Oxidation and Nitriding Tubes of Zr-1%Nb Zirconium Alloy

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Abstract **– *The work presents results of saturation of Zr-1% Nb tubes after processing in oxygen- and nitrogen- containing gas environments. The distribution of micro-hardness in the thickness of the tube and the thickness of the hardened layers, the weight gain was determined. It is found that the oxidation of the Zr-1%Nb alloy (T = 650°C, $P_{O2}=2.6\cdot10^{-1}$ Pa, τ = 3…20 h) makes a greater weight gain than nitriding (T = 650°C, τ = 5…20 h). The state of the surface of the inside and outside of Zr-1%Nb tubes for fuel cladding depending of the processings time was shown. The differences in saturation of outside and inside of the tube was showed. In particular, the hardness of internal surface of the tube is smaller relative to the outside after oxidizing and nitriding was found. The results of study of the outer and inner surface of fuel cladding in contact with gaseous environment containing oxygen and nitrogen are interesting for investigators of reactor materials.***

Keywords – zirconium alloy, oxygen, nirtrogen, surface hardnes, hardened layer, weight gain.

I. Introduction

Through a combination of unique physical, mechanical and nuclear properties the 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 [1, 2]. However, there are factors that significantly reduce the possibility of their use. In particular, a significant impact on service properties of zirconium provides an interstitial element – the oxygen, which easily reacts to him and takes 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 remains limited and controversial [3, 4]. Therefore, it is advisable to extend the knowledge about influence of the near-surface layers enriched with the 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.% and of nitrogen – 22 at.% [5, 6]. Furthermore, it should be noted that the dissolution of oxygen leads to formation of the ordered solid solutions (fig. 1).

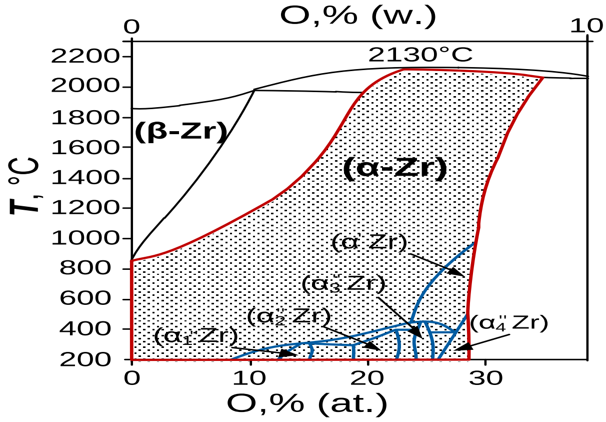


Fig. 1. Part of the binary phase diagram for the system Zr–O [5]

Purpose of the work – to establish of structural transformations (weight gain, the surface hardness, the depth of hardened zone) at saturation of Zr-1%Nb zirconium alloy after heat processing in a controlled oxygen- and nitrogen-containing gaseous mediums.

II. Materials and methods

The tubes of fuel cladding from Zr-1%Nb zirconium alloy that are made in Ukraine [7] were used as prototypes. The ring-samples of 3 mm width were cut from tube (fig. 2 *a*). After the chemical-thermal processing (CTP) the hardness of the outer and inner side of the ring-sample (fig. 2 *b*) was measured.

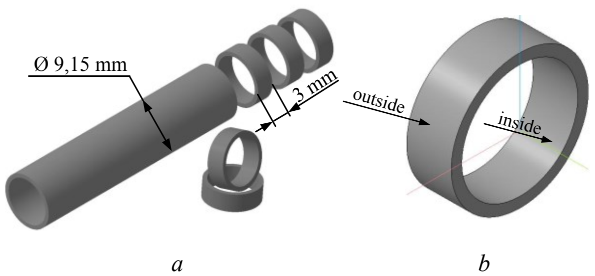


Fig. 2. Scheme cutting (*a*) and the general view of the sample (*b*)

The chemico-thermal processings of samples was carried out with the laboratory thermical equipment (fig. 3) in a controlled oxygen- and nitrogen-containing gas environments without inleakage into the reaction chamber of the furnace at various modes (tabl. 1).

