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ROLE OF SURFACE LAYER NANOSRTUCTURING IN IMPROVING MECHANICAL AND CORROSION PROPERTIES OF REACTOR MATERIALS

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The results of investigations into the influence of the ion-plasma treatment (IPT), including the ion implantation and ion-plasma coating deposition, on the mechanical properties and corrosion resistance of nuclear fuel cladding tubes made of zirconium alloy (Zr1%Nb) are presented. The tests of cladding samples have been performed at two temperatures between 20 and 350 °C. It is shown that the deposition of TiN, Ti+TiN, TiAlN, TiAlSiN, TiAlYN coatings improves mechanical properties of the sample surface, as well as, leads to the hardening of Zr1%Nb fuel cladding as a whole. The efficiency of hardening by implantation with (Zr, Mo) and gaseous (N_2, O_2) ions depends on the kind of ions and their energy. The nanostructure TiAlSiN and TiAlYN coatings improve the corrosion resistance of zirconium alloy. The results of experiments on hardening of fuel cladding tubes are explained by the state of the coating-surface interface.

INTRODUCTION

Development of the atomic engineering implies increasing the heat power of energetic units, extending the terms of company and fuel burning, providing nuclear power plant load following capability. All this substantially increases the load on the reactor structural materials and raises the requirements to their mechanical and corrosion properties. One of the ways for solving this problem is a material surface modification using the ion-plasma treatment (IPT) including the surface ion implantation and radiation-corrosion resistant coatings deposition. In any case IPT should not decrease the mechanical properties of structural materials.

Many publications [1–12] presents the results of investigations into the influence of electron, ion irradiation of materials or protective coating deposition on the change in the structure and mechanical characteristics of the surface layers and of the material as a whole. The authors of [1] give the results on the ion-helium plasma treatment of Zr1%Nb fuel cladding tubes by two modes: 1) "hard" mode with a plasma flow density $Q = 50$ J/cm^2 mode and "soft" mode with $Q = 25$ J/cm^2. For the first time, it has been found that the IPT provokes a grain reorientation α-Zr throughout the volume of the Zr1%Nb fuel cladding tube wall (similar to that in the case of complete recrystallization). This effect is realized only in the "soft" mode of treatment when no fritting occurs, and when elastic waves, generated by ion deceleration in the solid phase, are propagating throughout the tube wall thickness. From the results it follows that the IPT can lead to structure and strength changes not only in the surface layers but also in the whole material volume. In some publications the authors note a marked role of Zr alloy irradiation with gas and metal ions in the formation of surface layers with an increased hardness and coefficient of elasticity [3–6]. A similar result is reached by depositing protective multilayer multicomponent nanostructure ion-plasma coatings on Zr alloys [7–9]. Nanostructurization of the steel surface by the preliminary ultrasonic treatment and subsequent stabilizing treatment increases by 1.5 times the yield limit, the strength limit and plasticity [10]. Simultaneous increase of the strength and plasticity of steel can be reached by applying the treatment with low-energetic (1…3 keV) titanium ions in the argon atmosphere (under pressure of ~ 0.13 Pa) [11, 12].

Deposition of ion-plasma protective coatings on the Zr1%Nb fuel cladding tubes increases mechanical properties of tubes [9], as well as, protects the zirconium alloy against the high-temperature (1100 °C) oxidation in air during 1 hour [8] and increases its corrosion resistance [13]. However, the data concerning the IPT influence on the mechanical properties of structural materials are fragmentary and insufficient. Mechanical properties of Zr1%Nb fuel cladding tube samples subjected to IPT are partly presented in [4, 9].

The goal of this study is a continuation of the investigations into mechanical properties and corrosion resistance of fuel cladding tubes at different temperatures after IPT.

