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Описано закономірності впливу легування елементами втілення (O, N, H) на фізико-механічні властивості сплавів на основі цирконію. Наведено результати експериментальних досліджень щодо впливу обробки у контрольованому кисне- та азотовмісному середовищах на властивості зразків-кілець, вирізаних із цирконієвої оболонки тепловиділяючого елементу марки Zr-1 % Nb. Показано особливості стану внутрішньої та зовнішньої поверхонь після обробок

Ключові слова: цирконієві сплави, елементи втілення, приповерхневий шар, твердість, приріст маси, оболонка тепловиділяючого елементу

Описаны закономерности влияния легирования элементами внедрения (O, N, H) на физико-механические свойства сплавов на основе циркония. Приведены результаты экспериментальных исследований влияния обработки в контролируемом кислород- и азотсодержащих средах на свойства образцов-колец, вырезанных из циркониевой оболочки тепловыделяющего элемента марки Zr-1 % Nb. Показаны особенности состояния внутренней и внешней поверхностей после обработки

Ключевые слова: циркониевые сплавы, элементы внедрения, приповерхностный слой, твердость, прирост массы, оболочка тепловыделяющего элемента

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EFFECT OF OXIDATION AND NITRIDING ON THE PROPERTIES OF ZIRCONIUM ALLOYS

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1. Introduction

Due to the combination of unique physical and mechanical properties with the low cross section of absorption of thermal neutrons, zirconium and its alloys are widely used in nuclear technology. These properties make them non-alternative construction material for working in the active zone of thermal neutron reactors. However, some factors significantly reduce the possibility of their use. In particular, service properties of zirconium are essentially influenced by the interstitial elements – oxygen and nitrogen. Chemical-thermal treatment is one of the most effective methods of controlling the structure and characteristics of near-surface layers of metals, and as a result, they significantly affect functional properties of the material. Therefore, the expansion of ideas about the impact of the near-surface layer, enriched with interstitial elements, on properties of pipes made of Zr-1 % Nb alloy of heat generating elements (HGE), is quite appropriate.

It is known that the existence of oxygen or nitrogen in the lattice of zirconium inhibits absorption of the interstitial elements (for example, hydrogen) and affect anticorrosive characteristics. However, the problem of peculiarities of saturation of internal and external shell surfaces of heat generating elements with interstitial elements has not been studied sufficiently enough. Therefore, one of the relevant problems at present in the area of zirconium alloys is the establishment of influence of oxidation and nitriding on the properties of shell surfaces of the heat generating elements.

2. Literature review and problem statement

Zirconium alloys are important structural material for products of an active zone and the HGE of nuclear power plants (including shells of the HGE) [1–3]. For the purpose of nuclear safety, the nuclear shell of elements of nuclear reactors should meet increased requirements. The most vulnerable element of the HGE is the wall of a pipe [4, 5]. The key to effective use of zirconium alloys is provision of their proper structural-phase state. The peculiarity of the zirconium alloy is high sensitivity of structural-phase state to the content of interstitial elements [1]. Solubility of interstitial elements (oxygen, nitrogen, hydrogen) in α-zirconium has practical significance. According to the chart of states, oxygen has the highest solubility in α-zirconium that equals to 28 at. %, nitrogen has 22 at. % and hydrogen has the lowest – 7 % [6–8]. High solubility of oxygen in zirconium makes alloys of the "Zr-O" system very promising in terms of the practical use of oxygen alloying as a method of controlling the structure and properties of zirconium and its alloys. Among the interstitial elements in zirconium, oxygen and nitrogen are seen not only as a harmful impurity, but also as alloying elements.

In terms of diffusion mobility in Zr, hydrogen exceeds such interstitial elements as oxygen and nitrogen. Among the interstitial elements (O, N, C), only hydrogen has the lowest activation energy and quantum character of diffusion [9, 10]. Hydrogen has such characteristics in a wide range of temperatures. Hydrogen has the largest diffusion coefficient, while nitrogen has the lowest (Fig. 1).

The atomic radius of oxygen (R=0.066 nm) is significantly lower than the atomic radius of zirconium (R==0.16 nm). Therefore, when oxygen penetrates zirconium, it is placed in the interstices of the lattice of metal. A saturation of zirconium with oxygen leads to the formation of solid solutions that relate to the interstitial phases [11–13].

In the lattice of α-zirconium, oxygen atoms occupy octahedral position [14]. Octahedral interstices in the lattice of α-zirconium have trigonal symmetry. The equilibrium oxygen pressure in zirconium (p_{O2}) is very low – at temperature of 450 °C p_{O2}~$1{,}01^{-65}$ Pa [15].

