

THE EFFECT OF Cr, Cr-N AND Cr-O_x COATINGS ON DEUTERIUM RETENTION AND PENETRATION IN ZIRCONIUM ALLOY Zr-1Nb

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Depth distribution profiles of deuterium in zirconium alloy Zr-1Nb in initial state and with coatings Cr, CrN, and Cr₂O₃ after ion implantation with 15 keV/D⁺ at temperatures 350 °C to dose 1·10¹⁷ D/cm² and deuterium plasma of glow discharge at room temperature are determined by the method of nuclear reactions. It is shown that in studied range of temperatures and concentrations of deuterium coatings CrN and Cr₂O₃ act as barrier and protect zirconium from interaction with hydrogen isotope.

1. INTRODUCTION

Zirconium and its alloys play an important role in the nuclear field, given an optimized set of neutronic and mechanical properties [1]. However the mixture hydrogen is produced in the result of interaction of zirconium with coolant of water-cooled energetic nuclear reactors and as result nucleation and formation of hydride precipitates in zirconium alloys have been a key factor in limiting the lifetime of nuclear fuel cladding [2–5].

In order to solve this problem the barrier layers for hydrogen diffusion by modification of surface by ion-plasma treatment which includes irradiation of surface by gaseous and metal ions and deposition of vacuum-arc condensates are produced [6, 7]. To select the best coatings it is important to have a detailed understanding of the effect of coatings on hydrogen behavior.

In a recent study [8] we were described the methodology of determination of thickness and composition of plasma coatings of titanium and chromium nitrides obtained at different pressure of nitrogen in discharge chamber of plasma assembly.

The methods of saturation with deuterium (hydrogen) from gaseous phase and determination of its depth distribution profiles in zirconium alloy in initial state and in zirconium with coatings also are shown. The substitution of deuterium for protium allows the use of nuclear reactions to determine the depth distribution and concentration of hydrogen isotopes.

Permeability of coatings of CrN, CrAl, and Al₂O₃ on specimens of alloy Zr-1Nb in conditions of their saturation with deuterium was studied [9]. It was determined that in studied range of temperatures and pressures of deuterium the coating plays the role of barrier and protects zirconium from interaction with isotope of hydrogen.

During saturation of specimens by deuterium from gaseous phase deuterium doesn't penetrate in coating volume. Its near surface adsorption is detected. Up to 550 °C the amount of penetrated deuterium in the coatings is two and at T_{sat} = 550 °C even three orders less than for Zr-1Nb without coating.

It was shown [10, 11], that the vacuum-arc coatings of chromium and Cr-N effectively prevent oxidation of Zr-1Nb alloy tubes. Arc Ion Plating Technique produces Cr-O coating with high oxidation resistance and good mechanical properties [12], which can provide the

fretting-corrosion protection of fuel tubes in the nuclear reactor under normal operating conditions.

In addition to protecting the zirconium alloys from reacting with hydrogen the coatings can be used as an effective way to reduce tritium permeation through blanket components in a fusion device [13]. The application of a thin metal coating assumed to reduce tritium retention and permeation in ³He tubes used in the accelerator production of tritium (APT) device [14]. It is clearly important to study the behavior of hydrogen isotopes in materials under irradiation and at high concentrations.

The goal of present work was to investigate the effect of Cr, CrN, and Cr₂O₃ coatings on retention and permeation of deuterium through zirconium alloy Zr-1Nb at introduction of deuterium in the sample by way of ion implantation or plasma of glow discharge.

2. EXPERIMENTAL

Chromium coatings were deposited by the vacuum arc method from the two counter flows of metallic plasma with planetary rotation of samples on the system axis.

Chromium (99.9%) was used as cathodes. The temperature of samples during deposition did not exceed 500 °C. The initial vacuum in the system was at a level P₀ ≈ 7·10⁻⁴ Pa. The coating thickness was ≈ 1.5...5 μm. During deposition of Cr-N and Cr-O coatings, the working pressure was kept at 2 Pa by introducing reactive gas N₂ and O₂, respectively.