EXPERIMENTAL

Coatings were formed by vacuum-arc deposition method from two opposite flows of filtered plasma using the facility "Bulat-6". Rectilinear filters were used as plasma separators. Nanostructure TiAlN-base coatings were additionally doped with elements of Y and Si. Cathode materials were titanium and its alloys: 78Ti-16Al-6Si and 67Ti-28Al-5Y. The coating thickness was of the order of 4…5 μm that provided in the case of plasma filtration the absence of through pores. Choice of the coating composition was determined by the excellent properties of nitride multicomponent coatings, in particular, high mechanical properties, thermal stability, plasticity, corrosion resistance [14, 15]. Also, the multilayer coatings were formed on the base of alternating Ti/TiN layers. The coatings were deposited only on the external surface of Zr1%Nb cladding tube samples having the length of 80 and 9.2 mm in diameter.

The samples were irradiated with Zr, Mo, N_2, and O_2 ions using a gas-plasma source and high-voltage system of additional ion acceleration in the energy range from 1 to 15 keV with irradiation dose of $10^{17}…10^{18}$ ion/cm^2.

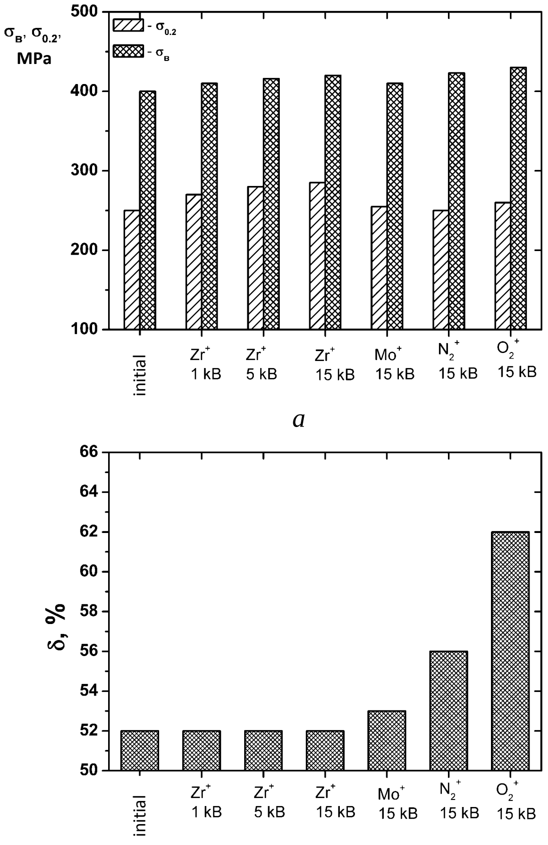
After IPT the samples were subjected to the tensile tests in the facility INSTRON-5581 and vacuum machine 1246Р-2/2300 at T = 20 and 350 °C in vacuum. The coating surface morphology was investigated with a scanning atomic force microscope (AFM) Nanoscope IIIa series Dimension 3000^{TM} in the periodic contact mode. Silicon probes with a nominal radius of the tip of 10 nm in radius were used. The nanohardness of the zirconium alloy surface before and after IPT was investigated with a device Nanoindentor G200 at the penetration depth of the indenter ~ 300 nm on the flat samples of 10×20×0.7 mm, cut from the fuel cladding tubes. Corrosion tests of the samples with coatings and without coatings were carried out on the potentiostat IPC-pro at room temperature in water (H_3BO_3 – 3 mg/dm^3, NH_4OH – 3 mg/dm^3, KOH – 12.3 mg/dm^3) being a heat carrier imitator of the WWER primary coolant circuit.

RESULTS AND DISCUSSION

Tensile tests at temperatures between 20 and 350 °C have shown that the deposition of ion-plasma coatings of all investigated compositions on the Zr1%Nb fuel element tubes results in hardening of their surface, as well as, in improvement of volume mechanical characteristics. At 20 °C the tensile strength of TiAlN, TiAlSiN, and TiAlYN coatings increases to 15% and the yield strength changes insignificantly in the coatings of all types. At 350 °C $\sigma_{в}$ increases by 12…21% and the yield limit $\sigma_{0,2}$ increases by 9% only for the $Ti_{77.9}Al_{19.2}Si_{2.7}N$ coatings. The elongation δ,% and the coefficient of elasticity are changing insignificantly.