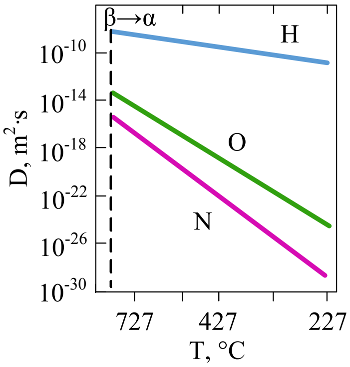


Fig. 1. Diffusion coefficients of oxygen, nitrogen and hydrogen in α-Zr [9, 10]

Oxygen relatively slowly diffuses in zirconium. Diffusive mobility of oxygen is by several orders of magnitude lower than the mobility of abnormally quick diffusants" – Fe and Ni [13].

The opinion about prevailing diffusion along certain crystallographic directions is quite common. An analysis, conducted in [16], revealed that the coefficient of diffusion anisotropy in α-zirconium at temperature of 670 K ($AD_{\|C}=D/D_{\perp C}$) is about 0.1.

Statistical processing of data on the diffusive mobility of oxygen atoms in zirconium was held in [17]. In paper [17], a dependence of the diffusion coefficient of oxygen in α-Zr on temperature was proposed. The authors also noted that in the temperature range of T=250...600 °C, the process of oxygen diffusion is controlled by the migration of oxygen atoms in basic planes. At T=600...1500 °C, it is controlled by the migration of oxygen atoms along the c axis.

In paper [18], it was found that oxygen in the amount of up to 3.11 % does not significantly affect the coefficient of oxygen diffusion in α-zirconium. At the same time, at greater oxygen content, due to the occurrence of interaction between oxygen atoms and their complexing, it is necessary to take into account its impact on the mobility of its own atoms. It should be noted that interstitial elements, penetrating the matrix of zirconium, lead to changes in the parameters of crystalline lattice and increase the area of α-Zr existence (Fig. 2). For example, oxygen content of up to 30 % defines a change in the c/a ratio from 1.598...1.602, and the presence of oxygen component up to 2.5 % of the mass increases the polymorphic zirconium conversion by 400 °C.

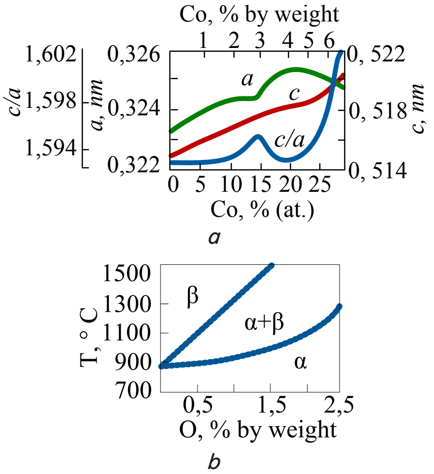


Fig. 2. Effect of oxygen on the characteristics of zirconium: *a* — on the parameters of lattice *a* and *c* [19]; *b* — on the existence of alpha-area [20]

It is common to assume that if the oxygen concentration in the surface layer of the sample reaches 30 at. % (~7 % by weight), the oxide film of ZrO_{2-x} composition is formed. Oxygen ions diffuse through the film and, reaching metal, increase its thickness (Fig. 3) [21].

Oxidation kinetics of zirconium alloys, for example in aqueous solutions (close to operating conditions), are described by function (1):

$$\Delta m = A \cdot t^n, \qquad (1)$$

where Δm is the mass increment per unit of area of the sample surface over time t; A and n are the constants. In the initial period of oxidation, exponent n is 0.33...0.5. When thickness of the film reaches 2...3 microns, the transition to linear oxidation (the "fracture" phenomenon) is observed and n=1.

Zirconium oxide ZrO_2 is polymorphic and, depending on the temperature rise, may exist in three crystalline modifications: monoclinic α, tetragonal β and cubic γ (Fig. 3).

Oxide films of thickness exceeding 3 microns consist mainly of columnar α-ZrO_2 crystals, but often contain inclusions of high-temperature modifications.

Such inclusions were discovered in the oxides of alloys Zr-l % Nb and Zr-2.5 % Nb after corrosion tests in different media (air, water vapor). The cause of these inclusions is the difference in parameters of the crystalline lattices of zirconium and zirconium oxides ZrO_x.

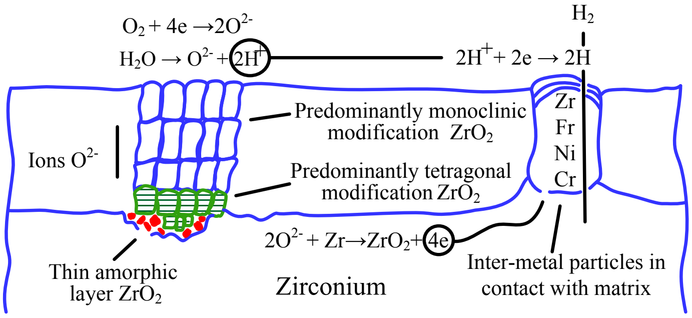


Fig. 3. Schematic representation of an oxide film [21]

At a certain oxidation stage, the level of compressing stresses in the outer layer of the film becomes insufficient to stabilize high-temperature modifications. This leads to a martensite conversion of tetragonal and cubic phase into monoclinic. Such conversions are accompanied by an increase in the film volume and formation of cracks and pores.

