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INFLUENCE OF THERMOCHEMICAL TREATMENT ON PROPERTIES OF TUBES FROM Zr-1%Nb ALLOY

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The influence of treatment in the controlled oxygen- and nitrogen-containing gas medium on the mass increment and properties of the subsurface layers of samples-rings, cut out of the fuel cladding tubes from Zr-1%Nb, has been established experimentally. Differences in the saturation of internal and external surfaces of zirconium tubes were described. Results of examining the hardness of external and internal subsurface layers of the ring-samples after oxidizing and nitriding are presented. It has been established experimentally that prolonged isothermal annealing at 750 ºC in the oxygen medium can lead to the initiation of a crack on the inner surface of zirconium tubes.

INTRODUCTION

Zirconium alloys are important structural material for products of an active zone and the nuclear fuel cladding (NFC) of nuclear power plants [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 NFC is the wall of a tube [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) 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.% [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.

Depending on the temperature-temporal and gas-dynamics parameters of zirconium interaction with oxygen-containing medium, in the subsurface layers of metal, an oxide film and/or only a diffusion layers is formed. In article [9] it was shown 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 until $T = 1205$ °C; at this temperature it is converted to tetragonal modification.

Recently, significant attention has been paid to study the mechanism of the air interaction (in fact, simultaneous action of oxygen and nitrogen) with a fuel cladding from zirconium alloys. 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 [10]. Using the chart p_{O_2}/p_{N_2}, which is presented in [11], it is possible to determine the bounds of stability of Zr, ZrO_2, and ZrN existence depending on temperature. According to the results of the studies, presented in the article [12], the mass increment of the nitrated sample are increases with an increase in oxygen in metal. With an increase in oxygen content, the grain dimensions decrease [10]. In article [13], 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.

Correlation between the volume content of oxygen and hardness, as well as distribution of oxygen concentration and hardness gradient in the subsurface layers after treatment in oxygen-containing mixture is shown in articles [6] and [14], respectively.

A number of papers give experimental data 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 NFC tube from Zr-1%Nb alloy in steam at temperature $T = 600$ °C, the microhardness of the external surface of the tube is higher relative to the internal surface [15].

Paper [16] also shows differences of saturation of the external and internal surfaces of the NFC tubes after saturation in oxygen medium. The authors do not explain this interesting scientific phenomenon, but only state the very fact of existence of a difference.

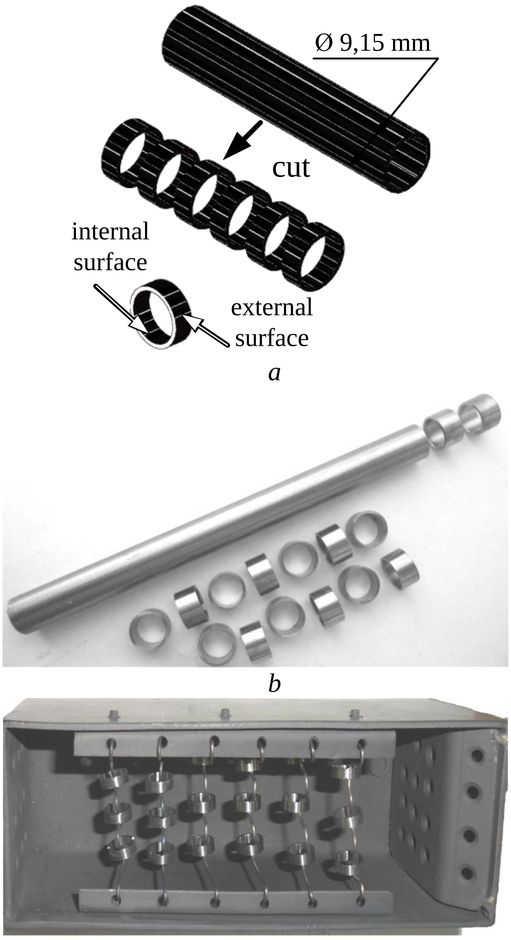
In paper [17], it was shown that solid solution strengthening of alloy Zr-2.5%Nb with oxygen causes a uniform distribution of dislocations, makes it difficult to separate them with the formation of sub-boundaries, and facilitates the effective relaxation of stresses near grain boundaries by forming deformation localization bands. It is the effective relaxation of stresses and the low mobility of dislocations, which determines the high shear stability at the microlevel that determine the good mechanical properties of the alloy under investigation.

