

## HYDROGEN BEHAVIOR IN CHROMIUM-COATED ZIRCONIUM ALLOY E-110 DURING DEPOSITION IN A GAS DISCHARGE

A. E. Evsin, L. B. Begrambekov,  
A. A. Gordeev, A. V. Grunin,  
S. V. Ivanova, and A. S. Kaplevskii

UDC 661.883.1:621.039.531+621.45.038.72

*The regularities and mechanisms of the processes characterizing the behavior of hydrogen in the zirconium alloy E-110 with a chromium coating were studied at different stages of the experiment: during irradiation of the substrate by ions from argon plasma and in the process of coating deposition. After ion bombardment of the zirconium, the hydrogen was retained in the interior and in the defects of the surface layer of the zirconium, and hydrogen trapping decreased with increasing residual gas pressure during irradiation in the range 1.3–30 mPa. The hydrogen atoms trapped during deposition of the chromium coating were retained primarily in the zirconium. As the pressure of the deuterium added to the residual gas during coating deposition increased, the trapping of deuterium atoms increased in the zirconium and remained unchanged in the chromium coating. Hydrogen atoms were observed to transition from the interior of the zirconium to the trapping centers in the oxide layer, which was accompanied by a reduction of the hydrogen desorption temperature and observed during ion irradiation of the substrate and coating deposition in a low vacuum.*

The zirconium-alloy parts used as elements in the core of a reactor are subjected to corrosion and hydrogen absorption, which causes premature removal from service, limits the service life of the reactor, and impedes any increases of the fuel burnup [1, 2]. One possible solution under consideration for the corrosion and hydrogen absorption problems is deposition of protective coatings on the parts. Positive test results on the corrosion and hydrogen resistance of coatings based on chromium and its compounds deposited on samples of zirconium alloys [3], including in a plasma discharge [4], indicate that they hold promise. However, the behavior of hydrogen in chromium-coated zirconium alloys during deposition has still not been studied. The present article is devoted to the study of the regularities and mechanisms of the processes characterizing the behavior of hydrogen at different stages of an experiment on the deposition of a chromium coating on samples of the zirconium alloy E-110 with 1% Nb in argon plasma.

### Experimental Procedure

The coating was deposited in a setup whose main parts are a spray chamber, where a gas discharge with a glowing cathode is ignited, a mass-spectrometric block based on a QMG 220 quadrupole mass spectrometer (Germany) connected with the spray chamber for monitoring the gases, an evacuation system, a working-gas (argon, deuterium) injection system, separated and independently controlled systems for powering the discharge, a target, and a substrate.

Samples of zirconium alloy E-110 with 1% Nb and dimensions  $7 \times 7 \times 1$  mm, prewashed in an ultrasonic alcohol bath, were used as substrates for deposition. Thermal cycling tests performed on coated samples showed that for acceptable adhesion the zirconium substrate should be irradiated with ions from argon plasma with residual gas pressure  $\leq 10$  mPa before

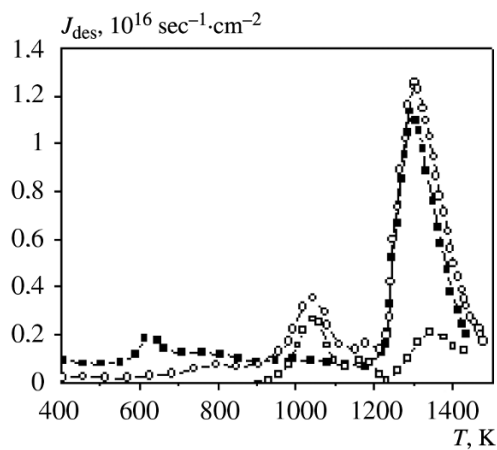


Fig. 1. Thermal desorption spectrum of hydrogen molecules from unirradiated (■) and irradiated (○) (by argon-plasma ions) samples of the zirconium alloy E-110 and the difference of the spectra (□).

coating deposition. Accordingly, the chromium coating is deposited in two stages: preliminary irradiation of the zirconium substrate by ions from argon plasma and direct deposition of the coating.

