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Reflection, re-emission and permeation of deuterium implanted in Ti–6Al–4V alloy

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Abstract

A Ti–6Al–4V alloy has been selected as the vacuum vessel structural material in the tokamak physics experiment (TPX) [1] and in the steady state tokamak JT-60 Super Upgrade (JT-60 SU) [2]. To determine the amount of hydrogen retained in titanium alloy during glow discharge cleaning and plasma operation the knowledge of the parameters such as a recombination coefficient K and a particles reflection coefficient R_N is necessary. Presence of the non-metallic impurities on the surface strongly affects both the above mentioned parameters. In the present work, the permeation behavior of deuterium has been investigated for deuterium implanted into Ti–6Al–4V membrane with an incident ion energy 150–1500 eV/D. R_N has been determined by means of the thermal desorption technique. The surface chemical composition was controlled in-situ by means of AES and SIMS analyses. Experimentally obtained values of R_N are larger than computer simulation results for both the clean Ti–6Al–4V surface and the surface layer with the concentration of the chemical elements same as that experimentally observed. The calculated values of R_N are not significantly different from one another. The amount of retained hydrogen was estimated for TPX condition taking into account the contribution of the reflected particles to the flux balance.

Keywords: Wall particle reflection; High Z wall material

1. Introduction

The hydrogen–titanium interaction has been studied for a number of years. A knowledge of it is of great interest in vacuum applications as well as in fusion reactor devices. The experimental activity was almost stopped when the decision not to continue studying titanium was made in the late 1970s [1]. At that time a number of other competing structural materials such as stainless steels, ferritic steels, nickel based alloys and vanadium based alloys had been investigated. The development of commercially available titanium alloys, such as Ti3Al–2.5V, Ti–6Al–4V, Ti–5Al–2.5Sn, Ti–15V–3Cr–3Sn–3Al and the use of titanium-based coatings in fusion have stimulated further research because of the lack of database on reflection, trapping and permeation for these alloys and coatings. Even for pure titanium the deviation of the experimentally measured trapping coefficient from computer calculations has been found for hydrogen energy below 1 keV [3]. The retention of hydrogen in Ti–6Al–4V alloy under TPX plasma conditions has been calculated in Ref. [1], where reflected particles were not taken into account, while in the present study the amount of retained hydrogen was estimated based on experimentally determined particles reflection coefficient with some assumptions from Ref. [4].

A number of factors can affect the above mentioned characteristics. It has been shown, that for the same hydrogen pressure, the equilibrium concentrations for Ti–6Al–4V alloy are roughly 0.6 of those for unalloyed titanium [5]. Brewer et al. [6] have observed that the hydrogen absorption is correlated with the amount of oxygen and nitrogen present on the surface. Sheft et al. [7] have observed the formation of titanium deuterides on the surface of titanium after low temperature (< 423 K) bombardment by 15 keV deuterium to fluences of 10^{23} m^{-2}. Therefore, it is important, that this investigation was undertaken with in-situ surface chemical control.

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2. Experimental

The membrane sample employed in the experiment was made from Ti-6Al-4V foils supplied by Furuuchi Kagaku. It was a disc of 1.3 cm in diameter and 0.1 mm in thickness, x_0. The initial bulk impurity and alloying elements concentrations were as follows: 6.12×10^4 wppm Al, 3.87×10^4 wppm V, 9.2 wppm Ca, 304 wppm Fe and 4.71 wppm Mg. The membrane was cleaned ultrasonically in acetone and then annealed in a vacuum of $(3-5) \times 10^{-6}$ Pa at 1023 K for about 6 h before the first experiment. It was welded to the stainless steel holder and could be heated up to 1073 K by an external resistive heater. A Pt/Pt–Rh thermocouple was used to measure the membrane temperature.

The experiments have been performed using the apparatus described in Ref. [8]. The experimental chamber is separated by the sample membrane into two parts: the upper chamber and the bottom chamber. The background pressure in the upper chamber being evacuated by a turbomolecular pump (TMP) was $(2-3) \times 10^{-6}$ Pa and that in the bottom chamber being evacuated by a TMP and ion pump (IP) was $(6-8) \times 10^{-7}$ Pa. The quadrupole mass spectrometers QMS1 and QMS2 are installed in the upper and bottom chamber, respectively, to evaluate the deuterium permeation or re-emission rate by measuring the partial pressures of D_2 and HD. A mass-separated D_2^+ ion beam with ion flux density $(0.1-2.5) \times 10^{16}$ D m^{-2} s^{-1} was used for irradiation of the membrane at the TDS experiments. During ion gun operation D_2 pressure in the target chamber was lower than 1.3×10^{-7} Pa due to employment of an ion channel with a mass separator and a differential pumping. The surface impurity composition was monitored by AES before, during and after ion gun operation. SIMS surface analyses by use of QMS1, which can be installed instead of AES, provide additional information on the chemical forms of surface contamination. To determine R_N the thermal desorption technique was used. It is based on measuring the bombarding ions in the solid below saturation at temperatures where re-emission and permeation can be neglected. R_N is then given by the fraction of ions not being trapped:

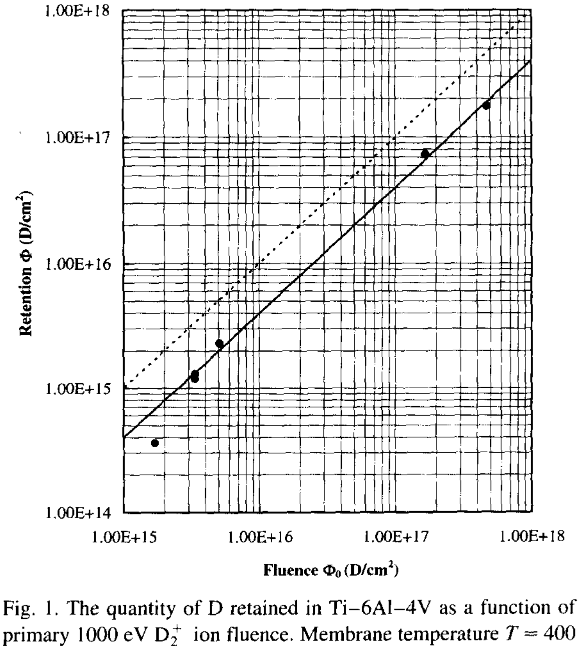

Fig. 1. The quantity of D retained in Ti–6Al–4V as a function of primary 1000 eV D_2^+ ion fluence. Membrane temperature $T = 400$ K. 100% retention is indicated by the dotted line.

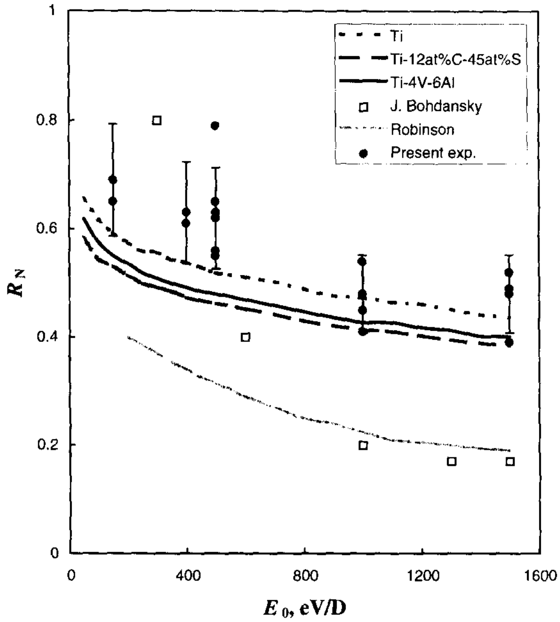

Fig. 2. Particle reflection coefficient versus the energy of primary ions with angle of incidence $\vartheta_0 = 50°$, obtained by TDS and the Monte-Carlo computer simulation results for the clean Ti, Ti–6Al–4V surfaces and for the Ti(12 at%)–C(45 at%)–S layer. The experimental result of Bohdansky et al. along with the theoretical calculation of Robinson from Ref. [3] for $\vartheta_0 = 90°$ are also shown.

$$R_N = 1 - \Phi/\Phi_0. \qquad (1)$$

The thermal desorption spectrums of HD and D_2 from both the upstream-side, by QMS1, and the downstream-side, by QMS2, have been measured to evaluate Φ.

A non-separated 3 keV D_2^+ ion beam in the bottom chamber with ion flux density 3.4×10^{16} D m^{-2} s^{-1} was used for the measurement of the permeation signal in the upper chamber by QMS1.

3. Results and discussion

Taking into account that thermal re-emission can be neglected for Ti only within the temperature interval of about 400–500 K [3,10], the ion bombardment with $I_0 =$

0.1×10^{16} D m^{-2} s^{-1} and angle of incidence $\vartheta_0 = 50°$, was carried out at a membrane temperature of 400 K.