Coatings were deposited on flat specimens (5×14×0.7 mm) produced from section of fuel tubes (alloy Zr-1Nb).

Before the deposition of coatings the surface of specimens was bombarded by ions of argon and chromium at negative potential from 0.5 to 1.35 kV.

Implantation of specimens by deuterium with energies 15 keV/D⁺ was performed by means of irradiation facility a schematic diagram of which is shown in Fig. 1.

The facility has an oil-free pumping system with a residual target-chamber pressure of ~ 1·10⁻⁴ Pa. The deuterium ion flux was 10¹⁴ cm⁻²·s⁻¹, dose – 1·10¹⁷ D/cm². The implantation temperature supported at 350 °C.

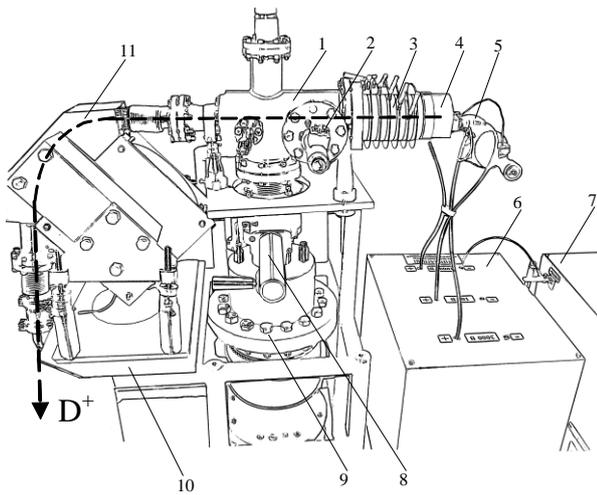


Fig. 1. Diagram of irradiation facility:
 1 – base chamber; 2 – Faraday cup; 3 – accelerating system; 4, 5 – ion injector with a gas inlet system;
 6 – electrical power supply for the ion injector;
 7 – high-voltage power supply 0...50 kV;
 8, 9 – vacuum-pumping system; 10 – bedplate;
 11 – magnetic mass-analyzer; the dotted line with an arrow – the path of the ion beam D^+

After cooling of specimens to room temperature the content of deuterium was measured by the method of nuclear reactions. The depth distribution profile of deuterium was measured by reaction $D(^3\text{He}, p)^4\text{He}$. Beams of ions $^3\text{He}^+$ with energies 0.3...1.4 MeV were obtained with electrostatic accelerator ESU-2. The result of nuclear reaction ($^3\text{He}, D$) is the birth of two particles: of proton and ^4He . For investigation of high depths the method of nuclear reactions (NRA) in geometry of back scattering with analysis of protons energy spectra is more beneficial. More detailed description of the method of deuterium concentration measurement in materials is presented in [8].

For study of surface morphology the scanning electron microscope JEOLJSM-7001F 00 was used.

3. RESULTS AND DISCUSSION

For testing of the methods of irradiation and further comparison of deuterium penetration in zirconium alloy with and without coating the retention and permeation of deuterium through zirconium alloy Zr-1Nb was firstly investigated. It is known that in studied range of temperatures hydrogen and its isotopes have high mobility in zirconium alloy [3].

Fig. 2 shows the depth distribution profiles of deuterium in alloy Zr-1Nb irradiated 15 keV/ D^+ at temperatures 350 °C to dose $1 \cdot 10^{17}$ D/cm². Data are shown for two types of initial samples with preliminary ion cleaning of sample surface and without.

It is seen that deuterium is detected over the entire depth available for the analyzing ions of $^3\text{He}^+$ with energy 1.4 MeV (probe depth). The depth profile can be divided into two parts: a peak at 0 depth with a decaying curve having a half-width of about 250 nm. Another part of the implanted gas (concentration of about 100 appm) is practically uniform distributed up to a depth of 2.5 μm .

