

Vasyl Trush, Alexander Luk'yanenko, Viktor Fedirko
Karpenko Physico-Mechanical Institute of the NAS of Ukraine, Lviv, Ukraine

THERMAL PROCESSING OF ZR-1 %NB TUBE IN OXYGEN- AND NITROGEN CONTAINING GASEOUS MEDIUMS

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Abstract. Zirconium alloys have unique properties (physical, mechanical, radiation) is therefore are an essential structural material for nuclear energy. A feature of these alloys is high affinity to the interstitial elements (O, N). Saturation of oxygen and nitrogen occurs during the technological and exploitation heating. The dissolved interstitial elements greatly effect on the properties of finished products. The proposed results of experimental researches will expand the notions of patterns of relationship of the influence of elements interstitial on the properties of the zirconium alloy. The work presents results of the saturation of Zr-1 %Nb tubes after processing in oxygen- and nitrogen- containing gas environments. The distribution of micro-hardness and the size of the hardened layers in the section of the tube wall and the weight gain were determined. It is found that the oxidation of the Zr-1 %Nb alloy ($T = 650\text{ }^{\circ}\text{C}$, $P_{\text{O}_2} = 2.6 \cdot 10^{-1}\text{ Pa}$, $\tau = 3 \dots 20\text{ h}$) makes a greater weight gain than after nitriding ($T = 650\text{ }^{\circ}\text{C}$, $\tau = 5 \dots 20\text{ h}$). The state of the surface of the inside and outside of Zr-1 %Nb tubes for fuel cladding depends of the processing time. The differences in saturation of outer and inner surfaces of the tube were registered. In particular, the hardness of internal surface of the tube is smaller relative to the outer surface after oxidation and nitriding processes. The results of study of the outer and inner surface of fuel cladding in contact with gaseous environment containing oxygen and nitrogen will be interesting for investigators of reactor materials.

Keywords: thermal processing, zirconium alloys, gaseous mediums, saturation, micro-hardness.

Introduction

Through a combination of unique physical, mechanical and nuclear properties (in particular, high melting point, excellent corrosion resistance) zirconium and its alloys are widely used in nuclear technology, making them non-alternative construction material for use in the reactor core on thermal neutrons.

Problem formulation

However, there are factors that significantly reduce the possibility of their use. In particular, interstitial elements have a significant impact on service properties of zirconium – the oxygen and nitrogen that easily react to it and take part in all the processes occurring in the material under various thermal, radiation, mechanical conditions.

Analysis of modern information sources on the subject of the article

Zirconium alloys is an important constructive material for the articles of active zone and fuel claddings of nuclear power plants (including the shells fuel claddings) [1–3]. To comply nuclear safety fuel claddings of nuclear reactors impose high demands. The most vulnerable element of fuel claddings is the tube wall (Fig. 1).

In particular, interstitial elements have a significant impact on service properties of Zr1 %Nb alloy – the oxygen and nitrogen that easily react to it and take part in all the processes occurring in the material

under various thermal, radiation, mechanical conditions, but data about the influence on the structure of surface remain limited and controversial [6–11]. Therefore, it is advisable to extend the knowledge's about influence of the near-surface layers enriched of interstitial elements on properties of Zr-1 %Nb cladding tubes. It should be noted, that the interactions of interstitial elements (oxygen, nitrogen) with the zirconium leads to the formation of an interstitial solid solution: a maximum solubility in the zirconium of oxygen is 28 at. % (Fig. 2, *a*) and of nitrogen – 22 at. % (Fig. 2, *a*) [12, 13]. Furthermore, it should be noted that the dissolution of oxygen leads to formation of the ordered solid solutions (Fig. 2, *a*).