Determining the mass increase ΔM (μg/mm^2) of samples was obtained by weighing them before and after the chemico-thermal processing on the electronic precision automatic scales firm «Voyager» to within 0.0001 grams. The micro hardness of samples was determined at device PMT-3M with a load 0,49 N at indenter. Metallographic study was performed by scanning with electron microscope (EVO 40XVP with microanalysis system INCA Energy).

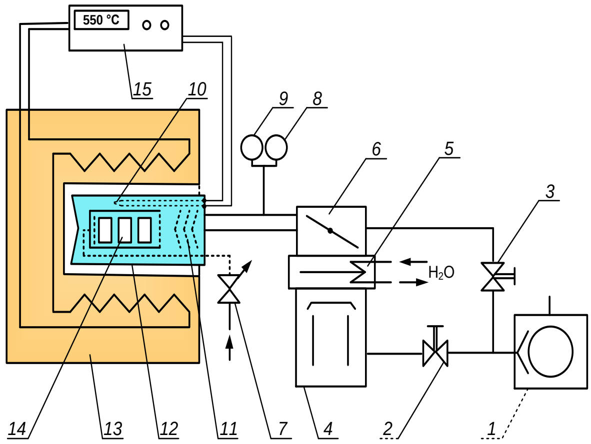


Fig. 3 Scheme of installation for chemical-thermal processing of the Zr-1%Nb alloy samples:
1 – backing vacuum pump; 2 – stopcock; 3 – the stopcock buy a pass; 4 – diffusion vacuum pump; 5 – trap diffusion pump; 6 – controlled valve; 7 – leak valve; 8 – thermocouple vacuum gauge; 9 – high ionization vacuum gauge; 10 – thermocouple; 11 – the system of screens; 12 – the reaction vial; 13 – furnace; 14 – container with a samples; 15 – heating furnace control system

TABLE 1

MODES OF CHEMICAL-THERMAL PROCESSING ZR1%NB ALLOYS

Number	Modes of chemical-thermal processing	Conditional denotation
1	before processing	**P0**
Processing in the oxygen-containing medium ($\boldsymbol{T}$ = 650°C, $\boldsymbol{P}_{O2}$=2,6·10^{-1} Pa)		
2	τ = 3 h	**P1**
3	τ = 5 h,	**P2**
4	τ = 10 h	**P3**
5	τ = 20 h	**P3**
Processing in the nitrogen medium ($\boldsymbol{T}$ = 650°C)		
6	τ = 5 h	**P5**
7	τ = 10 h,	**P6**
8	τ = 20 h	**P7**

Construction of the microhardness distribution curve of the tube thickness was performed basing on the method of least squares.

III. Results and discussion

Dissolving of the interstitial elements (in particular, oxygen, nitrogen) in zirconium alloys accompanied by the distortion of the crystal lattice and, consequently, results in the increase of hardness. The external and internal tube sides saturate with interstitial elements differently [8]. Therefore, after different modes of processing the micro-hardness of surface and near-surface layers on the inside and the outside of the tube were defined. According to the results of studies greater amount of oxygen was recorded on the outer wall surface than on the inner part of the tube (tab. 2). Therefore, it is to expect a difference in microhardness on the outside and inside surfaces of the tube.

TABLE 2

ELEMENT CONCENTRATION ON SURFACE OF TUBES OF ZIRCONIUM ALLOY ZR-1%NB ALLOY AFTER PROCESSING

Modes of CCT		Zr	Nb	O
		at.%	at.%	at.%
P0	Outside	78,64	2,65	18,71
	Inside	88,59	2,92	8,50
P3	Outside	43,81	0,94	55,25
	Inside	75,38	2,31	22,30

Indeed, according to the results of research (fig. 4, 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 to the outside of the tube and 325±15 $HV_{0,49}$ to 710±70 $HV_{0,49}$ inside surface of the tube. The thickness of the hardened near-surface layers after 20 h exposure: on the external side of tube – 75...90 µm, and the inside of tube – 65...80 µm. The probable cause of the greater surface microhardness and hardened layer's depths on outer surface of tube is that after penetration of the interstitial element (oxygen) is "seal" of the diffusion flux due the reducing of diffusion front. Weight gain after 20 h processing on the order of magnitude greater than after processing for 3 h. It should be noted that the processing on various time τ = 3...20 h only the solid solution of oxygen is formed in the surface layers of the metal which is vindicated by the hardness distribution curves (fig. 4)