The lower temperature limit is characterized by the formation of the TiD_2 surface layer [7], whose reflectory properties can be different from that of alloy. The quantity of D retained in Ti–6Al–4V was determined by subsequent flashing of the specimen temperature over 1123 K immediately after ion irradiation. The linear dependence of the number of particles released per unit surface area during the heating procedure, i.e. the retention Φ, on the primary ion fluence Φ_0 was observed for Φ_0 up to 5×10^{17} D cm^{-2}, Fig. 1.

The values of R_N obtained from the $\Phi(\Phi_0)$ dependence are shown in Fig. 2 along with the results of the Monte-Carlo computer simulation for the impurity-free Ti and Ti–6Al–4V surfaces. At energies below 1 keV a large deviation from the theoretical values has been observed [3], as supposed by author, most probably due to surface oxide. In the present study AES measurements revealed Auger electron peaks from alloying elements as well as from S, C and O, as shown in Fig. 3. The form of AES spectrum and SIMS analysis allowed the conclusion that carbon and oxygen were present on the surface in the form of TiC and TiO_2, respectively. The surface composition was almost stable during experiments because of the low ion flux density. Taking into account these experimental observations, the calculations were performed also for the Ti(12 at%)– C(45 at%)–S layer. The calculated values of R_N are not significantly different from one another for the different surface chemical composition and are smaller than that experimentally obtained, as shown in Fig. 2. It may be due to incomplete desorption even at temperatures up to 1173 K, or to the formation of volatile CD_4 or D_2O.

A SIMS measurement also confirmed the stable surface chemical condition before and during ion bombardment, but essential changes of the surface composition have been observed during subsequent increasing of the specimen temperature, as shown in Fig. 4. In particular, TiO^+ signals disappear at 1073 K, most probably due to oxygen dissolution in the bulk. At temperatures below 1073 K oxygen tends to segregate to the surface, that give rise to TiO^+ signal.

In Ref. [11] almost the same values of the activation energy for the hydrogen desorption from the neutron irradiated and un-irradiated Ti were obtained. Both values of activation energy agree with the reported value of the activation energy for hydrogen diffusion in β-Ti, E_D = 27.6 kJ/mol [12]. Therefore, it was assumed that the

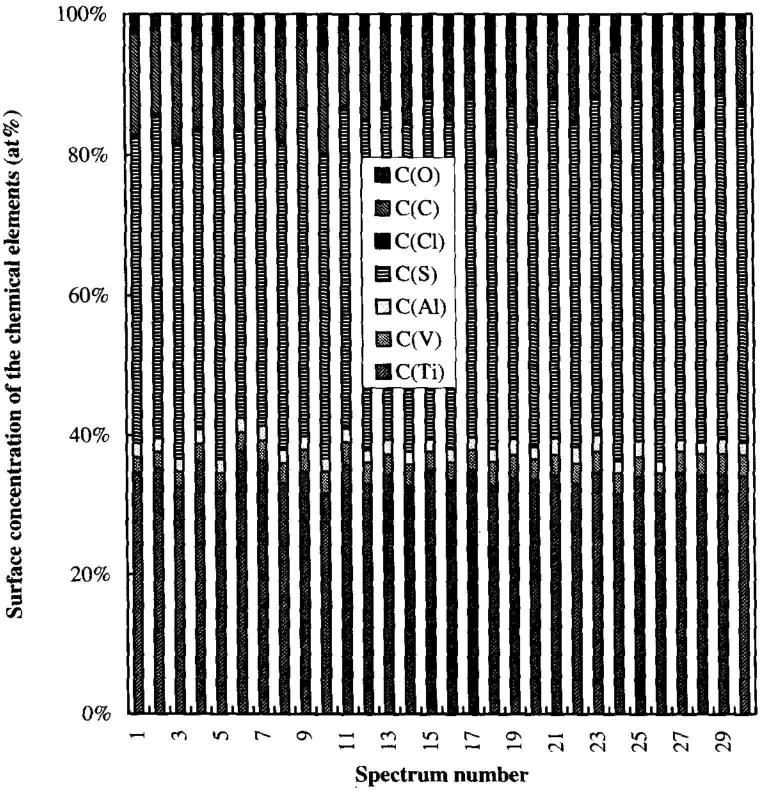

Fig. 3. Results of Ti–6Al–4V surface analysis by Auger electron spectroscopy. Spectra with the number 1–5, 17, 18; 6–10, 19, 20; 11–16, 21, 22; 23–26; 27–30 were obtained before and during ion bombardment with energies 1500, 1000, 500, 400 and 150 eV/D, respectively.