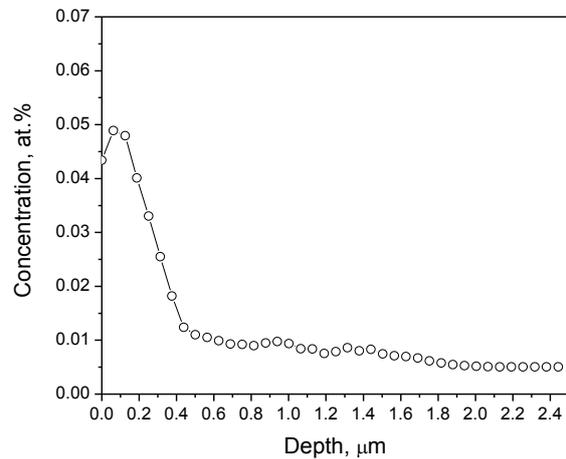


Fig. 2. Depth distribution profile of deuterium ion-implanted with the energy 15 keV/ D^+ at a temperature of 350 °C to dose $1 \cdot 10^{17}$ cm⁻² in initial Zr-1Nb (without coatings)

The peaks of the depth distribution profiles and the respective half-widths practically agree with the SRIM code simulations [15], indicating that a fraction of the implanted deuterium is trapped by the damage produced during self-implantation, even though the deuterium-induced dose is less than 1 dpa. The remaining part of deuterium is captured on the traps of no radiation origin and it may be distributed to depths much greater than depth of analysis.

Pre-ion cleaning makes a noticeable effect in the retention and distribution of ion-implanted deuterium.

Fig. 3 shows the depth distribution profiles of deuterium implanted with 15 keV/ D^+ at temperatures 350 °C to dose $1 \cdot 10^{17}$ D/cm² in chromium coatings on a Zr-1Nb substrate. Data are shown for two thicknesses of the chromium coatings – 1.5 and 3.5 μm .

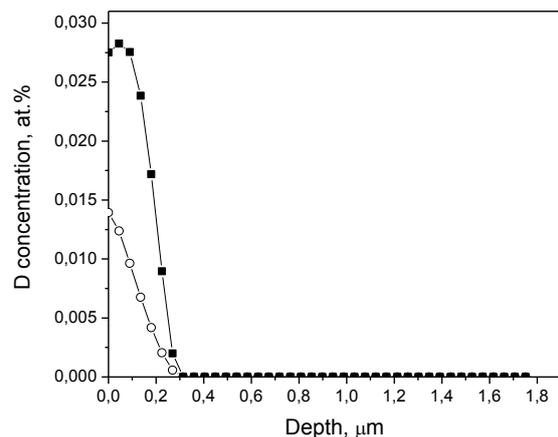


Fig. 3. Depth distribution profile of deuterium ion-implanted with the energy 15 keV/ D^+ at a temperature of 350 °C to dose $1 \cdot 10^{17}$ cm⁻² in Zr-1Nb with Cr coating thickness 1.5 (■) and 3.5 μm (○)

The figure shows the distribution of deuterium only in the near-surface region for the chromium coatings and a decrease in almost twice of magnitude of concentration of captured deuterium in comparison with the alloy Zr-1Nb. These facts indicate low retention of

deuterium in the traps at the irradiation temperature 350 °C.

Fig. 4 shows depth distribution profiles of deuterium ion-implanted in Cr coating with the energy 15 keV/D⁺ at room temperature and subsequent annealed at 350 °C.