In the case of ion implantation after irradiation with polyenergetic (15 to 60 keV) metals ions of Mo and Zr and gas ions of N_2 and O_2 (15 keV) in the samples of Zr1%Nb cladding tubes the gradient nanostructure layers are formed with increased values of the hardness and of the coefficient of elasticity. The hardness increases by a factor of 2.5…3 and the Young modulus – by 20…30% (120…140 GPa) measured by nano-indentation.

The irradiation with Zr ions leads to the tensile strength increase by 3…6% (the hardening efficiency increases with ion energy increasing from 1 to 15 keV), and the yield strength increases by 3.5…8%. A maximum hardening is observed under irradiation with gaseous ions of N_2 and O_2 having a 15 keV energy. The yield strength is not almost changed after implantation with ions of Mo, N_2, and O_2. The tensile strain δ_5 weakly depends on the kind of metal ions, and under irradiation with gas ions of N_2 and particularly of O_2 it increases from 8 to 20%, respectively (Fig. 1).



a

b

Fig. 1. Quantities $\sigma_{в}$, $\sigma_{0,2}$ (a) and δ (b) of Zr1%Nb cladding tubes as a function of the kind and energy of ions. Test temperature is 20 °C

The increase of δ_5 is provoked by the nanograin texturing in the alloy under the gas ion action similarly to the effect for the steel [3].

The tensile test of such samples at T = 350 °C has shown an appreciable increase of the yield limit $\sigma_{0,2}$ for all the irradiated samples. A maximum increase of $\sigma_{0.2}$ (by 16%) was obtained under irradiation with polyenergetic zirconium ions. The yield limit increases when the accelerating negative potential E_p, applied to the substrate with samples, is increasing. The value of δ_5 slightly decreases under irradiation with metal ions, and after irradiation with gas ions it increases by 10%. The presented results demonstrate a possibility of using the IPT method for hardening both the surface layers and the whole sample through the thickness of Zr-Nb fuel cladding tubes.

Table presents the mechanical characteristics of the investigated coatings.

Mechanical properties and roughness of coatings

Coatings	Thickness, μm	H, GPa	E, GPa	H^3/E^2, GPa	R_a, nm
TiN	5	31	438	0.16	47
(Ti+TiN)x	6	29	380	0.17	63
TiAlN	5	32	341	0.28	50
TiAlSiN	5	45	425	0.5	36
TiAlYN	5	33	352	0.29	21