Preliminary irradiation by ions from argon plasma was conducted under residual gas pressure 1.3–40 mPa ( $\text{H}_2\text{O}$  comprises >90% of its composition), argon pressure 130 mPa, irradiating ion energy 250 eV, ion flux density on the sample  $7.5 \cdot 10^{15} \text{ sec}^{-1} \cdot \text{cm}^{-2}$ , irradiation dose  $9 \cdot 10^{18} \text{ cm}^{-2}$ , and sample temperature 530 K.

The coating was deposited under residual gas pressures 4 and 13 mPa on the samples pre-irradiated by argon-plasma ions. In some cases, the deposition was conducted in a deuterium–argon mixture under residual-gas pressure 4 mPa. The argon pressure was kept the same; the deuterium pressure in different experiments was 4 and 10 mPa. The energy of the ions irradiating the surface of the coating formed during deposition did not exceed 20 eV. The temperature of the sample during coating deposition equaled 520 K, the coating deposition rate was  $\sim 0.5 \mu\text{m/h}$ , and the coating thickness was  $\sim 0.5 \mu\text{m}$ .

The regularities of the trapping of hydrogen isotopes and the character of their confinement at each stage were investigated by means of thermal desorption spectrometry (TDS). The MIKMA setup (Russia) was used to perform thermal desorption analysis [5]. The residual gas pressure in the chamber was no worse than  $7 \mu\text{Pa}$ . The rate of lineal heating of the sample equaled 5 K/sec. The molecules  $\text{H}_2$ , HD, and  $\text{H}_2\text{O}$  were detected during analysis. Desorption of other hydrogen or deuterium containing molecules was negligible.

### Experimental Results and Discussion

**Hydrogen gas exchange between the residual gas and a zirconium substrate at the stage of preirradiation of the substrate by argon-plasma ions.** The TDS spectra of hydrogen molecules desorbed from a zirconium sample irradiated by argon ions under residual gas pressure 20 mPa as well as from an unirradiated sample (maximum at 620 K) are shown in Fig. 1. At the same time, the total amount of hydrogen in the sample increased. The height of the peak at 1300 K increased and peaks appeared at 1050 and 1170 K.

The existence of the peaks at 1050 and 1300 K in the TDS spectra of hydrogen from zirconium samples annealed at 1500 K for 600 sec and held in gaseous hydrogen is mentioned in [6, 7]. The authors attribute the peak at 1300 K to desorption of hydrogen confined in the interior of the zirconium and at 1050 K to decomposition of the chemisorbed states of hydrogen on the zirconium surface.

The peak at 1300 K is dominant in the TDS spectra of hydrogen from samples before and after ion irradiation (Fig. 1), which makes it possible to accept the supposition stated in [6, 7] on the nature of this peak.

The integration of the spectrum of the irradiated sample showed that  $10^{17} \text{ cm}^{-2}$  atoms are desorbed in the region 980–1080 K; this is much greater than the number of adsorption centers on the surface. This does not permit attributing the

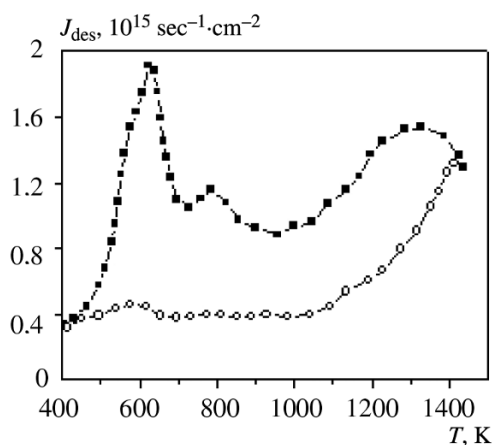


Fig. 2. Thermal desorption spectrum of hydrogen molecules from unirradiated (■) and irradiated (○) (by argon-plasma ions) samples of the zirconium alloy E-110.