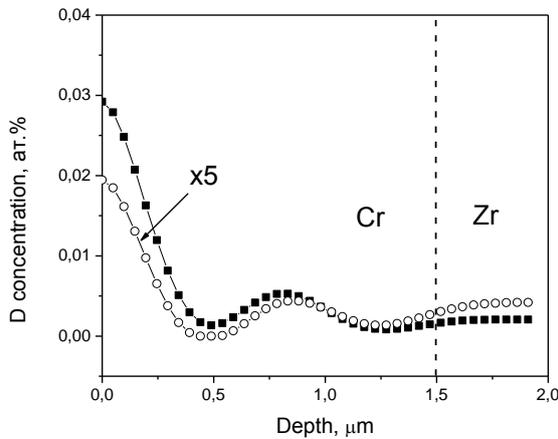


Fig. 4. Depth distribution profile of deuterium ion-implanted with the energy 15 keV/D at a room temperature to dose $1 \cdot 10^{17} \text{ cm}^{-2}$ (■) and subsequent annealing at 350 °C (○) in Zr-1Nb with Cr coating thickness 1.5 μm

Irradiation at room temperature causes the retention of nearly 80% of implanted deuterium. It is observed a peak at 0 depth and “tail” of deuterium distribution in the material. Since the coating had a thickness of 1.5 μm, the deuterium penetrated through the Cr coating into the substrate of an alloy Zr-1Nb. After annealing, the deuterium concentration decreased about five times on all depth in coating and Zr-1Nb substrate.

As can be seen from Fig. 3 the two-fold difference of the concentration of deuterium trapped chromium coating with different thicknesses – 1.5 and 3.5 μm are observed.

It is known that the process of hydrogen dissociation/association at metal-vacuum interface has a significant influence on hydrogen retention in metals. The back release is possible only through the formation of hydrogen molecule by way of surface recombination. The latter is governed by physical-chemical mechanisms that are highly sensitive to the surface condition and, in particular, to the surface chemical composition at the level of a fraction of a monolayer.

Fig. 5 shows microphotographs of surface of Cr coatings where any special features of surface morphology are not seen. A more detailed study will provide the new results needed to understand of the effect of chromium coatings on retention and permeation of deuterium under ion irradiation.

Fig. 6 shows the depth distribution profiles of deuterium in Cr₂O₃ and CrN coating on a Zr-1Nb substrate irradiated 15 keV/D⁺ at temperatures 350 °C to dose $1 \cdot 10^{17} \text{ D/cm}^{-2}$. As can see in these coatings the deuterium remained in a depth which corresponds to the calculated ranges of deuterium ions with energy of 15 keV. The retention is about 90% of implanted deuterium.

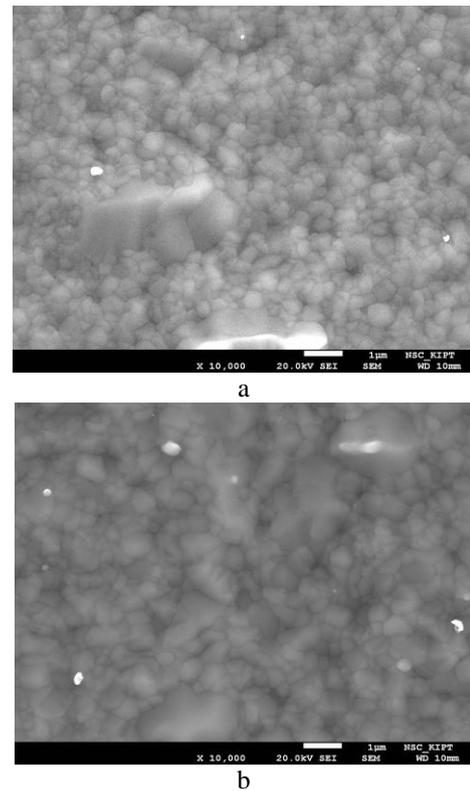


Fig. 5. Microphotographs of the surface of Cr coatings with thickness of 1.5 (a) and 3.5 μm (b)