Oxidized zirconium alloy is composed of several layers, in particular:

1) oxide;

2) metal, adjacent to the oxide layer ZrO with high content of oxygen;

3) metal layer outside the diffusion zone of oxygen.

At temperature T=300...500 °C, up to 15 % of oxygen, absorbed by the alloy in the oxidation process, is consumed for the formation of diffusion zone in the metal phase. Dissolving in the metal, oxygen can lead to zirconium embrittlement. It is known that zirconium materials, containing more than 10 at. % (2 % by weight) of oxygen, are virtually incapable of plastic deformation.

In paper [22], three basic types of characteristic grains of oxide film structures are distinguished: with mostly elongated grains, with mostly equilibrium grains and laminar structure.

Paper [23] explores in detail the phenomena, which are observed at changing the content of nitrogen in gas mixtures with oxygen. The microstructure of a layer at changing the content of nitrogen in the mix from 0 to 100 % greatly varies. In pure oxygen at T=900 °C, degradation of the oxide layer on zirconium slightly slows down. In the layer that contains up to 15 % of N_2, isolated ZrN particles appear, but the oxide base of the layer is still prone to degradation. At nitrogen concentration above 15 %, a continuous ZrN film, adjacent to metal, is revealed, and general deformation of the original zirconium sample is observed. At the same time, local penetration of the oxide into the base disappears. Finally, only in the atmosphere of pure nitrogen, oxide completely disappears from the system, only a continuous ZrN film is observed, oxide degradation and base deformation do not manifest themselves [23].

Fig. 4 shows a schematic, illustrating the structure of the surface layer formed on zirconium as a result of its consistent heating in different gas media at T=900 °C. Depending on the mode of heating, the following cases are possible:

a) at secondary heating in gas media, enriched by nitrogen at the bound of metal, a continuous ZrN film is always observed after the degradation of scale;

b) at secondary heating in oxygen, the ZrN film (formed earlier in the air or nitrogen) more or less quickly disappears; a zirconium plate may even quickly burn if the primary scale consisted of only ZrN;

c) at secondary heating in oxygen or in the air, the scale on the sample, which was formed as a result of the first heating, always forms the outer zone of the final oxide layer.

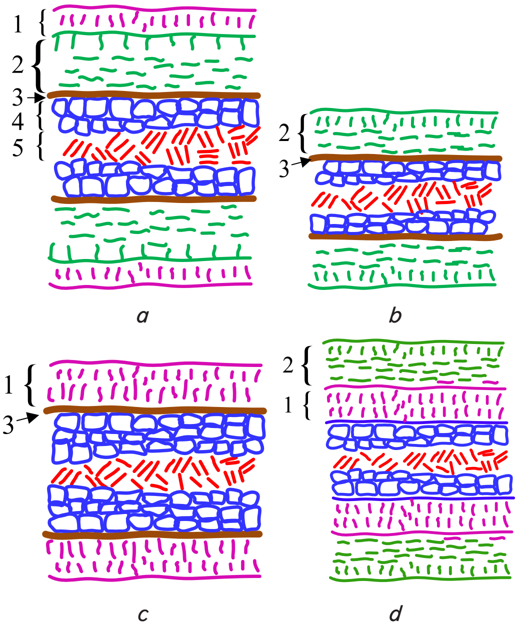


Fig. 4. Schematic of the structure of surface layer, formed on zirconium as a result of consistent heating at T=900 °C in different media [23]: *a* – oxygen → air; *b* – nitrogen → air; *c* – oxygen → nitrogen; *d* – air → oxygen

In paper [24], the following thermo-dynamically stable compounds were revealed: Zr_6O, Zr_3O, Zr_2O, ZrO and ZrO_2, as well as the Gibbs powers, at which the formation of the above compounds takes place, were established (Fig. 5).

The conditions of existence of different compounds were shown. Monoclinic compound ZrO_2 exists in the widest range of chemical potentials, while compounds Zr_6O, Zr_3O, Zr_2O, ZrO are stable only under strongly reducing conditions.

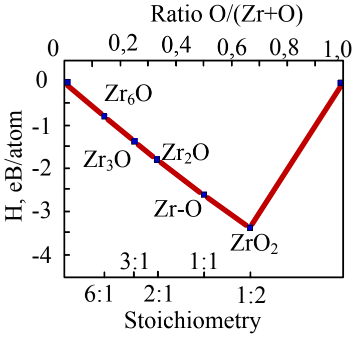


Fig. 5. Enthalpy of the formation of zirconium oxides [24]

Depending on the temperature-temporal and gas-dynamics parameters of zirconium interaction with oxygen-containing medium, in the near-surface layer of metal, an oxide film and/or only a diffusion layer is formed. Paper [10] also shows that in the "Zr-O" system there is only one stable oxide ZrO_2, which has several modifications. Low-temperature monoclinic α_{ZrO} modification is resistant to 1205 °C; at this temperature, it is converted to tetragonal.