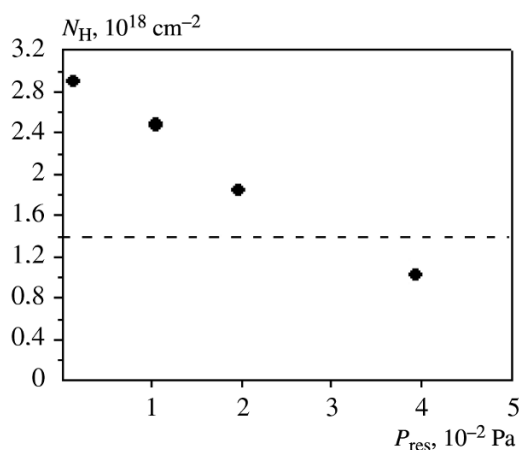


Fig. 3. The number of hydrogen atoms in a sample of alloy E-110 irradiated by ions from argon plasma versus the pressure of the residual gas: ---) hydrogen level in the unirradiated sample.

peak at 1050 K in the TDS spectrum to hydrogen desorption from the surface chemisorbed states. On the basis of this and the fact that 1050 K is less than the temperature 1300 K of the main maximum of the hydrogen desorption from zirconium, it can be supposed that the peak at this temperature is a consequence of hydrogen emission from trapping centers located in the oxidative surface region of zirconium. This is also supported by the presence of a peak at 1050 K in the TDS spectrum of hydrogen molecules [8] from zirconium oxide saturated with hydrogen by Sievert's method. The authors of this work attribute this peak to hydrogen desorption from clusters consisting of an oxygen vacancy and two trivalent ions.

It can be assumed that the small peak at 1170°C is also associated with hydrogen desorption from trapping centers in the oxidized region of zirconium but of a different type. It should be noted that ion irradiation can create hydrogen trapping centers in the surface region of the zirconium which are in addition to the existing ones.

The peak in the low-temperature part of the TDS spectrum of hydrogen molecules from zirconium (500–600°C) was mentioned in [7, 9] and attributed to hydrogen desorption from surface OH-groups. The presence of a peak at 620 K in the TDS spectrum of hydrogen molecules and water from an unirradiated sample as well as the absence of this peak in the spectra of the irradiated sample confirms this supposition (Figs. 1 and 2).

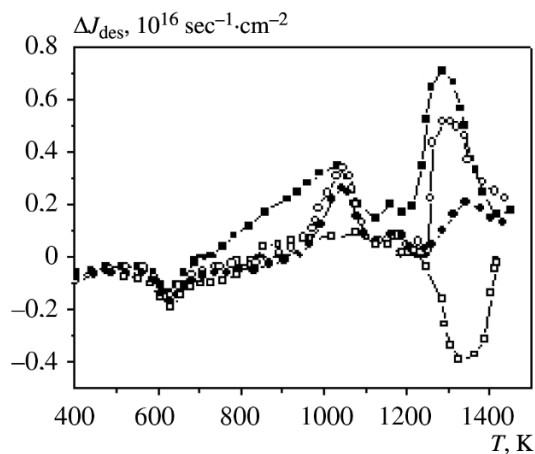


Fig. 4. Difference of the thermal desorption spectra of hydrogen molecules from a sample of the alloy E-110 before and after irradiation by ions from argon plasma under residual gas pressure 1.3 (■), 11 (○), 20 (●), and 40 mPa (□).