Therefore, in accordance with the above literature review, it was shown that physical-mechanical properties of zirconium are very 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 because of thermochemical treatment, the saturation of the subsurface layers with interstitial elements of finished NFC tubes is possible. However, there are very few studies dealing with the influence of the strengthened subsurface layers with oxygen or nitrogen.

Therefore, the aim of this paper is to study the influence of modes of thermochemical processing and a level of saturation by oxygen and nitrogen on the characteristics of external and internal shell surfaces of the heat generating elements. In fact, to predict functional properties of the NFC tubes, it is important to know depth of the strengthened subsurface layers and surface morphology after the treatment in gas media.

MATERIALS AND METHODS

We chose as the material of research the nuclear fuel cladding tubes made of zirconium alloy Zr-1%Nb, produced in Ukraine [18]. For kinetic studies, we used the samples-rings, which were cut out of an NFC tube (Fig. 1).



c

Fig. 1. Schematic (a) and general view (b) and placement of ring-samples in a container (c), which were cut from the NFC tube

Thermochemical treatment of zirconium alloys was performed in the controlled oxygen- and nitrogen-containing gas medium under different modes (Tabl. 1) using laboratory thermal equipment, which prevent leakage of air into the reaction chamber (Fig. 2).

Table 1

Modes of thermochemical processing
of ring-samples of Zr-1%Nb alloy

Number	Modes of thermochemical processing	Conditional denotation
1	Before processing (initial state)	*R*0
Processing in the oxygen-containing medium *O*1 (T = 650 °C, $P = 1.3\cdot10^{-1}$ Pa)		
2	τ = 3 h	*O*1-3
3	τ = 5 h	*O*1-5
4	τ = 10 h	*O*1-10
5	τ = 20 h	*O*1-20
Processing in the nitrogen medium *N* (T = 650 °C, $P_{N2}=1\cdot10^5$ Pa)		
6	τ = 5 h	*N*-5
7	τ = 10 h	*N*-10
8	τ = 20 h	*N*-20
Processing in the oxygen-containing medium *O*2 (T = 750 °C, $P = 1.3\cdot10^{-1}$ Pa)		
9	τ = 5 h	*O*2-5
10	τ = 10 h	*O*2-10
11	τ = 20 h	*O*2-20

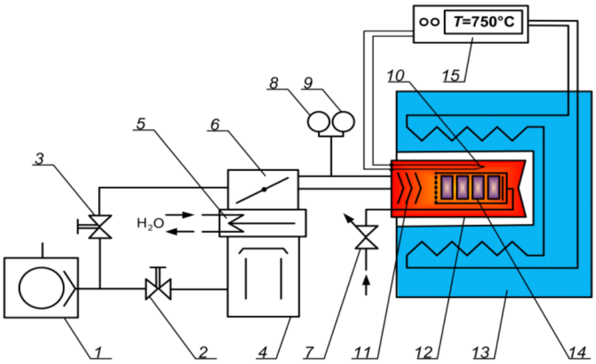


Fig. 2. Scheme of installation for thermochemical processing of the Zr-1%Nb alloy samples:
1 – vacuum pump; 2 – stopcock; 3 – the bypass stopcock; 4 – diffusion vacuum pump; 5 – trap of diffusion pump; 6 – controlled valve; 7 – leakage valve; 8 – thermocouple vacuum gauge; 9 – ionization vacuum gauge;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

Metallographic 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 N.