Recently, significant attention has been paid to studying the mechanism of the air interaction (in fact, simultaneous action of oxygen and nitrogen) with zirconium shell pipes. In particular, it was established that zirconium nitride is formed only in the absence of oxygen in the gas phase and, at the same time, at existence of oxygen in the metal phase [25]. Using the chart p_{O2}/p_{N2}, which is presented in [17], it is possible to determine the bounds of stability of Zr, ZrO_2, and ZrN existence depending on temperature.

The oxygen content in metal significantly influences a mass increment and the structure of zirconium samples at temperature of T=1100 °C. According to the results of the studies, presented in [26], the mass increment of the nitrated sample increases with an increase in oxygen in metal. With an increase in oxygen content, the grain dimensions decrease [27].

It was found that one of the negative consequences, which leads to existence of hydrogen in Zr may be inhibited hydride cracking [2]. According to research [2], the hydride phase is formed, when the local hydrogen concentration exceeds the maximum solubility in α-Zr. For example, boundary solubility of hydrogen in α-Zr at temperature T=300 °C is rather low and makes only 80...100 ppm. It is shown that the zirconium hydrides orientation is not uniform in thickness of the HGE pipes. One of the factors that determine their location is the stressed state of pipe surfaces. It was noted that on the internal part of a pipe, hydrides are mainly located along the radial planes, while on the external part hydrides tend to be located in the tangential direction.

In paper [29], some patterns of saturation of zirconium alloy Zry-4 after treatment in various gas media were established. In particular, it was shown that the highest mass increment of the given alloy is after treatment in the air, and the lowest is after treatment in pure nitrogen (Fig. 6).

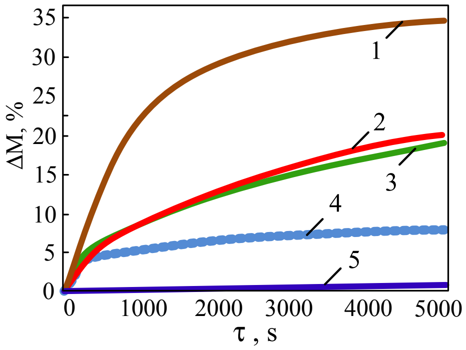


Fig. 6. Mass increment of zirconium alloy Zry-4 after treatment at T=1100 °C in various gas media [29]: 1 – air; 2 – O_2 → air; 3 – O_2; 4 – $O_2 \rightarrow N_2$; 5 – N_2

Correlation between the volume content of oxygen and hardness, as well as distribution of oxygen concentration and hardness gradient in the surface layer after treatment in oxygen-containing mixture is shown in articles [6] and [30], respectively.

We are acquainted with the works, demonstrating differences of saturation of the external and internal surfaces after treatment in gas and water media. In particular, it was established that after treatment of a HGE pipe from alloy Zr-1 % Nb in steam at temperature T=600 °C, the microhardness of the external surface of the pipe is higher relative to the internal surface [31].

Paper [32] also shows differences of saturation of the external and internal surfaces of the HGE pipes after saturation in oxygen mixture (Fig. 8). The authors do not explain this interesting scientific phenomenon, but only state the very fact of existence of a difference.

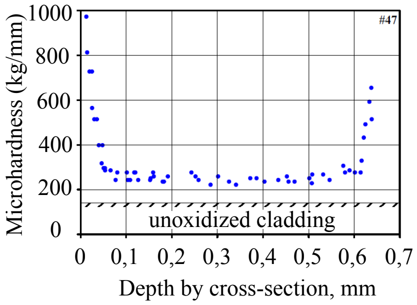


Fig. 7. Oxygen distribution in zirconium pipe from alloy E110 after treatment at T=1100 °C [32]

Article [33] establishes the influence of oxygen content on the fatigue durability of zirconium samples, cut from the HGE pipes. Paper [27] convincingly shows that oxygen improves fatigue durability both at room temperature and at elevated T=350 °C. The reason for the positive effect is explained by the formation of solid solution of interstitial elements in the matrix of metal.

There are also studies that show the change of fatigue properties of zirconium depending on hydrogen content. For example, in article [34], it was noted that with an increase in the content of hydrogen (in the range of 0...800 mkg/g), the number of cycles before destruction of alloy Zr-1,0Sn-0,3Nb-0,3Fe-0,1Cr, at temperature T=370 °C and amplitude of deformation εa=±0.5 %, the maximum stresses of a cycle increase. The authors explain such increase in the maximum destructive stresses of a cycle by the so-called hydrogen-induced softening that occurs due to certain formed hydrides.

In [35], it was indicated that an increase in the oxygen content leads to a decrease in the twinning process and the start of pores initiation at late stages of the uniform plastic deformation.

In paper [36], it was shown that solid-soluble strengthening of alloy Zr-2.5 % Nb with oxygen causes a homogeneous distribution of dislocations, makes their separation with boundary formation more difficult. Therefore, in the given work, it was hypothesized that solid-soluble strengthening may promote effective relaxation of stresses near grain bounds by the formation of bands of deformation localization.