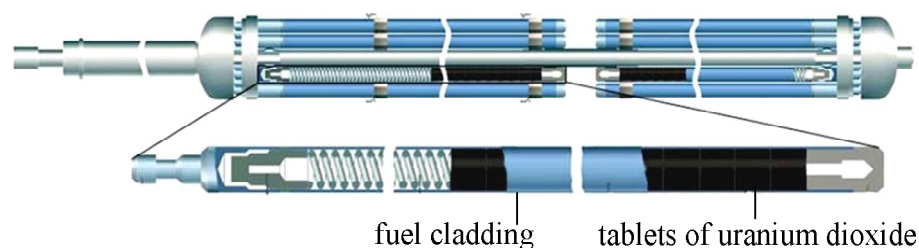


Fig. 1. The fuel claddings [4, 5]

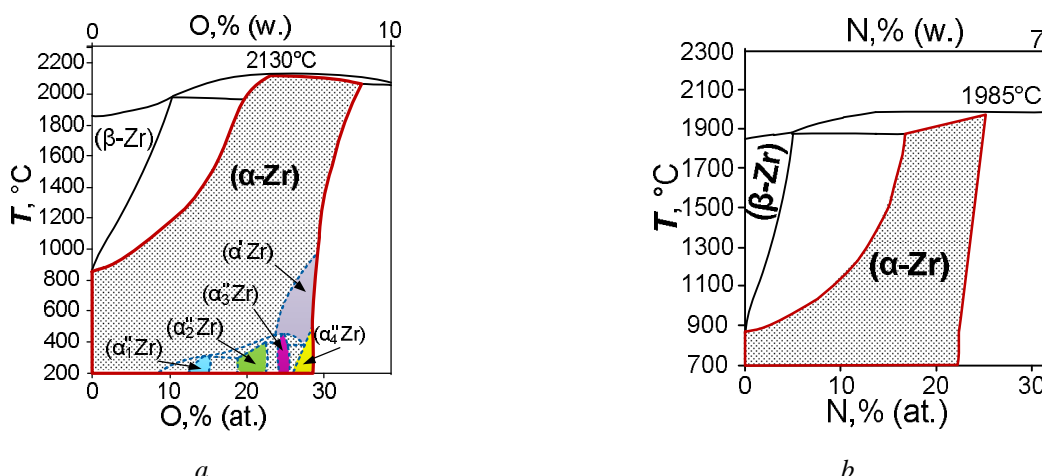


Fig. 2. Part of the binary phase diagrams for the systems Zr–O [5] and Zr–N [6]

Scientists in the field of zirconium alloys (J. Zhang, A.R. Oganov, X. Li, H. Dong and others) found that in the system Zr–O, there are several thermodynamically stable sub-oxides, namely: Zr_6O , Zr_3O , Zr_2O , ZrO and ZrO_2 (Fig. 3). These sub-oxides are characterized by their order and have special properties.

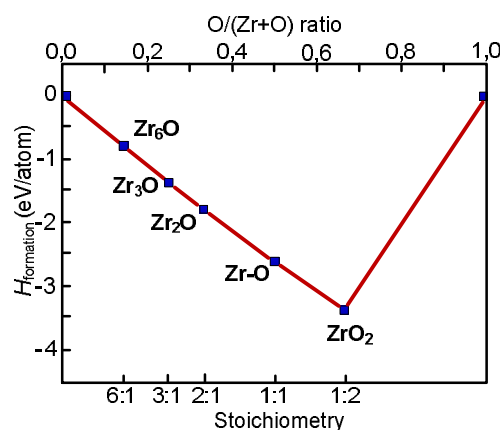


Fig. 3. Scheme of technological sample "Marine" with a sequence of the overlap-butt joint welding

Some researchers [15] noted that the hardening by oxygen leads to a non-homogeneous distribution of dislocations that complicate their separation and form sub-boundaries facilitates effective relaxation of stresses near the borders of grains by the formation of strain localization bands.

We know that strengthening zirconium by nitrogen gives better results than by oxygen [16]. The reason for this effect is that the ion radius of nitrogen is greater compared to one of oxygen ion. It should also be noted that the probability of absorption of nitrogen is lower than oxygen [17]. The presence of solid solution in hardened near-surface layers of zirconium alloys will improve the functional properties of finished products. Therefore, researchers in the field of zirconium alloys lead search of thermo-chemical treatment modes in order to form these strengthening layers. For example, scientists demonstrated the possibility of diffusion coatings formation on the zirconium in atmosphere of technically pure nitrogen [18]. However, a significant disadvantage of this treatment [18] is the high saturation temperature ($T = 900\text{ }^{\circ}\text{C}$) and the complexity of the process (putting into the reaction space TiH_2 titanium hydride) and formation small diffusion layer ($2\ldots 4\text{ }\mu\text{m}$) thick. In [19] it was proposed to strengthen the near-surface layer of zirconium by oxygen in three stages (Fig. 4).