Zirconium samples were weighed before and after treatment on the precision balance, produced by Voyager (OHAUS, Switzerland), with precision

±0.0001 g. Before weighting and treatment, the samples were washed in alcohol and dried.

RESULTS AND DISCUSSION

Depending on the availability of gas environment component (oxygen, nitrogen) the surface of zirconium tubes have gained a different shade (Fig. 3). For example, surface of ring-samples after treatment in the oxygen-containing atmosphere for 20 h (treatment *O*1-20) have changed light-metallic shade of tube surface to gray. Processing in nitrogen-containing atmosphere at isothermal holding 20 h (*N*-20 mode) – leads to a light golden shade of tube surface.

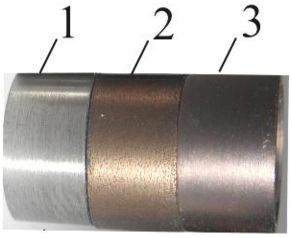


Fig. 3. General view of outer surface of the Zr-1%Nb ring-samples after processing by the modes: 1 – R0; 2 – N-20; 3 – O1-20

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. 4, curves 1, 2). Treatment in nitrogen-containing medium leads to a change in the mass of samples by the parabolic law (see Fig. 4, curves 3, 4).

This indicates that during treatment under modes *O*1 and *O*2, a dense (continuous) protective oxide film is not formed on the ring-samples within 20 h [8, 16]. Parabolic law of change in the mass of ring-samples during nitriding indicates the formation of a dense nitride film, which controls the process of high-temperature interaction of samples with nitrogen and slows down the absorption of the nitrogen [8, 16].

An increase in temperature of the treatment medium from $T = 650$ °C (mode *O*1) to $T = 750$ °C (mode *O*2) leads to an increase in the rate of interaction with the rarefied oxygen-containing medium approximately by 2.7 times (see Fig. 4, curves 1, 2).

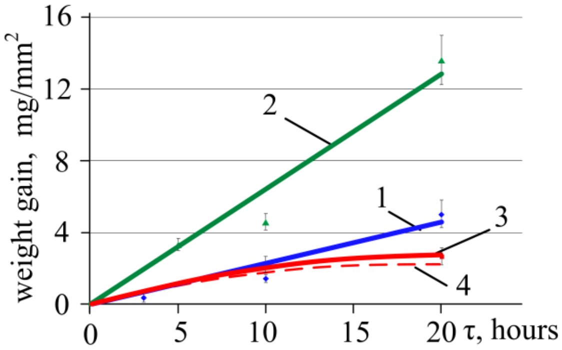


Fig. 4. The mass changes of ring-samples of zirconium Zr-1%Nb alloy under different treatment modes: 1 – O1 mode; 2 – O2 mode; 3 – mode N; 4 – the parabolic law of change in mass for compare

As evidenced by the results of measurement of microhardness before the treatment, in the subsurface layers, there is no a strengthened layer on both external and internal surfaces (Tabl. 2). According to research results (see Tabl. 2), the hardness of external surface of the ring-samples after treatment at $T = 650$ °C in the oxygen-containing medium (*O*1-3…*O*1-20) varies in the range from $H^{\text{surface}} = (375 \pm 30)$ $\text{HV}_{0.49}$ to $H^{\text{surface}} = (1190 \pm 90)$ $\text{HV}_{0.49}$ 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 (see Tabl. 2 and Figs. 5–7).

