\(_2\) + 2 % O\(_2\) plasma at 623 K for 1 h | <5 %                    | 17 %                                       | <5 %                           |
| Deuterium desorption during irradiation with ions of H\(_2\) + 30 % O\(_2\) plasma at 623 K for 1 h | <5 %                    | 70 %                                       | <5 %                           |

If the keeping of the uncoated sample (Mo + sorbent layer) at 623 K for 1 h was accompanied by the irradiation with 650 eV/at. ions of either H\(_2\) + 2 % O\(_2\) or H\(_2\) + 30 % O\(_2\) plasma, noticeable deuterium losses from the sorbent layer were not observed (table 1). Moreover, during subsequent TDS analysis of the irradiated sample deuterium desorbed at higher temperatures (figure 2). Thus, ion irradiation of the sorbent layer covered only by the genuine oxide film mitigates thermal desorption of deuterium. Analogous result was obtained by us earlier [1, 2] when titanium deuteride underwent the similar radiation test. As a possible reason of this phenomenon, it was proposed that low-energy protium ions captured in the surface region may hinder deuterium diffusion from the bulk and subsequent desorption [1, 2].

Irradiation of the yttria-coated samples by ions of hydrogen plasma with both oxygen concentrations did not cause deuterium desorption from the sorbent layer (table 1). At the same time, under irradiation of the nitride-coated sample with ions of H\(_2\) + 30 % O\(_2\) plasma, 17 % of deuterium atoms desorbed, and irradiation in H\(_2\) + 30 % O\(_2\) plasma provoked desorption of 70 % of deuterium (table 1). Experimental result with titanium nitride coating is supposed to be the consequence of the degradation of the coating’s barrier properties under ion irradiation. The failure of the barrier properties develops with the increase of oxygen contamination of plasma; therefore, one can believe that the interaction of oxygen with the surface of titanium nitride is a possible reason of the degradation.

After the irradiation of both types of coatings a peak at the temperature \(\approx 780\) K appeared in the deuterium TDS spectrum (figure 3). This maximum is inherent for TDS spectra of deuterium from the
irradiated uncoated sorbent layer (figure 2) and that allows for suggesting that the partial degradation of the coatings occurs, apparently, due to their sputtering by the impinging ions. EDX analysis confirmed the absence of the protective coatings on particular regions of the surface. This result indicates the necessity of application of protective coatings recovery system providing the protection of the neutron tube target during its service lifetime.

4. Conclusions
It is found that the temperature of deuterium desorption from titanium layer (sorbent layer) under linear heating is significantly increased if this layer is coated by a thin film of yttria or titanium nitride. It is shown that deuterium desorption from the samples with both types of coatings during prolonged keeping at the operating temperature of the neutron tube is very low. Yttria coating retain its barrier properties under irradiation by ions of both H₂ + 2% O₂ and H₂ + 30% O₂ plasma, whereas the irradiation of titanium nitride by ions of oxygen-contaminated plasma causes the degradation of its barrier properties and promotes the deuterium desorption from the sorbent layer. Sputtering of the protective coatings by the impinging ions requires the development of protective coatings recovery system providing the protection of the neutron tube target during its service lifetime.

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