This treatment leads to the formation of the $3\text{ }\mu\text{m}$ oxide layer thickness and $\sim 40\ldots 60\text{ }\mu\text{m}$ transitional diffusion layer. However, the above processing [19] is rather complicated from a technological point of view and therefore cannot find wide applications.

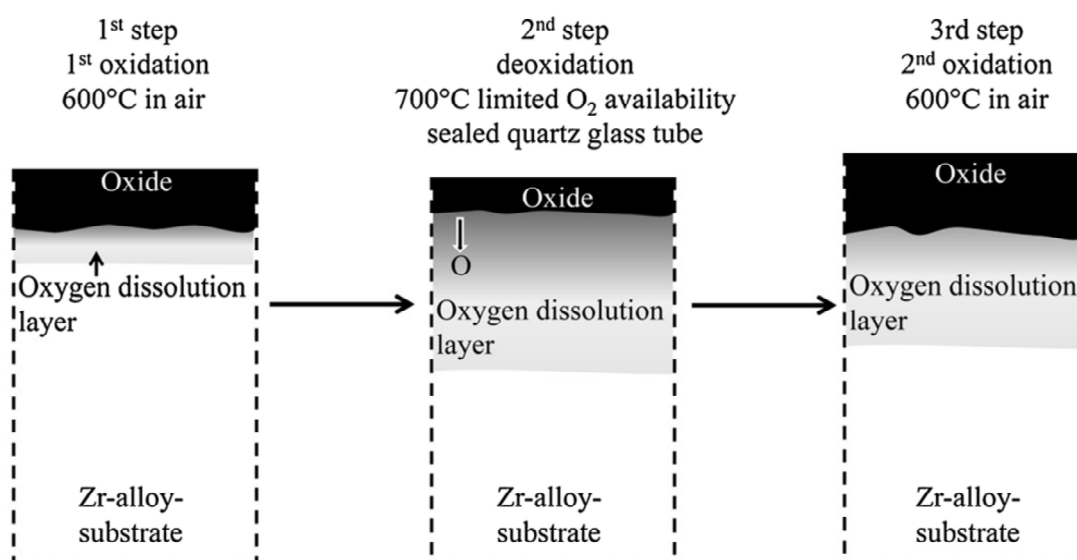


Fig. 4. Schematic layer sequences of oxidation process for an alloy with Nb-content $< 3\text{ wt } \%$ [19]

It should be noted that the regularities of diffusion layers formation have been established on samples of experimental zirconium alloys. In this work, the diffusion of near surface layers on the zirconium tubes is described, which will be important from a practical point of view.

Statement of purpose and problems of research

The purpose of the work is to establish structural transformations (weight gain, the surface hardness, the size of strengthening zone) by saturation of Zr-1 %Nb zirconium alloy after chemico-thermal treatment in a controlled oxygen- and nitrogen-containing gaseous mediums.

Experimental procedure and results

The tubes of fuel cladding from Zr-1 %Nb zirconium alloy that are made in Ukraine [20] were used for samples. The ring-samples of 3 mm width were cut from the tube (Fig. 5, *a*, *b*). After the chemical-

thermal processing (CTP) the hardness of the outer and inner sides of the ring-samples (Fig. 5, *a*) was measured.

The near surface layers saturated by interstitial elements are formed by diffusion saturation in oxygen- and nitrogen- containing controlled gas mediums, by different modes (Table. 1).