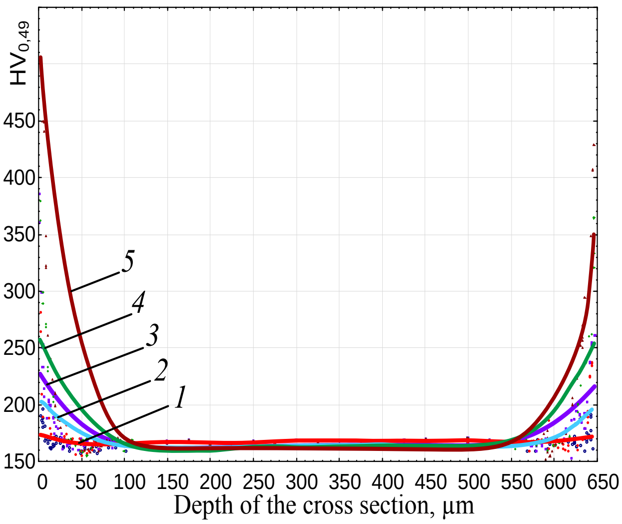


Fig. 4. The hardness distribution in the cross section of the Zr-1%Nb alloy tube after processing on modes:
1 – **P0**, 1 – **P1**, 3 – **P2**, 4 – **P3,** 5 – **P3**

Nitriding processing of Zr-1%Nb alloy's tubes leads to the same increase of surface hardness and distribution of hardness in nearsurface layers of tube as after oxidation, but the absolute values are somewhat smaller (fig. 5, table. 4).

TABLE 3

THE EFFECTS OF DIFFERENT MODES OF CTP IN AN OXYGEN ENVIRONMENT ON THE CHARACTERISTICS OF RING-SAMPLES FROM THE ZR-1%NB ALLOYS

Processing mode			P0	P1	P2	P3	P4
Microhardness $HV_{0,49}$	outside	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
	inside	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 $\Delta M/S$, µg/mm^2			-	0,424	1,174	1,477	5,043

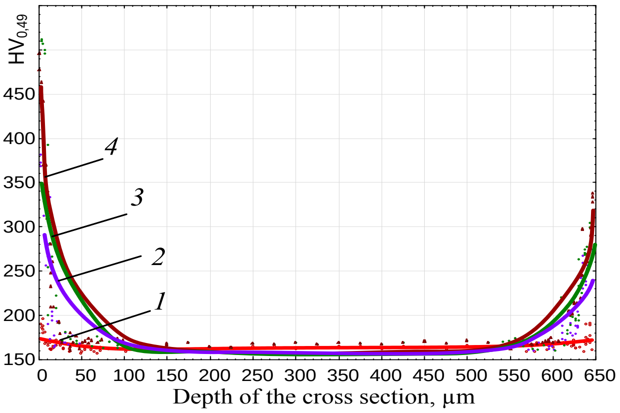


Fig. 5. The hardness distribution in the cross section of the Zr-1%Nb alloy tube after processing on modes: 1 – **P0**, 1 – **P5**, 3 – **P6**, 4 – **P7**

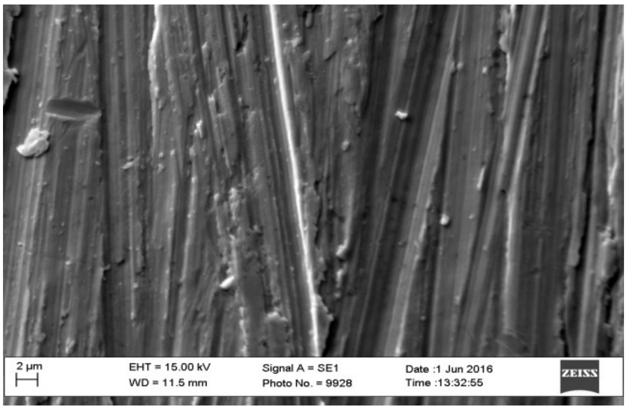
TABLE 4

THE EFFECTS OF DIFFERENT MODES OF CTP IN NITROGEN ENVIRONMENT ON THE CHARACTERISTIC OF RING-SAMPLES FROM THE ZR-1%NB ALLOYS