The experiments on the irradiation of zirconium by ions from argon plasma with different residual gas pressures showed that as the residual gas pressure increases in the range 1.3–30 mPa hydrogen trapping diminishes, and irradiation at 30 mPa even reduces the amount of hydrogen in the sample (Fig. 3). Figure 4 attests that as the residual gas pressure increases, hydrogen trapping diminishes in the surface oxide layer of the zirconium as well as in the interior of the sample, while the number of hydrogen atoms in the interior of the zirconium and in the sample as a whole does not fall below the level in an unirradiated sample. The latter fact indicates that even at 530 K a portion of the hydrogen atoms present in the interior of the zirconium is desorbed.

The authors of [7, 9] discovered that the presence of oxygen atoms on the surface of zirconium gives rise to hydrogen diffusion to the surface and lowers the desorption temperature for a portion of the hydrogen in the zirconium. It can be supposed that the observed changes in the character of the gas-exchange of zirconium with the residual gas during plasma irradiation are also a consequence of the increase in the oxygen concentration on the surface of the irradiated samples with increasing residual-gas pressure.

The oxygen content on the surface of the sample in the experiments described above was determined by irradiating the surface by ions of the products of dissociation of water molecules in the plasma as well as ion-irradiation activated reaction of water molecules of the sorbed layer with the surface. Both processes were intensified as a result of an increase in the residual-gas pressure. The conditions and mechanism of gas-exchange of zirconium with the residual gas, including the low-temperature desorption of a portion of the hydrogen atoms from the zirconium require further investigation.

**Regularities in the change of the character of hydrogen confinement in chromium-coated zirconium at the chromium deposition stage.** The TDS spectrum of the hydrogen molecules of a chromium sample was measured in order to establish the possibility of determining the region of trapping and confinement of hydrogen isotopes in chromium-coated zirconium samples and the shape of this spectrum was compared with the shapes of the TDS spectra of the hydrogen from zirconium samples before and after ion irradiation. It is evident in Fig. 5 that the maximum of the TDS spectrum of hydrogen from chromium is located at 700 K, i.e., a much lower temperature than the main desorption peak of hydrogen from zirconium (1300 K) and the peaks in the TDS spectrum of hydrogen from zirconium irradiated by argon atoms (1050, 1170 K) (see Fig. 1). This makes it possible to determine the number of hydrogen atoms confined in the coating and substrate by analyzing chromium-coated zirconium samples.

It is evident in Fig. 6 that the peaks of the thermal desorption of hydrogen from coated zirconium occur at the same temperature as in the TDS spectra of hydrogen from uncoated zirconium (1050, 1170, 1300 K), attesting that the zirconium oxide layer is preserved during the deposition of chromium. The total amount of hydrogen in the sample after coating depo-

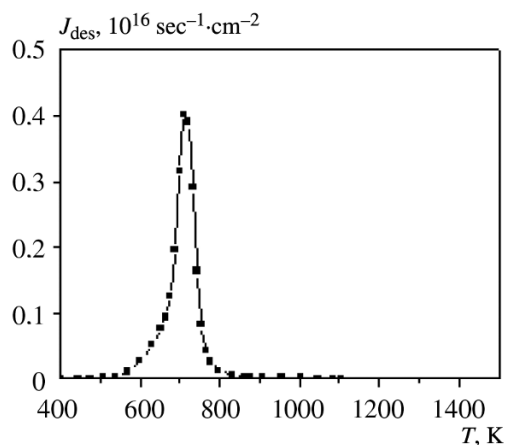


Fig. 5. Thermal desorption spectrum of hydrogen molecules from a chromium sample.