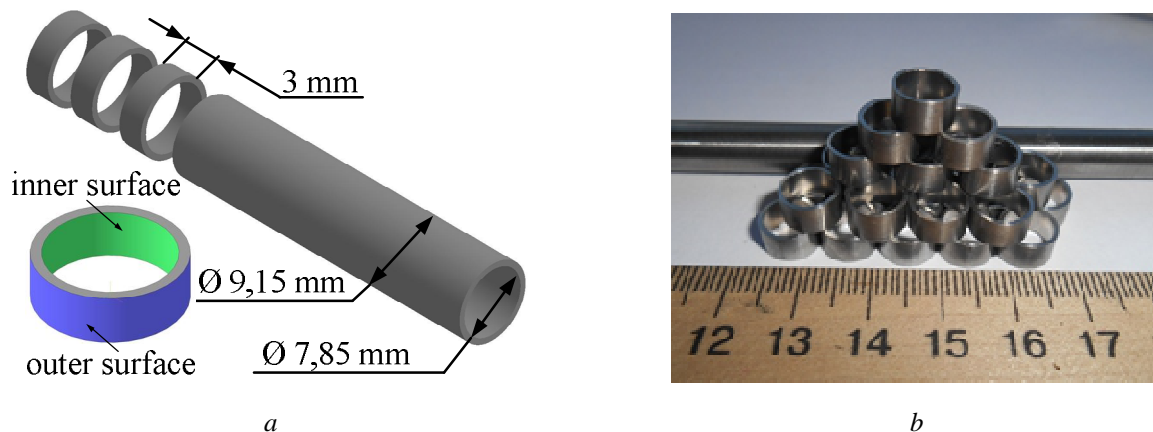


Fig. 5. Scheme cutting (*a*) and the general view of the samples (*b*)

Table 1

Modes of chemical-thermal processing of ring-samples of Zr-1 %Nb alloy

Number	Modes of chemical-thermal processing	Conditional denotation
1	before processing	P0
Processing in the oxygen-containing medium ($T = 650\text{ }^{\circ}\text{C}$, $P_{\text{O}_2} = 2,6 \cdot 10^{-1}\text{ Pa}$)		
2	$\tau = 3\text{ h}$	P1
3	$\tau = 5\text{ h}$	P2
4	$\tau = 10\text{ h}$	P3
5	$\tau = 20\text{ h}$	P4
Processing in the nitrogen medium ($T = 650\text{ }^{\circ}\text{C}$, $P_{\text{N}_2} = 1 \cdot 10^5\text{ Pa}$)		
6	$\tau = 5\text{ h}$	P5
7	$\tau = 10\text{ h}$	P6
8	$\tau = 20\text{ h}$	P7

The chemical-thermal processing of Zr-1 %Nb alloy performed on laboratory thermal equipment (Fig. 6) without leakage of air into the reaction chamber.

Determination of the mass increase ΔM ($\mu\text{g}/\text{mm}^2$) of samples was obtained by weighing them before and after the chemico-thermal processing on the electronic precision automatic scales “Voyager” with precision of measurements at 0.0001 grams. The micro hardness of samples (Fig. 7) was determined with PMT-3M device with a load 0.49 N at indenter. Construction of the micro hardness distribution curve of the tube wall thickness was performed basing on the method of least squares.

Metallographic study was performed by scanning with electron microscope (EVO 40XVP with microanalysis system INCA Energy).