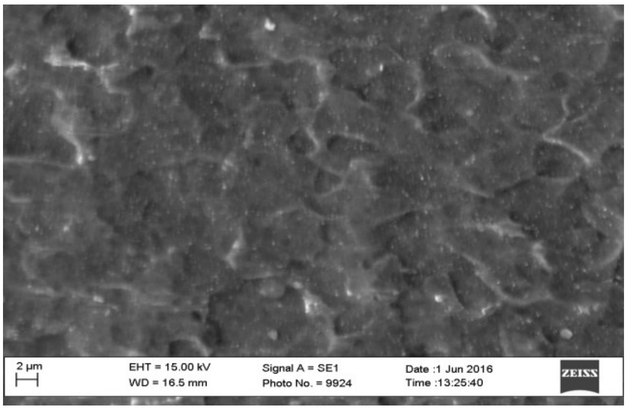
Processing mode			P0	P5	P6	P7
Microhardness $HV_{0,49}$	outside	Size hardened layer, µm	10…20	70…80	75…85	80…90
		ΔH	55	275	375	445
		surface	225±15	440±25	545±35	615±35
	core		170±10	165±15	170±15	170±20
	inside	surface	205±10	360±20	385±25	445±35
		ΔH	35	195	215	275
		Size hardened layer, µm	6…15	55…65	60…70	70…85
Weight gain $\Delta M/S$, µg/mm^2			-	0,960	2,253	2,675

The surface hardness after nitriding at different m odes of processings ranges from 440±20 $HV_{0,49}$ to 615±35 $HV_{0,49}$ hardness units to the outside of the tube and 360±20 $HV_{0,49}$ to 445±35 $HV_{0,49}$ with internal side of the tube. The thickness of the hardened near-surface layer after 20 h exposure: on the outside of the tube is 85…100 µm, and the inside of the tube – 70…90 µm. The reason for lower hardness of nitrided tube is due that the diffusion mobility of nitrogen at the processing temperature in zirconium is lower than for oxygen.

The state of the surface of the cladding studied with an electron microscope before processing (fig. 6) and after oxidation (fig. 7) and nitriding (fig. 8) for τ = 20 h. As seen from the photographs, the differences in the state of the various surfaces of the fuel cladding tube before CTP processing (fig. 6) were observed. On the outer surface the machining traces (fig. 6 *a*) are observed, and on the inner surface – they are missing (fig. 6 *b*).



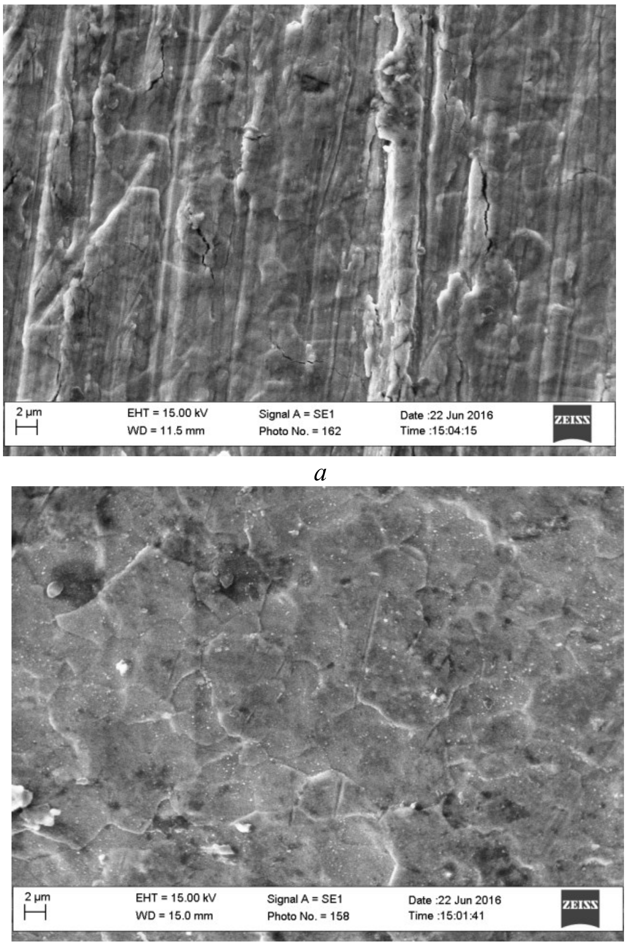
a



b

Fig. 6. The outside (*a*) and the inside (*b*) surfaces of tubes from Zr-1%Nb alloy before the CTP modes