Therefore, in accordance with the above literature review, it was shown that physical-mechanical properties of zirconium are sensitive to the content of interstitial elements. It should be noted that the works mainly describe the impact of volume content of oxygen, nitrogen or hydrogen on characteristics of zirconium alloys. At the same time, it is necessary to consider that as a result of chemical-thermal treatment, the saturation of the near-surface layer with interstitial elements of finished HGE pipes is possible. However, there are very few studies dealing with the influence of the strengthened near-surface layer with oxygen or nitrogen.

In particular, today the problem of establishing the influence of saturation with oxygen and nitrogen on the characteristics of external and internal shell surfaces of the heat generating elements has not been solved. In fact, to predict functional properties of the HGE pipes, it is important to know depth of the strengthened near-surface layer and surface morphology after the treatment in gas media.

3. The aim and tasks of the study

The aim of present work is to establish the impact of chemical-thermal treatment in controlled oxygen and nitrogen containing gas media on the hardness of near-surface layers of zirconium HGE pipes.

In particular, this will make it possible to assess the influence of oxidation and nitriding on differences of formation of the strengthened near-surface layer on the external and internal surfaces of shells of heat generating elements.

To achieve the set goal, the following tasks had to be solved:

– to establish a change in the mass of samples-rings from alloy Zr-1 % Nb after treatment in the oxygen- and nitrogen-containing gas media;

– to reveal the influence of temperature on the rate of interaction of zirconium alloy with the gas medium;

– to explore the state of external and internal surfaces of samples-rings, cut from the HGE pipes after treatment in gas media;

– to establish hardness of external and internal surfaces of samples-rings after oxidation and nitriding.

4. Materials, treatment modes and methods for examining the characteristics of material

We chose as the object of research the pipes made of zirconium alloy Zr-1 % Nb, produced in Ukraine [37]. For kinetic studies, we used the samples-rings, which were cut out of an HGE pipe.

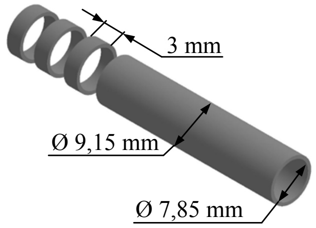


Fig. 8. Schematic of cutting the samples-rings from a shell of a heat generating element

Thermal treatment of zirconium alloys was performed using laboratory equipment without leakage in the controlled oxygen- and nitrogen-containing gas media under different modes (Table 1).

Metalographic research into the samples in the original and strengthened states was performed using the scan electronic microscope (EVO 40XVP (Carl Zeiss, Germany)). Microhardness distribution along the samples intersection was determined using the device PMT-3M (LOMO, St. Petersburg) at load 0.49 H.

The influence of chemical-thermal treatment on the studied material was assessed according to the following parameters of strengthening of the near-surface layer: surface hardness increment (2):

$$\Delta HV=(HV^{surface}-HV^{core}), \qquad (2)$$

where $HV^{surface}$ is the hardness of titanium surface; HV^{core} is the hardness of zirconium core and dimensions of strengthened layer – l μm.

Table 1

Modes of chemical-thermal treatment of samples of zirconium alloy, Zr-1% Nb

No. of treatment	Mode of CTT	Conditional designation
1	Before treatment	P0
P1 – T=650 °C, $P=1,3\cdot10^{-1}$ Pa		
2	t=3 h	P1-3
3	t=5 h	P1-5
4	t=10 h	P1-10
5	t=20 h	P1-20
A – T=650 °C, $P_{N2}=1\cdot10^{5}$ Pa		
6	t=5 h	A-5
7	t=10 h	A-10
8	t=20 h	A-20
P2 – T=750 °C, $P=1,3\cdot10^{-1}$ Pa		
9	t=5 h	P2-5
10	t=10 h	P2-10
11	t=20 h	P2-20

Weighing of zirconium samples was performed before and after chemical and thermal treatment. Before treatment, the samples were washed in alcohol, dried and weighed on the precision balance produced by Voyager (OHAUS, Switzerland) with precision ±0.0001 g.

5. Results of experimental research into the treatment of zirconium alloy in controlled oxygen- and nitrogen-containing media

It was established that the character of changes in the mass of samples, which were treated in oxygen-containing medium (mode P1) approximates the linear law (Fig. 9, curves 1, 2). Treatment in nitrogen-containing medium leads to a change in the mass of samples by the parabolic law (Fig. 9, curves 3, 4).

This indicates that during treatment under modes P1 and P2, a dense protective oxide film is not formed on the samples-rings within 20 h [8, 16]. Parabolic law of change in the mass of samples-rings during nitrading indicates the formation of a dense nitride film, which controls the process of high-temperature interaction with nitrogen and slows down absorption by the nitrogen samples [8, 16].