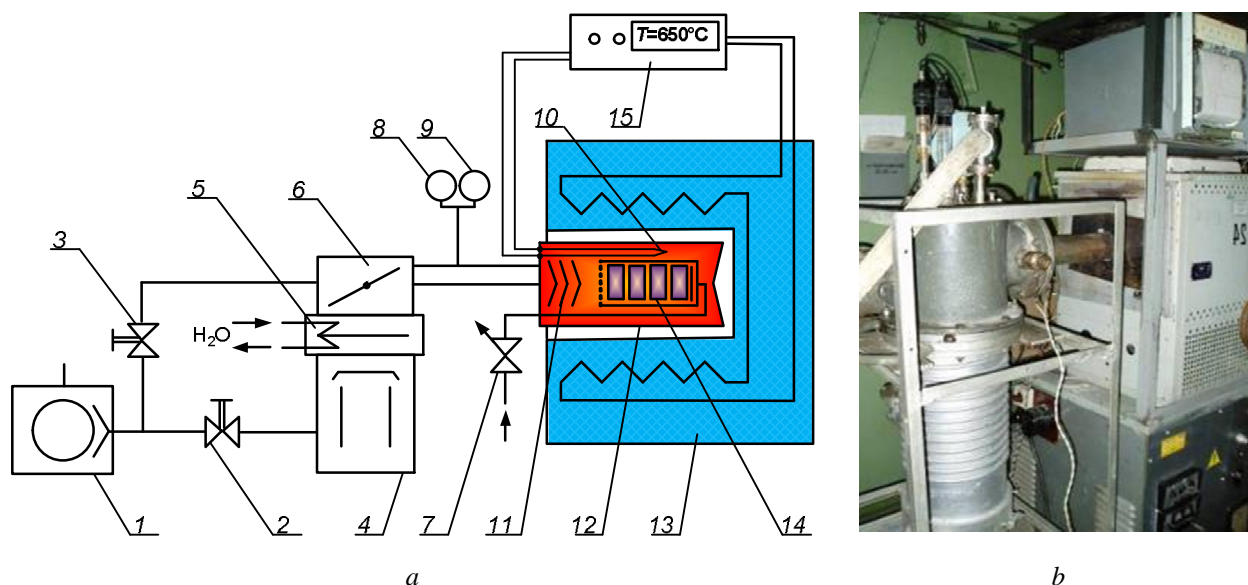


Fig. 6. Scheme of installation (a) for chemical-thermal processing of the Zr-1 %Nb alloy samples and general view equipment (b): 1 – vacuum pump; 2 – stopcock; 3 – the bypass stopcock; 4 – diffusion vacuum pump; 5 – trap of diffusion pump; 6 – controlled valve; 7 – leakage valve; 8 – thermocouple vacuum gauge; 9 – ionization vacuum gauge; 10 – thermocouple; 11 – the system of screens; 12 – the reaction chamber; 13 – furnace; 14 – container with a samples; 15 – heating control system of furnace

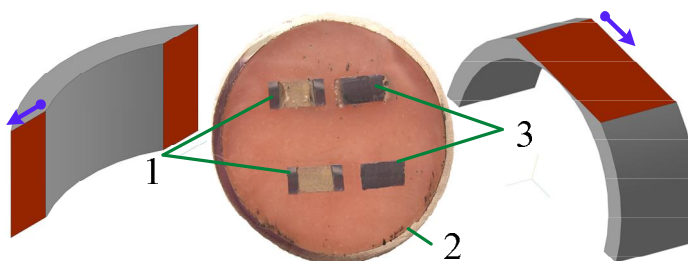


Fig. 7. Oblique ground joint for determining near-surface layer of the tube wall:

1 – on the inner surface; 2 – the general view of the sample in the pouring;
3 – on the outer surface (by arrows indicate the direction of determining the micro hardness)

Dissolving of the interstitial elements (in particular, oxygen, nitrogen) in zirconium alloys is accompanied by the distortion of the crystal lattice and, consequently, results in the increase of hardness. The external and internal tube sides are saturated with interstitial elements differently [21]. Therefore, the micro hardness of surface and near-surface layers on the inside and the outside of the tube were defined after different modes of processing. According to the results of studies greater micro hardness (oxygen amount) were recorded on the outer wall surface than on the inner part of the tube (Table 2).

Table 2

Element's concentration on the surface of Zr-1 %Nb alloy tubes after processing

Element, at. %	Modes of chemical-thermal processing			
	P0		P3	
	Outer surface	Inner surface	Outer surface	Inner surface
Zr	78,64	88,59	43,81	75,38
Nb	2,65	2,92	0,94	2,31
O	18,71	8,50	55,25	22,30

Depending on the availability of gas environment component (oxygen, nitrogen) the surface of zirconium tubes have gained a different shade (Fig. 8). For example, surface of ring-samples after treatment in the oxygen-containing atmosphere for 20 h (treatment P4) have changed light-metallic shade of tube surface to gray. Processing in nitrogen-containing atmosphere at isothermal holding 20 hour (P7 mode) – leads to a light golden shade of tube surface.



Fig. 8. The general view surface of the Zr-1 %Nb tubes after processing by the modes: 1 – P0, 2 – P4, 3 – P7

Indeed, according to the results of research (Fig. 9, Table 3) the hardness of the surface after oxidation at different processing modes ranges from 375 ± 30 HV_{0.49} to 1190 ± 95 HV_{0.49} hardness units on the outside of the tube and 325 ± 15 HV_{0.49} to 710 ± 70 HV_{0.49} on the inside surface of the tube.