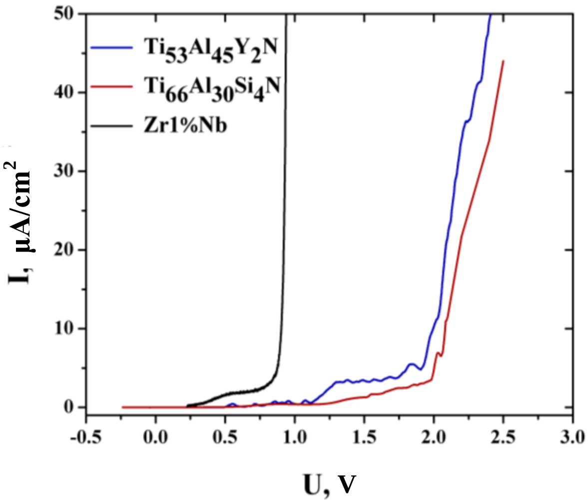
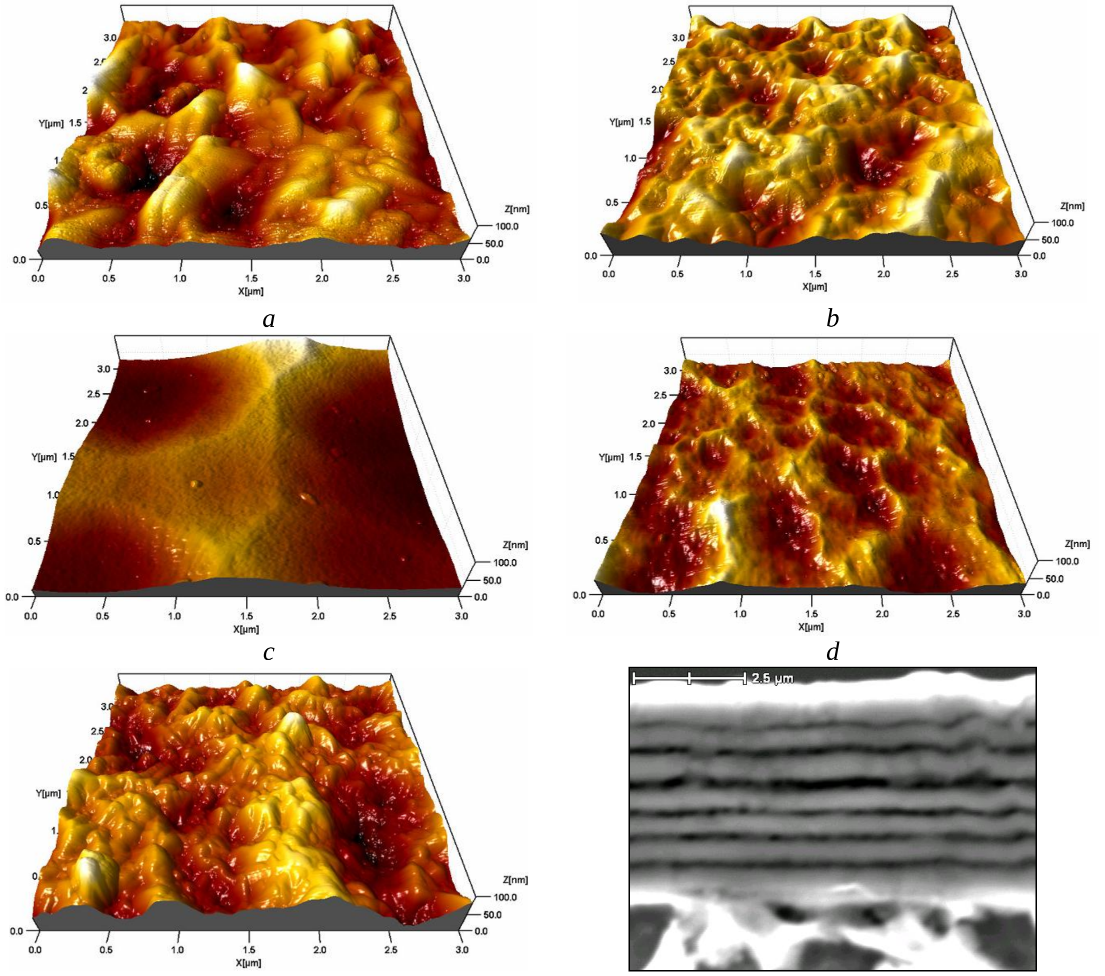


Fig. 2. Anode polarization curves obtained for the coatings in the reactor water on the Zr1%Nb alloy at temperature of 20 ^{o}C

The results show a strong dependence of the properties of coatings on their composition, nevertheless all they can be used for hardening the surface layers and the whole cladding tubes made of zirconium alloy. The high value of H^3/E^2 indicates high erosion resistance of the obtained coatings and low value of R_a, about their high quality.

Fig. 2 demonstrates the anode polarization curves obtained for the samples of zirconium alloy with coating and without coatings. It is seen that the corrosion potential of the zirconium alloy with coatings increases from 0.8 to 1.8 V, i. e. the investigated coatings increase the corrosion resistance of the alloy in the reactor water. Consequently, the service life of fuel claddings will be significantly increased.