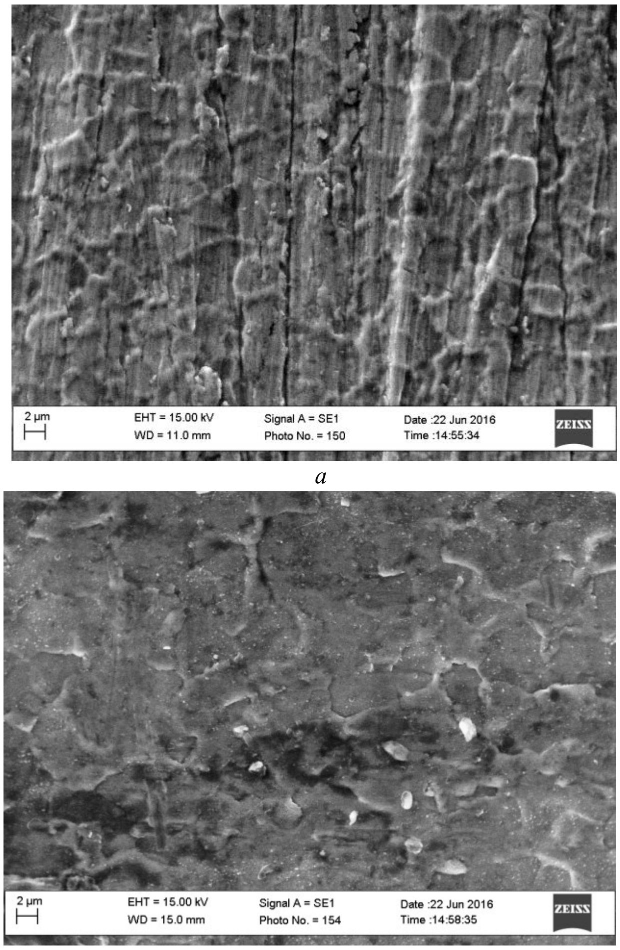
Oxidation and nitration resulting in minor visible changes on the surface of the tubes of Zr-1%Nb alloy (figs. 7, 8). On the outer surface of the tubes after oxidation (fig. 7 *a*) and nitriding (fig. 8 *a*) formation of thin films based on the interstitial elements can be observed, which flattens microroughness and should enhance the surface roughness. On the inner surface of the tubes after oxidation (fig. 7 *b*) and nitriding (fig. 8 *b*) we observed the similar surface condition with the size of the grain boundaries 2…5 µm.



a

b

Fig. 7. The outer (*a*) and inner (*b*) surfaces' view of tubes of Zr-1%Nb alloy after processing at CTP mode ***P3***



a

b

Fig. 8. The outer (*a*) and inner (*b*) surfaces' view of tubes of Zr-1%Nb alloy after processing at CTP mode ***P7***

Conclusion

The influence of processing ($\boldsymbol{T}$ = 650°C, τ = 3...20 h) the zirconium alloy in the controlled oxygen- and nitrogen-containing gaseous mediums on the hardness of surface and the hardness gradient of nearsurface layers, weight gain was showed. Differences in surface saturation of inner and outer sides of the tube by oxygen and nitrogen are established. On the outer side of Zr-1%Nb alloys tubes the microhardness of surface and gradient in near-surface layer is greater than on the inner side at the saturation in oxygen- and nitrogen-containing environments. We found that the thermal processing ($\boldsymbol{T}$ = 650°C) in oxygen-containing gaseous atmosphere leads to greater weight gain and depth of hardened zone regarding to processing in a nitrogen atmosphere.

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