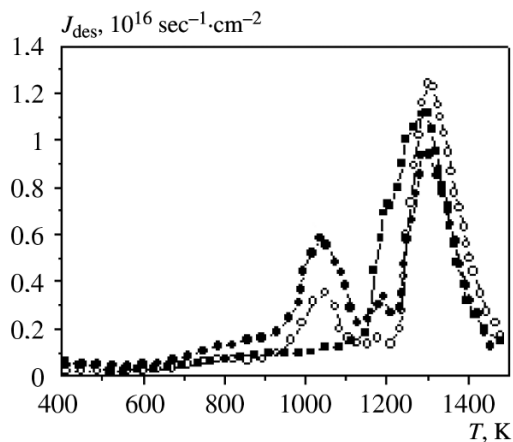


Fig. 6. Thermal desorption spectrum of hydrogen molecules from a sample of the zirconium alloy E-110 after preliminary ion irradiation ( $\circ$ ) and after deposition of a chromium coating under residual gas pressure 13 ( $\bullet$ ) and 4 mPa ( $\blacksquare$ ).

sition changed very little for residual gas pressures 13 and 4 mPa in the deposition process. However, during the deposition of the chromium layer the hydrogen was redistributed between the trapping centers located in the zirconium and its oxide layer. In the case of chromium deposition under residual gas pressure 4 mPa, a portion of the hydrogen from the zirconium (peak at 1300 K) and almost all hydrogen from the low-temperature trapping centers in the oxide layer (peak at 1050 K) became concentrated in the higher-temperature trapping centers (peak at 1170 K) as well as centers located in the oxide. Conversely, when the residual gas pressure during coating deposition was 13 mPa, the hydrogen content in the trapping centers with desorption temperature 1050 K decreased significantly owing to the hydrogen from zirconium, while the amount of hydrogen in the trapping centers with desorption temperature 1170 K increased very little.

The facts presented above attest that upon chromium deposition definite changes occurred in the oxide layer of the zirconium that changed the character of the hydrogen confinement. It should be noted that the number of hydrogen atoms transferred from the zirconium into the oxide layer is all the greater, the higher the residual gas pressure during the coating deposition process. This effect is probably of the same nature as the reduction of the temperature of hydrogen desorption from zirconium under irradiation by argon-plasma ions.

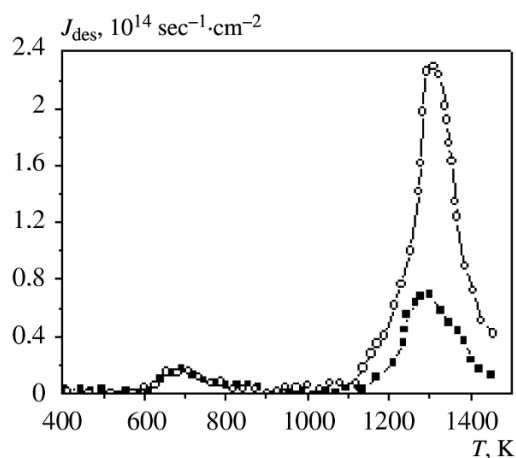


Fig. 7. Thermal desorption spectrum of HD molecules from a sample of the zirconium alloy E-110 with a chromium coating, deposited under deuterium pressure 4 (■) and 10 mPa (○).

In connection with the difficulty of determining the amount of hydrogen trapped in a coated sample and the region of hydrogen confinement accompanying the redistribution of the hydrogen atoms between the trapping centers in the zirconium and its oxide layer, experiments were performed with the addition of an admixture of deuterium to the argon plasma at the deposition stage. The experiments showed that most of the trapped deuterium atoms penetrate into the zirconium and remain confined there; in addition, as the deuterium pressure increases, the number of particles trapped in the zirconium increases (Fig. 7). Probably, this is a consequence mainly of two factors: the dissolution of hydrogen isotopes in zirconium, in contrast to their dissolution in chromium, is an exothermal process with a high heat of solution ( $Q_s = -0.67$  eV/atom [10]) and the comparatively high temperature of the sample secures a quite high rate of deuterium diffusion.

The desorption of the deuterium atoms confined in the chromium coating ( $\sim 10^{15}$  cm $^{-2}$ ) was approximately the same at both deuterium pressures. Thus, as the pressure increased, the trapping of deuterium in the sample as a whole increased as a result of increased trapping in zirconium. However, it is important to note that the total amount of deuterium trapped in a coated sample during the experiments ( $\leq 2 \cdot 10^{16}$  cm $^{-2}$ ) was found to be significantly less than the amount of hydrogen present in the zirconium initially ( $\sim 1.4 \cdot 10^{18}$  cm $^{-2}$ ).