The procedure of vacuum-arc deposition of coatings includes the stage of plasma cleaning of a metal part surface.



a *b* *c* *d* *e* *f*

Fig. 3. AFM images of the coating surface morphology: TiN (a); TiAlN (b); TiAlSiN (c); TiAlYN (d), and $(Ti+TiN)_x$ (e); SEM image of the multilayer $(Ti+TiN)_x$ coating fracture (f)

It is performed by surface bombardment before the coating deposition with gas and/or metal ions having energies of 1…3 keV. The process of condensate formation also goes under conditions of continuous bombardment with ions of lower energies leading to the formation of periodically repeated compression and tensile stresses [10, 16]. It follows from these publications that such a surface treatment forms at the coating-substrate interface a cellular structure from extruded and intruded zones, i. e. the surface of periodically repeated peaks and pits of a submicron size. Elastic waves being formed, penetrate deep into the material and cause its volume hardening [16]. The “coating-substrate” interface structure is distinctly reflected on the coating surface morphology shown in Fig. 3. The cellular structure size depends on the coating composition and deposition process parameters. A sandwich-like structure of the multilayer coating is clearly seen on its fracture (see Fig. 3,f).

Theoretical justification for the necessity of forming a multilevel profile of a self-coordinated deformation profile at the interface of two heterogeneous media to provide the conditions for compatibility of their interfacing is given in [10–16]. There experimentally confirmed is a high efficiency of improving the macromechanical characteristics of material by nanostructuring its surface or by depositing nanostructure coatings.

The hardening is explained on the base of a new approach to the description of a solid being deformed as a multilayer system. The surface layers of the loaded solid are considered as an independent subsystem, and their interface with the substrate plays an important functional role.

Just this thing determines the efficiency of improving the mechanical characteristics of the whole material. The investigation of the mechanism of surface layer hardening by nanostructurization has revealed a new effect of periodically repeated “chess” distribution of stresses and strains at the coating-substrate interface in the loaded solid [16].

The effect under consideration is the base of mesomechanics of the new metal hardening method providing the improvement of all the general mechanical characteristics including the strength and plasticity. Strain hardening of the surface layer has a direct influence on the deformed material as a whole. This conclusion is confirmed in the case of depositing thin coatings on the material. There are optimum values of the thickness of hardened surface layers providing the increase of all the mechanical characteristics of the material including its plasticity [16].

It is necessary to form a “chess-board” with a minimum cell size on the “coating-surface” interface. Thus, it is possible to reach a quasi-homogeneous stress distribution and to hamper the appearance of stress microconcentrates which generate a neck, main crack and material fracture.

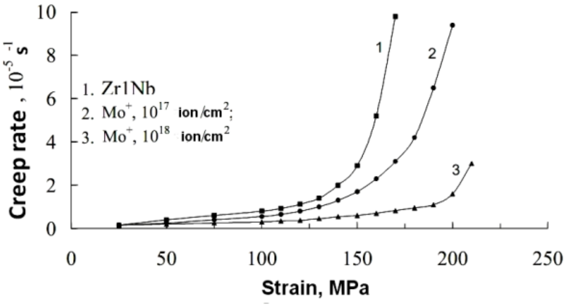


Fig. 4. Creep rate of Zr1%Nb samples as a function of the applied stress at T = 430 °C after implantation with Mo ions [3]

A significant role of the nanostructured surface layer consists in hampering the deformation defect accumulation in the material volume that leads to the material hardness increase. This observation is confirmed by the creep resistance increase in the Zr1%Nb alloy being implanted molybdenum ions.

This promotes the pinning of dislocations and increases the level of stresses which are necessary for activation of dislocation sources near the layer surface providing the yield strength increase, creep rate decrease (Fig. 4) and material hardness increase [3].

CONCLUSIONS

Proceeding from the results, given in the papers concerning the IPT effect on the strength properties of Zr1%Nb cladding tube samples, some key points can be noted.

Ion implantation and ion-plasma coating deposition increase the hardness and coefficient of elasticity of Zr1%Nb surface layer.

Usually the hardening occurs throughout the tube thickness too. The hardening efficiency is determined by a complex set of IPT constituents which the formation and passage of elastic waves, due to the ion slowing down in the solid phase of Zr1%Nb alloy, depend on.

Deposition of nanostructure ion-plasma coatings improves the corrosion resistance of zirconium alloys in the reactor water.

For prediction of the change in the macromechanical characteristics it is very important to take into account the effect of “chess” distribution of stresses and strains at the modified surface layer-substrate interface. The type of the interface formed and the nanodimension of the produced cellular structure play an essential role in the resulting effect.