An increase in temperature of the treatment medium from T=650 °C (mode P1) to T=750 °C (mode P2) leads to an increase in the rate of interaction with the rarefied oxygen-containing medium (Fig. 9, curves 1, 2) approximately by 2.7 times

As evidenced by the results of measurement of microhardnes before the treatment, in the near-surface layer, there is no a strengthened layer on both external and internal surfaces (Table 2). According to research results (Table 3), the hardness of external surface of the samples-rings after treatment at T=650 °C in the oxygen-containing medium (P1-3...P1-20) varies in the range from $HV^{surface}=375\pm$

±30 $HV_{0,49}$ to $HV^{surface}$=1190±90 $HV_{0,49}$ units of hardness. The presence of a dense nitride film and lower coefficient of nitrogen diffusion in zirconium explain approximately the same dimensions of the strengthened layer at temperature of T=650 °C after oxidation in the rarified gas medium and nitriding at atmospheric pressure of nitrogen (Table 4).

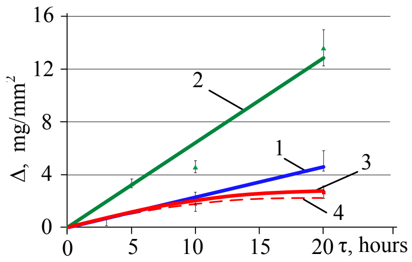


Fig. 9. A change in the mass of samples-rings of zirconium alloy Zr-1 % Nb under different treatment modes: 1 — P1 mode; 2 — P2 mode; 3 — mode A; 4 — parabolic law of change in mass

Table 2

Characteristics of the samples from Zr-1 % Nb alloy after treatment in the nitrogen-containing medium of different treatments at T=650 °C

Treatment mode			P0	A-5	A-10	A-20
Micro-hardness $HV_{0,49}$	External side	l, μm	10...20	45...55	50...60	55...65
		ΔHV	55	275	375	445
		$HV^{surface}$	225±15	440±25	545±35	615±35
	Matrix, HV^{core}		170±10	170±15	165±15	170±15
	Internal side	$HV^{surface}$	205±10	360±20	385±25	445±35
		ΔHV	35	195	215	275
		l, μm	6...15	40...45	45...55	55...60

Table 3

Characteristics of the samples of Zr-1 % Nb alloy after treatment in the oxygen-containing medium at T=650 °C

Treatment mode			P1-3	P1-5	P1-10	P1-20
Micro-hardness $HV_{0,49}$	External side	l, μm	45...55	50...65	65...70	70...75
		ΔHV	210	350	380	1020
		$HV^{surface}$	375±30	515±35	550±50	1190±90
	Matrix, HV^{core}		165±10	165±15	170±15	170±15
	Internal side	$HV^{surface}$	325±15	375±30	410±45	710±70
		ΔHV	160	210	240	540
		l, μm	40...50	45...50	50...55	60...65

Table 4

Characteristics of the samples from Zr-1 % Nb alloy after treatment in the oxygen-containing medium at T=750 °C

Treatment mode			P0	P2-5	P2-10	P2-20
Micro-hardness $HV_{0,49}$	External side	l, μm	10...20	55...65	75...80	95...105
		ΔHV	55	700	815	1320
		$HV^{surface}$	225±15	880±55	1000±65	1510±70
	Matrix, HV^{core}		170±10	180±10	185±10	190±10
	Internal side	$HV^{surface}$	205±10	735±60	865±75	1205±80
		ΔHV	35	555	680	1015
		l, μm	6...15	50...55	65...70	85...91

It was found that with an increase in the duration of maintaining in oxygen-containing medium (P1 mode), the hardness of the internal surface of the sample-ring increases from $HV^{surface}$=325±15 to $HV^{surface}$=710±70. The hardness of the inner surface of the sample-ring after treatment in the nitrogen-containing medium (mode A) at similar temperature and time parameters grows less, in particular from $HV^{surface}$=360±20 to $HV^{surface}$=445±35.

An increase in temperature (P2 mode) intensifies the interaction of samples-rings with oxygen-containing gas medium (Table 4) and increases the mass increment of samples. Despite formation of a penetrating oxide film, the main interaction process is the dissolution of oxygen in the matrix; therefore, it does not affect characteristics of the near-surface layers of metal.

With an increase in temperature of interaction with rarefied oxygen-containing medium, the rate of surface hardness increment (Fig. 10) is lower than the difference of rates of mass increment of samples (Fig. 9). This behavior may be explained by the fact that dependence of hardness on the oxygen content in zirconium is not linear in nature [16].

Treatment in the oxygen-containing medium leads to a linear change of the surface hardness of samples-rings. Treatment in nitrogen-containing medium leads to a parabolic dependence of surface hardness of samples-rings on time (Fig. 10).