The thickness of the hardened near-surface layers after 20 h exposure on the external side of tube is 75...90 μm , and the inside of tube is 65...80 μm . The probable cause of the greater surface micro hardness and hardened layer's depths on outer surface of tube is "seal" of the diffusion flux due the reducing of diffusion front that appears after penetration of the interstitial element (oxygen). The weight gain after 20 h processing is much greater than after processing for 3 h. It should be noted that after the processing for various duration $\tau = 3 \dots 20$ h, only the oxygen solid solution is formed in the near-surface layers of the metal, which is shown on the hardness distribution's (Fig. 9).

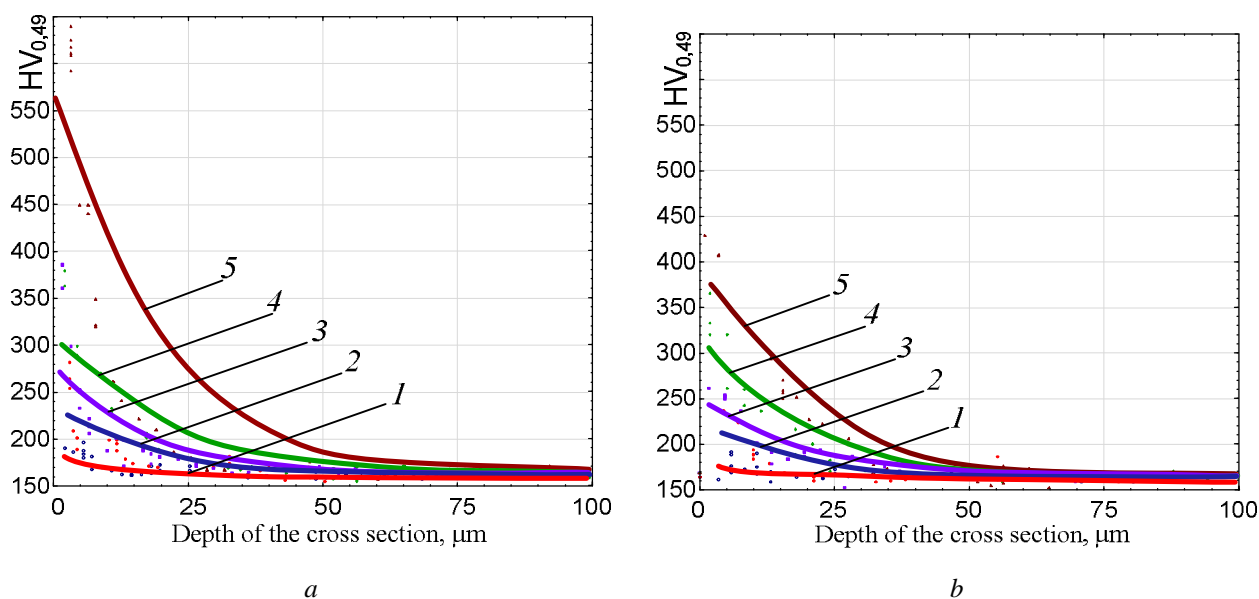


Fig. 9. The hardness distribution in the cross section of the outer (a) and inner (b) surface of the Zr-1 %Nb tubes after processing by the modes: 1 – P0, 2 – P1, 3 – P2, 4 – P3, 5 – P4

Table 3

**The effects of different modes of CTP in oxygen environment
on characteristics of ring-samples from the Zr-1 %Nb alloy**

Processing mode			P0	P1	P2	P3	P4
Micro hardness HV _{0,49}	Outer surface	Size hardened layer, μm	10...20	45...55	50...65	65...75	75...90
		ΔH	55	210	350	380	1020
		surface	225±15	375±30	515±35	550±50	1190±90
	core		170±10	165±10	165±15	170±15	170±15
	Inner surface	surface	205±10	325±15	375±30	410±45	710±70
		ΔH	35	160	210	240	540
		Size hardened layer, μm	6...15	40...50	45...50	50...60	65...80
Weight gain ΔM/S, μg/mm ²			—	0,424	1,174	1,477	5,043

Nitriding of Zr-1 %Nb alloy's tubes leads to the same increase of surface hardness and distribution of hardness in near-surface layers of tube as after oxidation, but the absolute values are somewhat smaller (Table 4, Fig. 10).