REFERENCES

1. Yu.A. Perlovich, M.G. Isaenkova, M.M. Grekhov, O.A. Krymskaya, V.I. Polskyij. Change of the texture and structure change in the volume of cladding tubes made of Zr-base alloy under ion-plasma surface treatment // *Proceedings of 19th International Conference “Radiation Damage Physics and Radiation Materials Science”,* 2010, Alushta, p. 125-126.

2. Yu. Perlovich, M. Grekhov, M. Isaenkova, V. Fesenko, B. Kalin, V. Yakushin. Bulk structure and texture changes in cladding tubes from Zr-based alloys under ion-plasma surface treatment // *Problems of Atomic Science and Technology.* 2004, N 3, p. 59-65.

3. V.A. Belous, E.V. Karasyova, G.I. Nosov, V.I. Sokolenko, G.I. Nosov, V.M. Khoroshikh, O.V. Borodin, G.N. Tolmachova. The effect of ion irradiation on the creeping and hardness of zirconium alloy Zr1Nb surface // *Vestnik Tambov State University.* 2010, v. 15, N 3, p. 910-911.

4. V.A. Belous, P.N. V’ygov, A.S. Kuprin, S.A. Leonov, G.I. Nosov, V.D. Ovcharenko, L.S. Ozhigov, A.G. Rudenko, A.G. Savchenko, G.N. Tolmachova, V.M. Khoroshikh. Investigation of the influence of ion-plasma treatment on mechanical properties of zirconium alloy Zr1Nb // *Journal of Physical Surface Engineering,* 2013, v. 11, N 1, p. 97-102.

5. J.G. Han, J.S. Lee, W. Kim, Dong S. Sun, Kie H. Chung. Zirconium oxide formation and surface hardening behavior by nitrogen implantation under

oxygen atmosphere in Zircaloy-4 // *Surface and Coatings Technology*. 1997, v. 97, p. 492-498.

6. I.P. Chernov, E.V. Berezneeva, P.A. Beloglazova, S.V. Ivanova, I.V. Kireeva, A.M. Lider, G.E. Remnev, N.S. Pushilina, Y.P. Cherdantsev. Physico-mechanical properties of the zirconium alloy surface modified by a pulsed ion beam // *Technical Physics*. 2014, v. 59, issue 4, p. 535-539.

7. V.A. Belous, S.A. Leonov, G.I. Nosov, V.M. Khoroshikh, N.S. Lomino, G.N. Tolmmachova, M.A. Brovina, I.G. Ermolenko. Modification of E110 alloy by deposition of multilayer Zr/ZrN coatings and ion irradiation // *Journal of Physical Surface Engineering*. 2009, v. 7, N 1-2, p. 76-81.

8. A.S. Kuprin, V.A. Belous, V.N. Voyevodin, V.V. Bryk, R.L. Vasilenko, V.D. Ovcharenko, E.N. Reshetnyak, G.N. Tolmachova, P.N. V'yugov. Vacuum-arc chromium-based coatings for protection of zirconium alloys from the high-temperature oxidation in air // *Journal of Nuclear Materials*. 2015, v. 465, p. 400-406.

9. V.A. Belous, P.N. V´ygov, A.S. Kuprin, S.A. Leonov, G.I. Nosov, V.D. Ovcharenko, L.S. Ozhigov, A.G. Rudenko, V.T. Savchenko, G.N. Tolmachova, V.M. Khoroshikh. Mechanical characteristics of Zr1Nb alloy tube after deposition of ion-plasma coatings // *Problems of Atomic Science and Technology*. 2013, №2(84), p. 140-143.

10. V.E. Panin, V.P. Sergeev, A.V. Panin, Yu.I. Pochivalov. Surface layer nanostructuration and nanostructure coating deposition as an effective method of hardening advanced structural and instrumental methods // *The Physics of Metals and Metallography*. 2007, v. 104, N 6, p. 650-660.

11. S.S. D’yachenko, I.V. Ponomarenko, S.N. Dub. Role of steel object surface condition on the behavior during deformation // *Met. Sci. Heat Treat.* 2015, v. 57, N 5, p. 245-253.