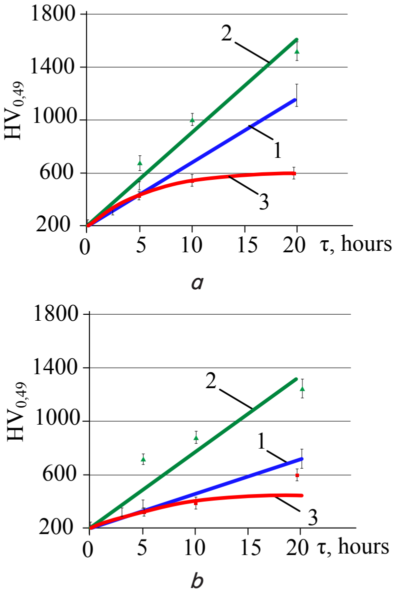
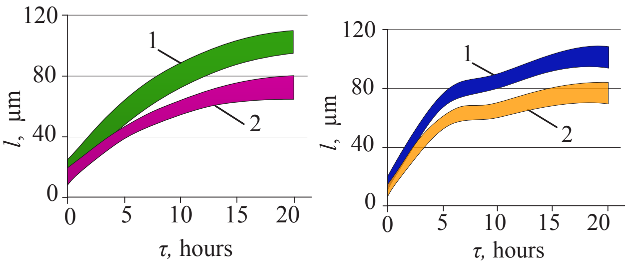


Fig. 10. A change in the hardness of samples-rings after treatment under modes P1 (1), P2 (2), A (3): *a* — external surface; *b* — internal surface

We noted a difference in the rates of growth of the strengthened layer from external and internal side of the wall of a sample-ring, regardless of technological gas media (Fig. 11).

The roughness of external and internal surfaces of the samples-rings is different (Fig. 12, *a*, *b*): roughness of the internal surface is slightly lower. After oxidation under P1-20 mode, the difference in roughness decreases due to the oxide film growth and healing of surface defects.

It should be noted that an increase in the temperature up to T=750 °C in the rarified oxygen-containing medium (mode P2-20) to great extent reduces roughness of the external and internal surfaces of samples-rings (Fig. 13, *a*, *b*).



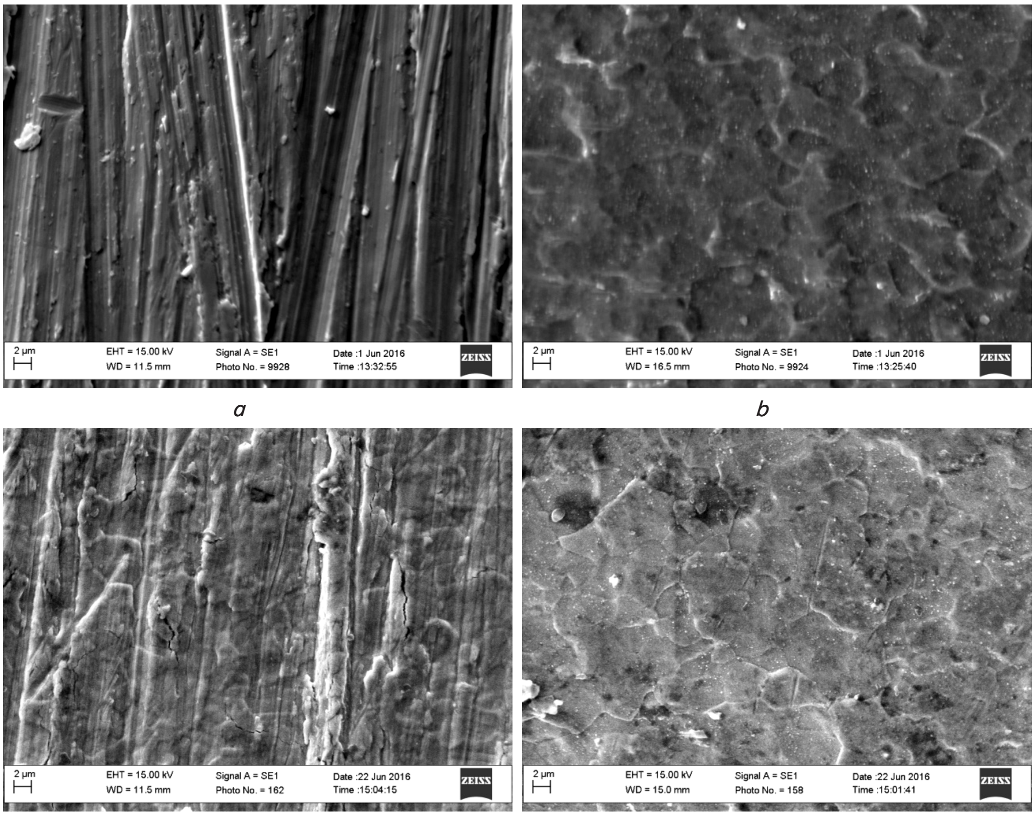
a *b*

Fig. 11. A change in the dimensions of strengthened layer on the external surface (1) and internal surface (2) of samples-rings after treatment under modes: *a* – P1; *b* – A

After treatment in oxygen-containing medium for 20 hours under P2 mode, cracks on the internal surface of samples-rings were observed. The cause of cracking is perhaps the stresses that occur during cooling, resulting from the difference between coefficients of thermal expansion of oxide and the matrix of metal.