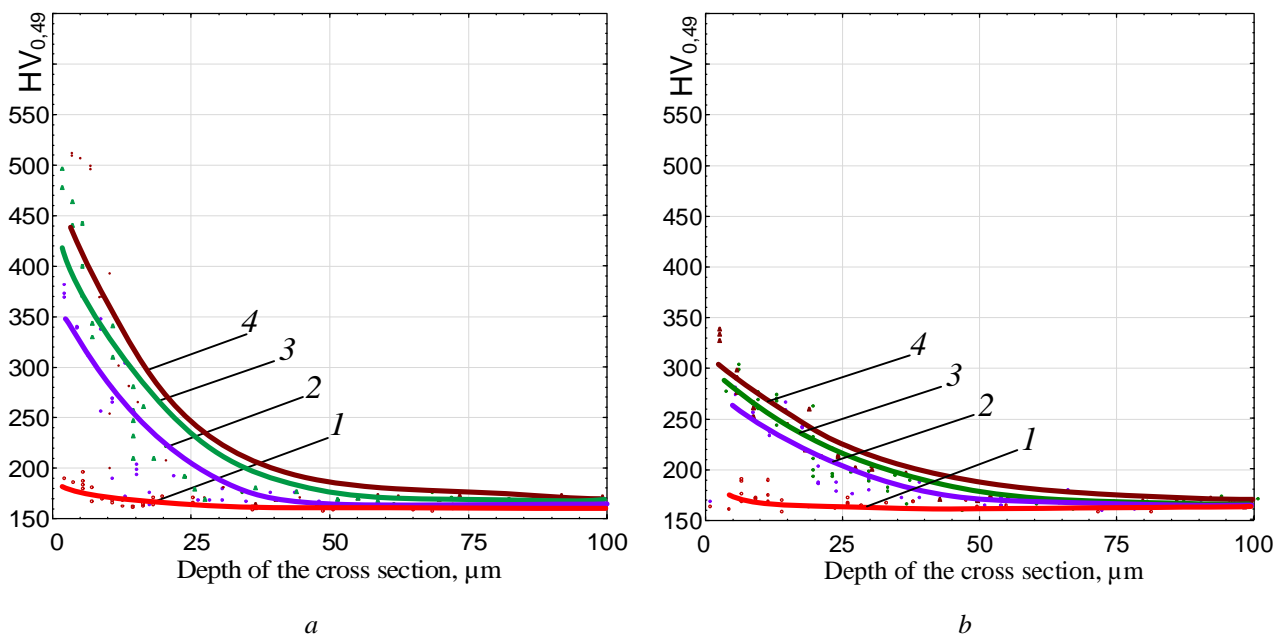


Fig. 10. The hardness distribution in the cross section of the outer (a) and inner (b) surface of the Zr-1 %Nb tubes after processing on modes: 1 – P0, 2 – P5, 3 – P6, 4 – P7

Table 4

**The effects of different modes of CTP in nitrogen environment
on the characteristic of ring-samples from the Zr-1 %Nb alloy**

Processing mode			P0	P5	P6	P7
Micro hardness HV _{0,49}	Outer surface	Size hardened layer, μm	10...20	70...80	75...85	80...90
		ΔH	55	275	375	445
		surface	225±15	440±25	545±35	615±35
	core		170±10	165±15	170±15	170±20
	Inner surface	surface	205±10	360±20	385±25	445±35
		ΔH	35	195	215	275
		Size hardened layer, μm	6...15	55...65	60...70	70...85
Weight gain ΔM/S, μg/mm ²			–	0,960	2,253	2,675

The surface hardness after nitriding at different modes of processing varies from 440 \pm 20 HV_{0.49} to 615 \pm 35 HV_{0.49} hardness units on the outside of the tube and 360 \pm 20 HV_{0.49} to 445 \pm 35 HV_{0.49} on the internal side of the tube. The thickness of the hardened near-surface layers after 20 h exposure on the outside of the tube are 85...100 μm , and the inside of the tube – 70...90 μm . The reason for lower hardness of nitrided tubes is due to the diffusion mobility of nitrogen at the processing temperature in zirconium alloy is lower than of oxygen.

Oxidation and nitriding are resulting in minor visible changes on the surface of the tubes of Zr-1 %Nb alloy (Fig. 11).