Table 2

Characteristics of the samples from Zr-1%Nb alloy after treatment in the gas medium at different modes

Gas media	Treatment mode	External surface		Matrix, H^{core}, $\text{HV}_{0.49}$	Internal surface	
		H^{surface}, $\text{HV}_{0.49}$	Size Hardened layer *l*, μm		H^{surface}, $\text{HV}_{0.49}$	Size Hardened layer *l*, μm
Before processing	*R*0	225±15	10…20	170±10	205±10	6…15
Nitrogen T=650 °C	*N*-5	440±25	45…55	170±15	360±20	35…45
	N-10	545±35	50…60	165±15	385±25	45…55
	N-20	615±35	55…65	170±15	445±35	50…60
Oxygen, T=650 °C	*O*1-3	375±30	45…55	165±10	325±15	40…45
	*O*1-5	515±35	55…65	165±15	375±30	45…50
	*O*1-10	550±50	60…70	170±15	410±45	50…55
	*O*1-20	1190±90	70…80	170±15	710±70	60…65
Oxygen, T=750 °C	*O*2-5	880±55	55…65	180±10	735±60	50…55
	*O*2-10	1000±65	75…80	185±10	865±75	65…70
	*O*2-20	1510±70	95…105	190±10	1205±80	85…91

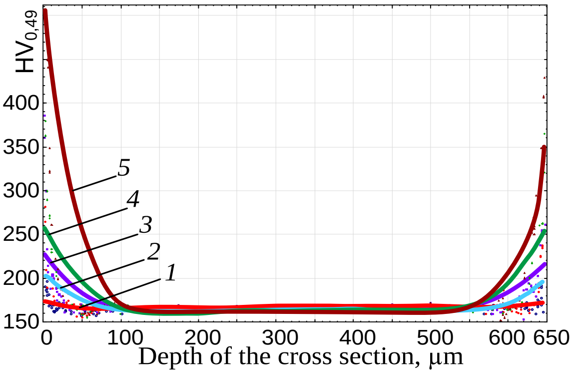


Fig. 5. The hardness distribution in the cross section of the Zr-1%Nb tubes after processing by the modes: 1 – R0; 2 – O1-3; 3 – O1-5; 4 – O1-10; 5 – O1-20

It was found that with an increase in the duration of maintaining in oxygen-containing medium (*O*1 mode), the hardness of the internal surface of the sample-ring increases from $H^{\text{surface}} = (325 \pm 15)$ $\text{HV}_{0.49}$ to $H^{\text{surface}} = (710 \pm 70)$ $\text{HV}_{0.49}$. The hardness of the inner surface of the sample-ring after treatment in the nitrogen-containing medium (mode *N*) at similar temperature and time parameters grows less, in particular from $H^{\text{surface}} = (360 \pm 20)\ \text{HV}_{0.49}$ to $H^{\text{surface}} = (445 \pm 35)\ \text{HV}_{0.49}$.

An increase in temperature (*O*2 mode) intensifies the interaction of zirconium samples with oxygen-containing gas medium (see Tabl. 2 and Fig.7) and increases the mass increment of samples (see Fig. 4).

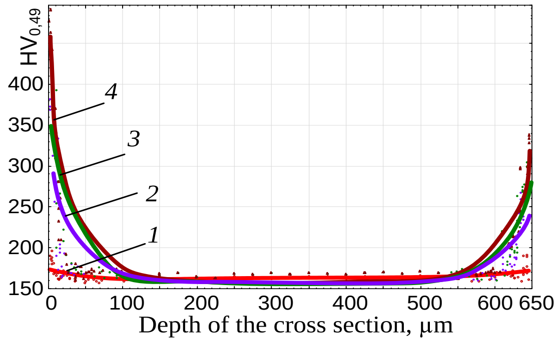


Fig. 6. The hardness distribution in the cross section of the Zr-1%Nb tubes after processing by the modes: 1 – R0; 2 – N-5; 3 – N-10; 4 – N-20