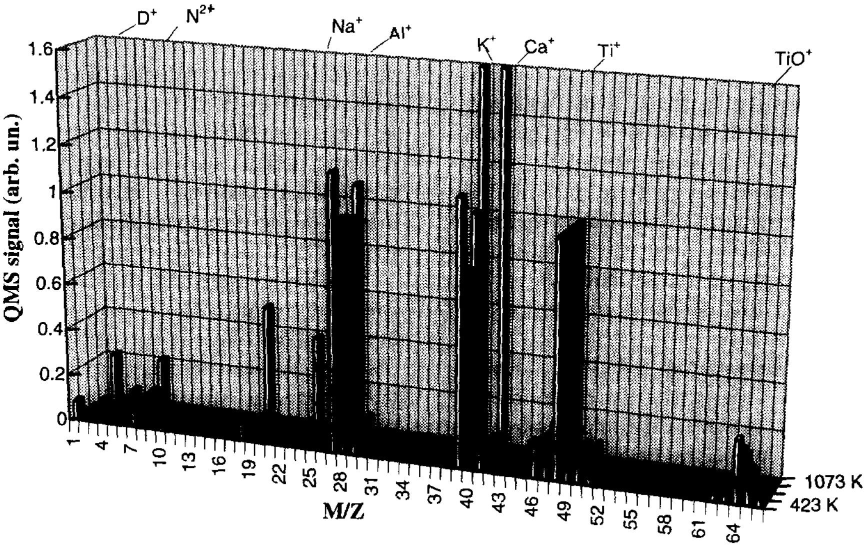

Fig. 4. Positive secondary ion mass spectrum for 1000 eV D_2^+ ion bombardment of Ti-6Al-4V at membrane temperatures 423, 623, 773 and 1073 K. All signals are normalized to the Ti^+ signal at each temperature.

desorption rate is controlled by the hydrogen diffusion in the specimen. It has been shown [13] that for diffusion-limited flow, the diffusivity can be obtained from

$$D = x_0^2/2\pi^2 t_b, \tag{2}$$

where t_b is the breakthrough time (defined as the intercept of the permeation curve's steepest tangent with the horizontal tangent before the beam is turned on). t_b was determined from the permeation data shown in Fig. 5. The calculation of the deuterium diffusivity by using Eq. (2) gives value of approximately four orders of magnitude smaller than that of published data for deuterium diffusivity in pure Ti near 873 K [9]. This indicates a possible influence of the surface-limited processes in the deuterium transport through the Ti-6Al-4V membrane.

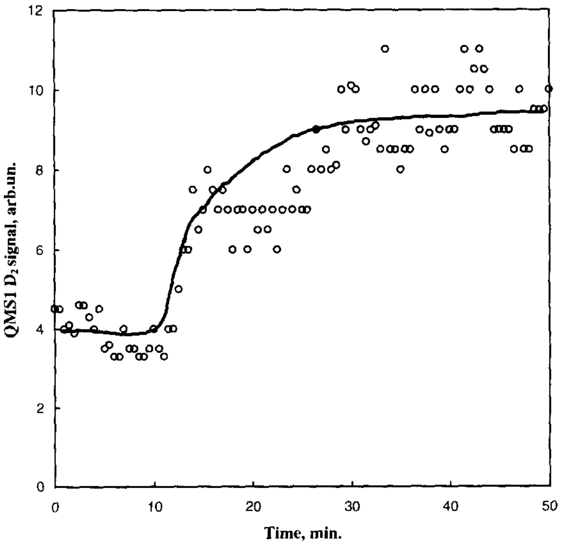

Fig. 5. Time history of the deuterium permeation for implantation of 3 keV D_2^+ into Ti-6Al-AV at temperature 873 K. Beam flux is 3.4×10^{16} D/m^2 s. The maximum permeation flux, J_P, at this temperature is 0.7×10^{16} D/m^2s.

4. Estimation of hydrogen retention

To estimate hydrogen inventory, calculations of tritium retention in the first wall of TPX [1] and ITER [4] were used. The first wall of both tokamaks will be exposed to mainly two sources of hydrogen: (1) fluxes of molecular hydrogen and low energy ions (200-300 eV) during glow discharge cleaning (GDC) and (2) flux of higher energy charge-exchange neutrals during plasma operation. TPX plasma conditions are summarized in Table 1 of [1].