On the outer surface of the tubes after oxidation (Fig. 11, *b*) and nitriding (Fig. 11, *c*) thin films are formed based on the interstitial elements and as result micro roughness smoothing can be observed. On the inner surface of the tubes after oxidation (Fig. 11, *f*) and nitriding (Fig. 11, *g*) we observed the similar surface condition with the grain size 2...5 μm .

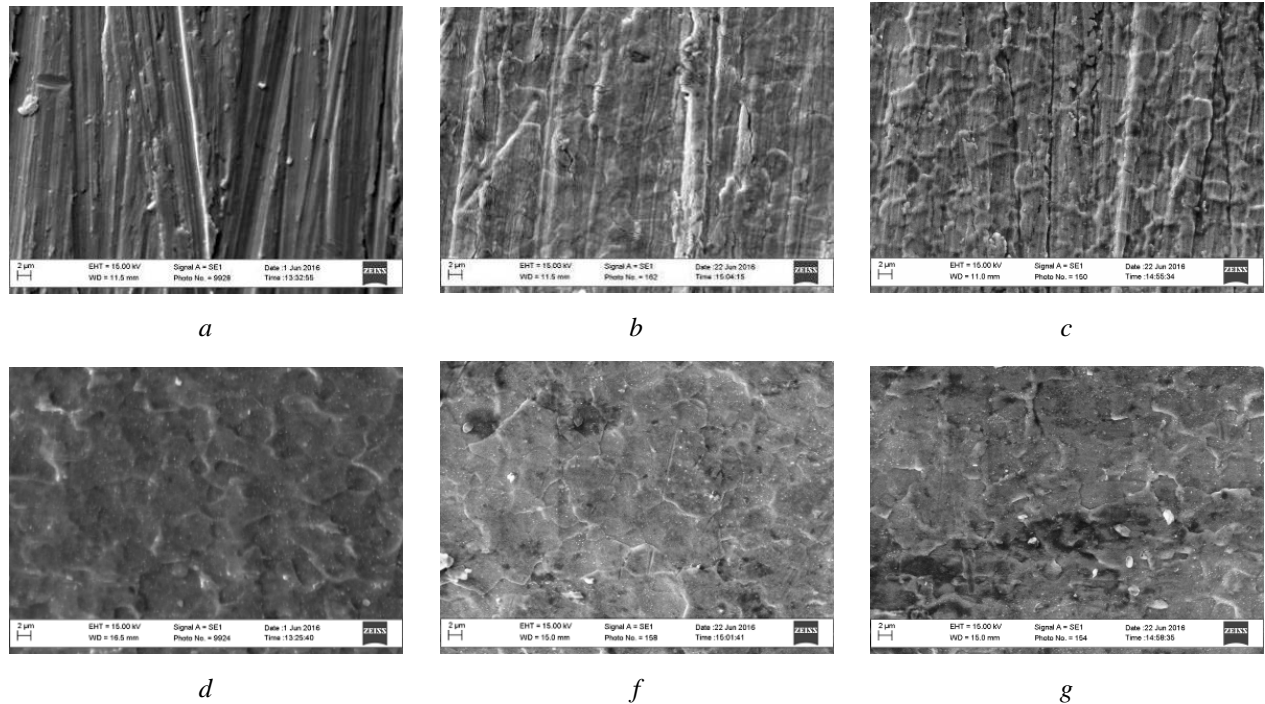


Fig. 11. The outer surface (*a, b, c*) and the inner surface (*d, f, g*) of tubes from Zr-1 %Nb alloy after the CTP modes: P0 – *a, d*; P4 – *b, f*; P7 – *c, g*

Conclusions

The influence of processing ($T = 650^{\circ}\text{C}$, $\tau = 3\text{--}20\text{ h}$) the Zr-1 %Nb zirconium alloy in the controlled oxygen- and nitrogen-containing gaseous mediums on the hardness of surface and the hardness gradient of near-surface layers and on the weight gain was shown. Differences in surface saturation of inner and outer sides of the tube by oxygen and nitrogen are noted. The micro hardness of surface on the outer side of Zr-1 %Nb alloys tubes and gradient in near-surface layer is greater than on the inner side after the saturation in oxygen- and nitrogen-containing environments. We found that the thermal processing ($T = 650^{\circ}\text{C}$) in oxygen-containing gaseous atmosphere leads to greater weight gain and depth of hardened zone compared to processing in a nitrogen atmosphere.

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