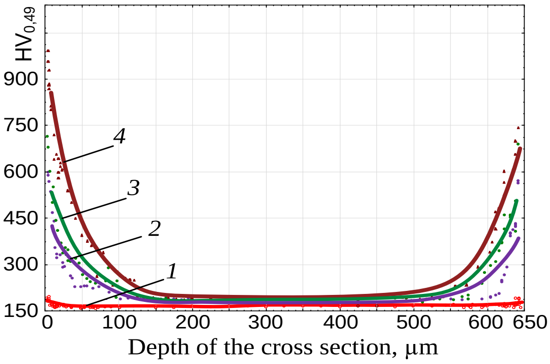


Fig. 7. The hardness distribution in the cross section of the Zr-1%Nb tubes after processing by the modes: 1 – R0; 2 – O2-5; 3 – O2-10, 4 – O2-20

With an increase in temperature of interaction with rarefied oxygen-containing medium, the rate of surface hardness increment is much lower than the difference of rates of mass increment of samples (compare Fig. 8 with Fig. 4). This behavior may be explained by the fact that dependence of hardness on the oxygen content in zirconium is not linear in nature [16].

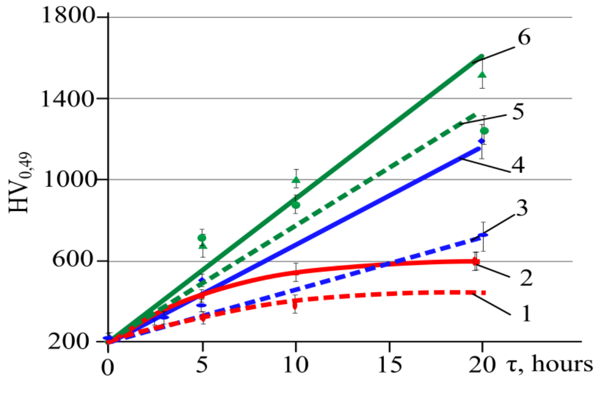


Fig. 8. The changes in time of the hardness of the outer surface (2, 4, 6) and the inner surface (1, 3, 5) of ring-samples after treatment by the modes: 1, 2 – N; 3, 4 – O1; 5, 6 – O2

Treatment in the oxygen-containing medium leads to a linear change of the surface hardness of samples-rings. This indicates the absence of a dense surface oxide film, which is a substantial diffusion barrier. Treatment in nitrogen-containing medium leads to a parabolic dependence of surface hardness of ring-samples on time (see Fig. 8).

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. 9). In all cases, the strengthened layer on external side was thicker than on internal side.

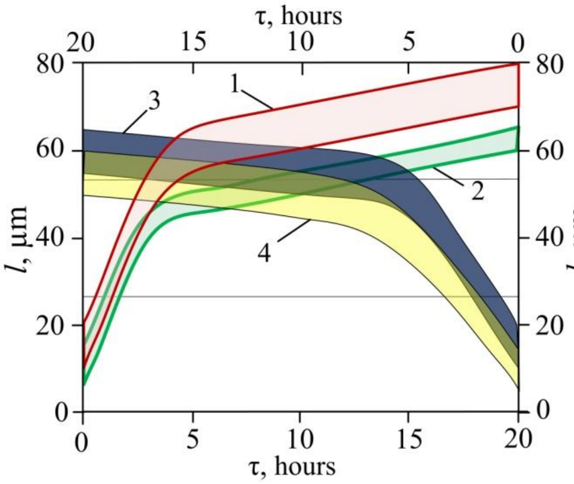


Fig. 9. A change in the dimensions of strengthened layer on the external surface (1, 3) and internal surface (2, 4) of ring-samples after treatment under modes: 1, 2 – O1; 3, 4 – N. Comment: for the nitriding regime N (curves 3, 4), see the upper scale of abscissas

It is interesting to note, that after treatment in oxygen-containing medium at 750 °C for 20 h (*O*2-20 mode), cracks on the internal surface of ring-samples were observed (Fig. 10).