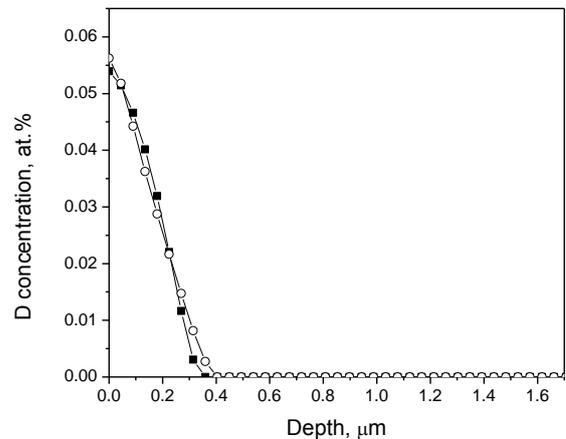


Fig. 6. Depth distribution profile of deuterium ion-implanted with the energy 15 keV/D at 350 °C to dose $1 \cdot 10^{17} \text{ cm}^{-2}$ in Cr₂O₃ (■) and CrN (○) coatings

Both coatings exhibit the same character of deuterium retention in the range profile, although the structure of the surface of these coatings is somewhat different (Fig. 7).

As noted in the introduction coatings may be used as an effective way to reduce tritium permeation in a fusion device and in ³He tubes used in the accelerator production of tritium (APT) device. The tritium gas pressure that will exist within both types of devices and the continuous tritium injection into the walls raise a valid concern about tritium retention and/or permeation through the walls into surrounding cooling water. Neither of these conditions is desirable for devices operation. Holdup in the walls will make it difficult for device to meet its production goals and extract the

tritium from the walls. High levels of permeation will necessitate a costly tritium removal system for the cooling water.

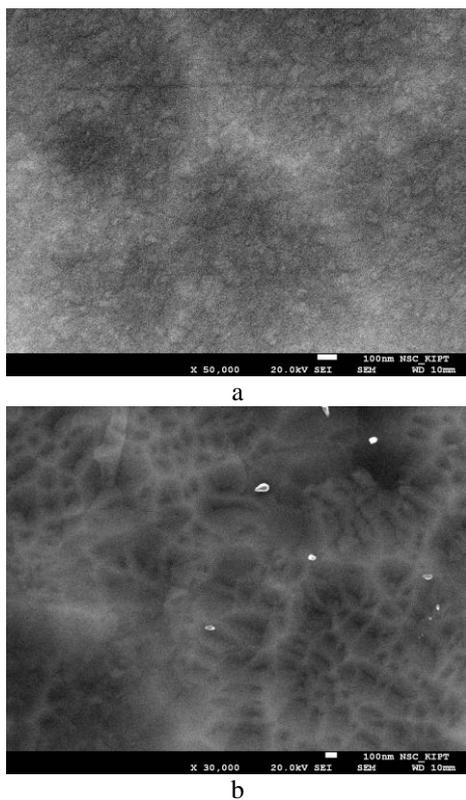


Fig. 7. Microphotographs of the surface of Cr_2O_3 (a) and CrN (b) coatings with thickness of $5 \mu\text{m}$

In presented paper we investigated the retention and permeation of deuterium through Cr , CrN and Cr_2O_3 coatings under the influence of deuterium glow gas-discharge plasma. Deuterium was used for these experiments, because the migration of deuterium and tritium through materials is very similar [16]. Specimens were irradiated with deuterium ions from glow gas-discharge plasma at voltage on electrodes 1000 V and density of ion current 20 A/m^2 . Maximal irradiation dose was $1 \cdot 10^{19} \text{ D}_2^+/\text{cm}^2$. The specimens were irradiated at room temperature.