The concentration of hydrogen which will result from exposure to molecules during GDC is given by the hydrogen solubility in Ti-6Al-4V alloy $C = 7.22\exp(45.94 \times 10^3/RT)P^{1/2}$ (derived from Fig. 4 in Ref. [5]), where C is the hydrogen concentration in appm, $R = 8.3145$ J K^{-1} mol^{-1} is the gas constant, T is the wall temperature in K and P is the hydrogen pressure in Pa. For $P = (0.1-0.4)$ Pa, that corresponds to 20% of total gas pressure during GDC, $C(623\text{ K}) = (1.63-3.26) \times 10^4$ appm.

The equilibrium concentration due to the low energy ion flux can be deduced by balancing the incoming flux ϕ_H with the outgoing recombination flux [4]

$$\phi_H = KC^2 \tag{3}$$

where K is the recombination coefficient. It will be assumed, that the water-cooled back surface of the wall is impermeable to hydrogen, since calculated release to the region between the plates tends to be less than 5% of front release [1]. For $\phi_H = 6 \times 10^{18}$ H m^{-2} s^{-1}, taking into account $R_N = 0.64$ obtained in the present study, using recombination coefficient for pure α and β-titanium $K_\alpha(623\ \mathrm{K}) = 1.8 \times 10^{-33}$ m^4 s^{-1}, $K_\beta(623\ \mathrm{K}) = 1.3 \times 10^{-35}$ m^4 s^{-1} [1] (for Ti–6Al–4V K is expected to be between these values) gives $C = (0.34\text{–}3.7) \times 10^{26}$ H m^{-3}, that corresponds to $C = (0.6\text{–}6.3) \times 10^3$ appm.

During a tokamak discharge the wall pumping effect can be expected as well as for the vanadium wall in Ref. [4], where the wall pumping time constant, τ_p, is defined as

$$\tau_p = (D/K) \times (1/\phi_{in}) \qquad (4)$$

where D is the diffusion coefficient, ϕ_{in} is the incident flux. Using $\phi_{in} = 1 \times 10^{21}$ H m^{-2} s^{-1}, $K_\alpha(423\ \mathrm{K}) = 1.38 \times 10^{-37}$ m^4 s^{-1} [1], $K_\beta(423\ \mathrm{K}) = 3.6 \times 10^{-40}$ m^4 s^{-1} [1] and $D(423\ \mathrm{K}) = 5 \times 10^{-13}$ m^2 s^{-1} [9] gives $\tau_p = 3.6 \times 10^3$ s for α-Ti and $\tau_p = 1.39 \times 10^6$ for β-Ti. If an inhibiting coating layer has reduced the inward flux to 0.2% of the original value it result in $\tau_p = 1.8 \times 10^6$ s, $\tau_p = 6.35 \times 10^8$ s for α-Ti and β-Ti, respectively. The maximum hydrogen concentration at 423 K will be given approximately by the fluence over the diffusion depth x since τ_p is greater than the pulse length Δt_a,

$$C = (\phi_{in} \times \Delta t_a)/x, \qquad (5)$$

where $x \approx (D\Delta t_a)^{1/2}$ at $\Delta t_a = 10^3$ s it results in $C = 7.7 \times 10^5$ appm.

5. Conclusions

Reflection of low energy deuterium ions of 150–1500 eV/D from Ti-6Al-4V membrane has been measured by using the thermal desorption technique that is based on the measurement of the bombarding ions in the solid below saturation at temperatures where re-emission and permeation can be neglected.

The surface chemical composition has been controlled by means of AES and SIMS that allows to obtain the R_N dependence on the energy of primary ion at the known concentration of the subsurface contamination. No correlation of the slight change in the surface chemical composition and the scatter in experimental data for R_N has been observed.

Experimentally obtained values of R_N are compared with the Monte-Carlo computer simulation results for both the clean Ti-6Al-4V surface and Ti(12 at%)-C(45 at%)-S layer. The calculated values of R_N are not significantly different from one another for the different surface chemical compositions and are smaller than that experimentally obtained. This is most probably due to incomplete desorption even at temperatures up to 1173 K, or to the formation of volatile CD_4 or D_2O.

The knowledge of particle reflection coefficients enables the determination of the hydrogen inventory more precisely, but still there is large uncertainty due to the scatter in experimental data for K. The measurement of the recombination coefficient at the present experimental conditions is a goal of the further study.

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