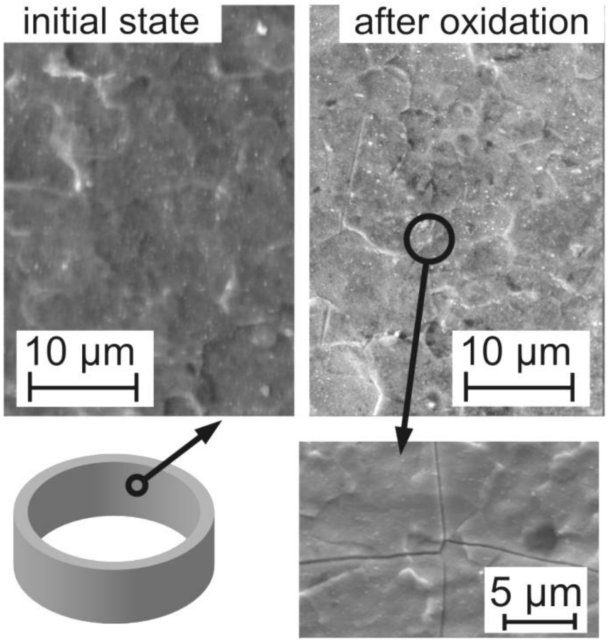


Fig. 10. View of inner surface of Zr-1%Nb tube samples after treatment under mode O2-20

The cause of cracks appears to be the stresses arising during cooling resulting from the difference between the coefficients of thermal expansion of the oxide and the metal matrix and the effect of the ratio of the volume of the oxide to the volume of the metal (Pilling-Badworth ratio) on the concave surface.

CONCLUSION

Analysis of the results obtained allows us to draw the following conclusions:

– change in mass of sample-rings at the treatment under reduced oxygen pressure (mode *O*1 and *O2*) is close to a linear law, while at the treatment at atmospheric pressure in nitrogen (mode *N*) the law mass change is close to parabolic;

– the strengthened layer on external side of Zr-1%Nb ring-samples was thicker than on internal side at all modes of heat treatment in the controlled oxygen- or nitrogen containing gas medium;

– the hardness of the outer surface of the tube samples as upon oxidation and upon nitriding higher than the hardness of inner surface.

The researches in the direction of the study of influence of different modes of thermochemical processing of samples-rings Zr-1%Nb alloy on their short-term and long-term mechanical properties and interaction with hydrogen are in process.

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ВЛИЯНИЕ ХИМИКО-ТЕРМИЧЕСКОЙ ОБРАБОТКИ НА СВОЙСТВА ТРУБОК ИЗ СПЛАВА Zr-1%Nb

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Экспериментально установлено влияние термической обработки в контролируемых газовых средах, содержащих кислород и азот, на прирост массы и свойства поверхностных слоев образцов-колец, вырезанных из твэльных трубок. Описаны различия в насыщении внутренних и внешних поверхностей циркониевых трубок. Определена твердость внешней и внутренней поверхностей образцов-колец после окисления и азотирования по разным режимам. Экспериментально обнаружена продолжительность изотермической выдержки в кислородной смеси, которая может привести к образованию трещины на внутренней поверхности циркониевых трубок.

ВПЛИВ ХІМІКО-ТЕРМІЧНОЇ ОБРОБКИ НА ВЛАСТИВОСТІ ТРУБОК ЗІ СПЛАВУ Zr-1%Nb

В.С. Труш, В.М. Федірко, О.Г. Лук'яненко, М.А. Тихоновський, П.І. Стоєв

Експериментально встановлено вплив термічної обробки в контрольованих газових середовищах, що містять кисень та азот, на приріст маси та властивості приповерхневих шарів зразків-кілець, вирізаних з твельних трубок. Описано відмінності в насиченні внутрішніх і зовнішніх поверхонь цирконієвих трубок. Представлені результати твердості зовнішніх та внутрішніх поверхонь зразків-кілець після окислення та азотування за різними режимами. Експериментально виявлено тривалість ізотермічної витримки в кисневій суміші, яка може призвести до утворення тріщини на внутрішній поверхні цирконієвих трубок.