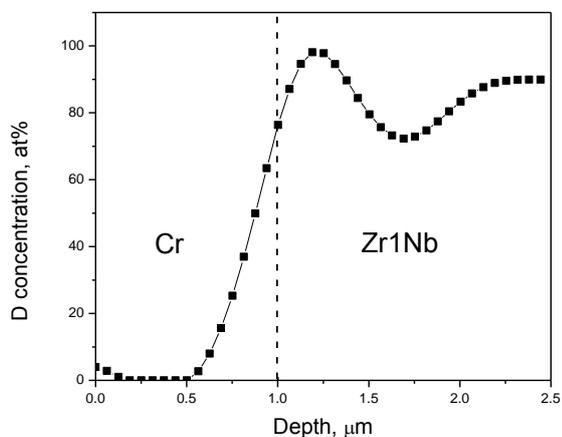


Fig. 8. Depth distribution profile of deuterium for Cr coatings after exposed to a deuterium plasma at room temperatures to dose $1 \cdot 10^{19} \text{ D}_2^+/\text{cm}^2$

Fig. 8 shows the depth distribution profiles of deuterium for Cr coating with thickness $1.5 \mu\text{m}$ exposed to a deuterium plasma at room temperatures to dose $1 \cdot 10^{19} \text{ D}_2^+/\text{cm}^2$.

Almost 30% of implanted deuterium atoms are trapped on region between 0.8 and $2.5 \mu\text{m}$. Retention in Cr coating is very low and a small peak attributed to deuterium absorption on surface is present at 0-depth.

As shown in Fig. 8 the thickness of Cr coating decreased almost twice. The reason for such effects likely involves effects of sputtering. This assumption is confirmed by comparing the structure of the surface of the original coating and after plasma exposure (Fig. 9). It is seen that the surface sputtered.

Thus chromium coating shows weak trapping of deuterium (see Fig. 3), which could be considered as a positive feature, but at the same time because of the good permeability at saturation of the plasma, can not be considered a good protective coating.

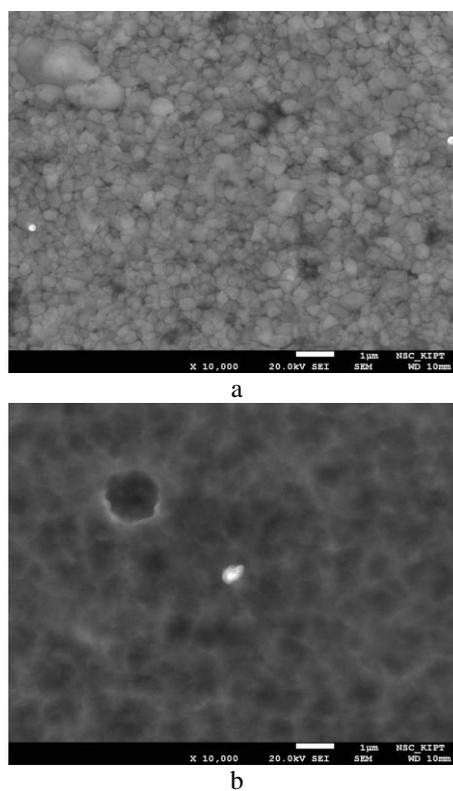


Fig. 9. Microphotographs of the surface of Cr coatings initial (a) and after exposed to a deuterium plasma at room temperatures to dose $1 \cdot 10^{19} \text{ D}_2^+/\text{cm}^2$ (b)

Fig. 10 shows the depth distribution profiles of deuterium for Cr_2O_3 and CrN coatings with thickness $5 \mu\text{m}$ exposed to a deuterium plasma at room temperatures to dose $1 \cdot 10^{19} \text{ D}_2^+/\text{cm}^2$.

It is seen that deuterium atoms are trapped near the surface. The quantity of trapped deuterium is about 0.35% of implanted deuterium dose. The lower deuterium retention and permeation in Cr_2O_3 and CrN coatings may be due to several effects.

As noted above if the coating material has a higher recombination rate coefficient for deuterium than the bulk material, the deuterium release from the surface should be increased, lowering the deuterium concentration. The coating may have poor solubility of

deuterium. A reduction in the concentration at the near surface may be associated with effects of sputtering due to the high density of ion flux. A more detailed study will need to understand of the effect of CrN and Cr₂O₃ coatings on retention and permeation of deuterium under ion irradiation.