6. Discussion of results of the oxidation and nitriding effect on the characteristics of HGE pipes

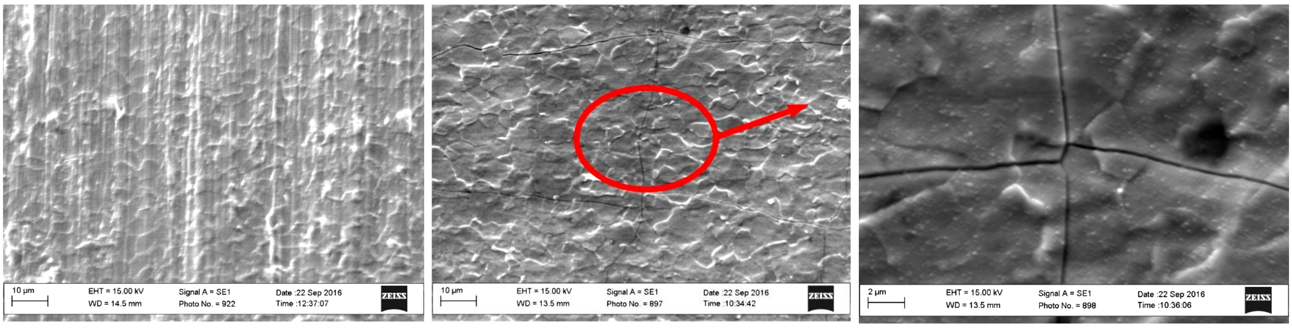
The influence of treatment in controlled oxygen- and nitrogen-containing media on characteristics of surfaces of the HGE pipes from alloy ZR-1 % Nb was established.



a *b*

c *d*

Fig. 12. View of surface (magnification ×2000) of the sample, cut out of the HGE pipe made of Zr1 % Nb alloy, in its original state P0 (*a, b*) and after treatment under mode P1-20 (*c, d*): *a, b* – external surface, *c, d* – internal surface



a *b* *c*

Fig. 13. View of surface of the sample, cut out of the shell of a heat generating element of pipe of Zr1 % Nb alloy, after treatment under mode P2-20: *a* – external surface (magnification ×1000), *b* – internal surface (magnification ×1000), *c* – internal surface (magnification ×5000)

An important result of the work is that it shows thicknesses of strengthened near-surface layer of the internal and external surfaces of the HGE pipes after treatment in the gas media. The dependence of the mass increment of samples cut from the HGE pipes was established, depending on the composition of gas reaction medium.

The key to reproduction of treatment results is high stability of operation of vacuum equipment. However, this equipment is unique in its design and is made up of complex nodes. These specialized nodes include: high-temperature electric oven, water cooling system, vacuum pumps, gas pressure control system in operating chamber, etc. Therefore, one of the difficulties (disadvantages) of the conducted studies is the high complexity of maintaining the thermal laboratory equipment.

It should also be noted that samples-rings of small width (3 mm) were used for the studies. It is known that the HGE pipes have a much larger length (3.2 m). Therefore, the downside of the work is that during the treatment of finished zirconium pipes, the near-surface layer might be saturated in a different way than the sample-ring. This is because it might be quite difficult to distribute evenly the gas component (oxygen, nitrogen) in the inside of a long pipe. Thus, it would be appropriate to direct further research towards the development of a possibility to saturate the HGE pipes. It is also necessary to establish the influence of oxidation and nitriding on the resource of the HGE tubes.

It is known that the penetration of hydrogen into the near-surface layer of the HGE pipes is one of the dangerous phenomena. A presence of other interstitial elements (oxygen, nitrogen) inhibits the penetration of hydrogen into zirconium matrix. Therefore, the promising continuation of studies will be to define an assessment of the hydrogenation of oxidized and nitrated HGE tubes and the impact of such treatment on their resource.

7. Conclusions

1. It was shown that a change in the mass of samples-rings at decreased pressure (P1mode) is close to a linear law. At the same time, during nitriding at atmospheric pressure (mode A), a change in the mass of samples-rings approaches the parabolic law.
2. An increase in the temperature of medium from 650 °C to 750 °C (P2 mode) was found to increase the rate of interaction with the rarefied oxygen-containing medium by ~2.7 times.
3. We established differences in the morphology of external and internal surfaces of samples-rings, cut out of the HGE pipes both before and after the treatment. In particular, it was shown that after oxidation the internal surface of zirconium samples-rings is characterized by a lower relief (a small number of microcavities and microcracks is observed) compared to the external surface. The reason for this phenomenon might be a more intense growth of an oxide film and healing of surface defects.
4. It was shown that the hardness of external surface of the samples-rings, both at oxidizing and nitriding, is higher than that of the internal surface. For example, treatment of the samples-rings in oxygen-containing medium ($T=650$ °C, $P=1.3\cdot10^{-1}$ Pa, $\tau=20$ h) leads to the hardness formation on the external surface – $HV_{0,49}=1190\pm90$, and on the internal surface – $HV_{0,49}=1190\pm90$.

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