### Conclusion

The behavior of hydrogen in chromium-coated zirconium alloy E-110 during irradiation of a zirconium substrate by ions from argon plasma and in the deposition process was studied. The trapping of hydrogen atoms under ion bombardment of zirconium did not exceed  $1.5 \cdot 10^{18}$  cm $^{-2}$ ; in addition, as the residual gas pressure increased in the range 1.3–30 mPa, the amount of trapped hydrogen decreased. After irradiation, the hydrogen was confined in the interior of the zirconium as well as in defects in the surface oxide layer of the zirconium.

The trapping of hydrogen atoms during chromium deposition did not exceed  $2 \cdot 10^{16}$  cm $^{-2}$ . It was found that the hydrogen atoms trapped during coating deposition are confined predominately in the zirconium. As the pressure of the deuterium added to the residual gas increased, the number of deuterium atoms trapped increased in the zirconium but decreased in the chromium coating.

It was found that hydrogen atoms migrate from the interior of the zirconium into trapping centers in the oxide layer and that this process is accompanied by a reduction of the hydrogen desorption temperature and is observed under ion irradiation of the substrate and coating deposition in a low vacuum. This process is thought to be associated with an increase in the concentration of oxygen atoms on the surface of zirconium, but the mechanism of the process is unclear and requires further study.

## REFERENCES

1. A. S. Zaimovskii, A. V. Nikulina, and N. G. Reshetnikov, *Zirconium Alloys in Nuclear Power*, Energoatomizdat, Moscow (1994).
2. S. V. Ivanova, A. K. Shikov, and O. V. Bocharov, "Hydrogen saturation of zirconium articles during the fabrication and operation processes – a factor limiting the service life in VVER and RBMK reactors," *Metalloved. Term. Obrab. Met.*, No. 8, 40–47 (2003).
3. I. A. Petel'guzov, "Effect of protective aluminum and chromium coatings on the oxidation of zirconium and its alloys," *Vopr. At. Nauki Tekhn. Ser. Fiz. Rad. Povr. Rad. Materialoved.*, No. 2(78), 114–119 (2012).
4. L. V. Selezneva, B. V. Bushman, Yu. V. Dubrovskii, et al., "Interaction of hydrogen with zirconium alloy coated with vacuum ion-plasma coatings," *Vopr. At. Nauki Tekhn. Ser. Termoyad. Sintez*, No. 2, 108–111 (2008).
5. L. B. Begrambekov, A. A. Airapetov, S. V. Vergyazov, et al., "Removal of oxygen from carbon-graphite composite and stainless steel in deuterium glow discharge," *ibid.*, No. 3, 29–34 (2010).
6. J.-M. and R. Gilbert, "The interaction of hydrogen with polycrystalline zirconium. I. Sticking coefficients and binding states," *Appl. Surf. Sci.*, **18**, 315–324 (1984).
7. W. Peterson, R. Gilbert, and G. Hoflund, "The interaction of hydrogen with polycrystalline zirconium. II. The effect of preadsorbed oxygen," *Appl. Surf. Sci.*, **24**, 121–124 (1985).
8. K. Park and D. Olander, "Hydrogen dissolution in and release from nonmetals. III. Tetragonal Zirconia," *J. Am. Ceram. Soc.*, **74**, 72–77 (1991).
9. D. Asbury, G. Hoflund, W. Peterson, et al., "TPD and ESD studies of the interaction of hydrogen and oxygen on polycrystalline zirconium," *Surf. Sci.*, **185**, 213–226 (1987).
10. Y. Fukai, *The Metal-Hydrogen System: Basic Bulk Properties*, Springer, NY (2005).