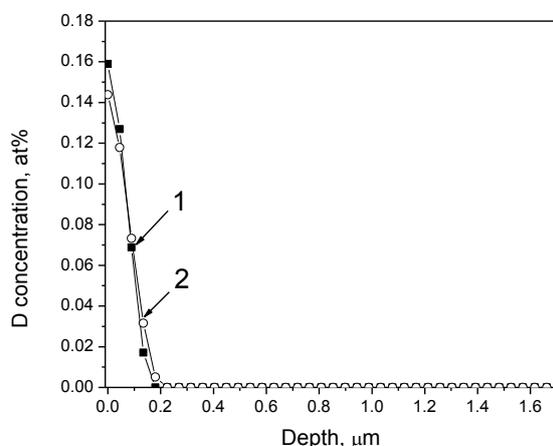


Fig. 10. Depth distribution profile of deuterium for Cr₂O₃ (1) and CrN (2) coatings after exposed to a deuterium plasma at room temperatures to dose $1 \cdot 10^{19} D_2^+ / cm^2$

CONCLUSION

The depth distribution profiles of deuterium in zirconium alloy Zr-1Nb in initial state and with coatings Cr, CrN and Cr₂O₃ were observed by the NRA method. The effect of vacuum-arc coatings on retention and penetration of deuterium in zirconium alloy Zr-1Nb at introduction of deuterium in the sample by way of ion implantation or plasma of glow discharge was investigated.

It is found that the pure chromium coatings with thickness of 1.5 μm provide a low retention of deuterium in the traps at the irradiation temperature 350 °C. At the same time, they show high permeability at irradiation with high-density plasma flux.

The CrN and Cr₂O₃ coatings significantly reduce the hydrogen (and its isotopes) permeation into material when introduced both by ion implantation method and by plasma glow discharge. In these coatings experimental depth profile of deuterium correlates to the calculated distribution of implanted D⁺ ions, so the deuterium does not leave the implanted layer.

These results indicate that CrN and Cr₂O₃ coatings should be effective for use in nuclear devices.

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ВЛИЯНИЕ ПОКРЫТИЙ Cr, Cr-N и Cr-O_x НА УДЕРЖАНИЕ И ПРОНИКНОВЕНИЕ ДЕЙТЕРИЯ В СПЛАВЫ ЦИРКОНИЯ Zr-1Nb

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В исходном сплаве циркония и в сплаве с Cr-, CrN- и Cr₂O₃-покрытиями методом ядерных реакций измерены профили распределения дейтерия, имплантированного с энергией 15 кэВ/D⁺ при температуре 350 °С до дозы 1·10¹⁷ D/см² и внедренного при воздействии плазмы тлеющего разряда. Показано, что в исследованном интервале температур и концентраций покрытия CrN и Cr₂O₃ выступают барьером и защищают цирконий от взаимодействия с изотопом водорода – дейтерием.

ВПЛИВ ПОКРИТТІВ Cr, Cr-N та Cr-O_x НА УТРИМАННЯ І ПРОНИКНЕННЯ ДЕЙТЕРІЮ В СПЛАВИ ЦИРКОНІЮ Zr-1Nb

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У вихідному сплаві цирконію і в сплаві з Cr-, CrN- і Cr₂O₃-покривами методом ядерних реакцій виміряні профілі розподілу дейтерію, який імплантований з енергією 15 кеВ/D⁺ при температурі 350 °С до дози 1·10¹⁷ D/см² і впроваджений при впливі плазми тліючого розряду. Показано, що в дослідженому інтервалі температур і концентрацій покриття CrN і Cr₂O₃ виступають бар'єром і захищають цирконій від взаємодії з ізотопом водню – дейтерієм.