12. I.V. Doshchechkina, S.S. D’yachenko, I.V. Ponomarenko, I.S. Tatarkina. Improving the plasticity of thin cold-rolled steel sheets for cold stamping // *Steel Transl.* 2016, v. 46, N 5, p. 364-367.

13. E. Alat, A.T. Motta, R.J. Comstock, J.M. Partezana, D.E. Wolfe. Multilayer (TiN, TiAlN) ceramic coatings for nuclear fuel cladding // *Journal of Nuclear Materials*. 2016, v. 478, p. 236-244.

14. V.A. Belous, A.S. Kuprin, S.N. Dub, V.D. Ovcharenko, G.N. Tolmachova, E.N. Reshetnyak, I.I. Timofeeva, P.M. Litvin. Structure and mechanical properties of Ti-Al-Si-N protective coatings deposited from separated plasma of a vacuum arc // *Journal of Superhard Materials*. 2013, v. 35, issue 1, p. 20-28.

15. S. PalDey, S.C. Deevi. Single layer and multilayer wear resistant coatings of (Ti, Al)N: a review // *Mater. Sci. Eng. A.* 2003, v. 342, p. 58-79.

16. V.E. Panin, V.P. Sergeev, A.V. Panin. *Nanostructuring of the surface layers of construction materials and nanostructured coating deposition*. Tomsk: Tomsk Polytechnic University, 2013, 2nd issue, p. 254.

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РОЛЬ НАНОСТРУКТУРИРОВАНИЯ ПОВЕРХНОСТНЫХ СЛОЕВ В ПОВЫШЕНИИ МЕХАНИЧЕСКИХ И КОРРОЗИОННЫХ СВОЙСТВ РЕАКТОРНЫХ МАТЕРИАЛОВ

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Представлены результаты влияния ионно-плазменной обработки (ИПО), включающей ионную имплантацию и осаждение ионно-плазменных покрытий, на механические свойства и коррозионную стойкость образцов из твэльных трубок циркониевого сплава Zr1%Nb. Испытания проведены при двух температурах: 20 и 350 °С. Показано, что нанесение покрытий TiN, Ti+TiN, TiAlN, TiAlSiN, TiAlYN приводит к различному повышению механических свойств не только поверхности образцов, но и к объемному упрочнению трубок из сплава Zr1%Nb. Эффективность упрочнения при имплантации металлическими (Zr, Mo) и газовыми (N_2, O_2) ионами зависит от вида и энергии ионов. Наноструктурные покрытия TiAlSiN, TiAlYN увеличивают коррозионную стойкость циркониевого сплава. Полученные экспериментальные результаты по упрочнению твэльных трубок объясняются состоянием интерфейса между покрытием и подложкой.

РОЛЬ НАНОСТРУКТУРУВАННЯ ПОВЕРХНЕВИХ ШАРІВ У ПІДВИЩЕННІ МЕХАНІЧНИХ І КОРОЗІЙНИХ ВЛАСТИВОСТЕЙ РЕАКТОРНИХ МАТЕРІАЛІВ

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Представлені результати впливу іонно-плазмової обробки (ІПО), що включає іонну імплантацію і осадження іонно-плазмових покриттів, на механічні властивості і корозійну стійкість зразків з твельних трубок цирконієвого сплаву Zr1%Nb. Випробування проведені при двох температурах: 20 і 350 °С. Показано, що нанесення покриттів TiN, Ti+TiN, TiAlN, TiAlSiN, TiAlYN призводить до різного підвищення механічних властивостей не тільки поверхні зразків, але і до об'ємного зміцнення трубок зі сплаву Zr1%Nb. Ефективність зміцнення при імплантації металевими (Zr, Mo) і газовими (N_2, O_2) іонами залежить від виду і енергії іонів. Наноструктурні покриття TiAlSiN, TiAlYN збільшують корозійну стійкість цирконієвого сплаву в два рази. Отримані експериментальні результати по зміцненню твельних трубок пояснюються станом інтерфейсу між покриттям і підкладкою.