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MECHANICAL AND ACOUSTIC CHARACTERISTICS OF OXIDIZED, NITRIDED AND OXYNITRIDED Zr-1%Nb ZIRCONIUM ALLOY

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The effect of the gaseous medium composition during thermo-chemical treatment (TCT) on the mechanical properties and acoustic parameters of Zr-1%Nb zirconium alloy was studied. It is shown that TCT in oxygen-nitrogen contained gaseous media significantly increases the surface hardness and does not worsen the mechanical characteristics (including their plasticity) of zirconium alloy which is used as a material for case of fuel nuclear rod. It is established that TCT in different mediums also influences on acoustic parameters of the Zr-1%Nb alloy. Noticeable changes in the acoustic parameters observed at the initial stage of deformation are associated with the features of the destruction of a thin film formed on the zirconium alloy surface after TCT.

INTRODUCTION

Zirconium alloys are one of the main structural materials for core products and fuel elements of nuclear power reactors [1, 2]. They are widely used in nuclear power engineering due to a unique complex of properties: low neutron capture cross-section, high corrosion resistance, high melting point, and good mechanical properties. Zirconium alloys are widely used for the production of parts for nuclear reactors: fuel cladding and structural components of the fuel assembly (guide thimbles, central tube, rigid angles, channel pipes).

For nuclear safety, increased requirements are needed for the fuel rod elements of nuclear reactors. The most important components of fuel rod elements are cladding tubes, which provide the necessary mechanical strength and dimensional stability of the structure, protect nuclear fuel and distribution products from the action of the coolant.

Cladding tubes are operated in difficult conditions while being exposed to temperature, radiation, corrosive environment and mechanical stress. Outside, they undergo corrosion upon contact with a coolant with a temperature of up to 380 °C, and from the inside – corrosion under the action of moisture, hydrogen, fluorine, iodine, caesium and other elements released from the fuel during the operation of fuel rod elements. Cladding tubes are also constantly under the influence of mechanical stress from the weight of fuel pellets and their expansion during operation [1, 2]. The material and design of a fuel rod element have to provide reliable operation for a long time under extremely difficult operating conditions. Therefore, high requirements are needed for the materials of fuel rod cladding in terms of strength, ductility and creep resistance [3, 4].

Zr-1%Nb zirconium alloy is used as a material for fuel rod element cladding, successfully operating in pressurized water-cooled reactors at a temperature of 300 ºC. During operation in a reactor, damage accumulates in fuel rod cladding leading to structure and property change under the influence of a whole set of external and internal factors. Sometimes this leads to the destruction of the fuel rod cladding. The critical processes that limit the service life of the material in the reactor are water corrosion and hydrogenation [5–13]. In order to reduce the negative impact of these processes, research is currently underway to create new and improve existing zirconium alloys that can work reliably for a long time in reactor conditions at a temperature of 400 °C and above. In this regard, new methods are being developed for applying protective coatings and modifying surface zirconium and its alloys. The main objectives of surface modification of cladding tubes are to strengthen the surface layers to reduce wear of the tubes under the influence of cavitation and friction processes, as well as to slow down the formation of hydrides.

A promising method for the purposeful formation of the phase-structural state of the surface layer of metal is thermo-chemical treatment (TCT), in particular, the method of controlled thermodiffusion saturation of surface layers with oxygen and nitrogen, developed at the Karpenko Physico-Mechanical Institute of the NAS of Ukraine (Lviv).

Thermodiffusion saturation provides the formation of hardened near-surface layers for various functional purposes on both zirconium and titanium [14–19]. An important feature of this method is the possibility of treatment of long and complex products, such as tubes. The efficiency of TCT depends on the correct choice of treatment parameters: temperature, time and pressure. These parameters allow controlling the size and properties of the surface modified layer after TCT. To substantiate the expediency of using TCT, it is necessary to conduct comparative tests of samples in the initial state and after TCT.

The purpose of the work is to study the influence of the composition of the medium during TCT on the mechanical and acoustic characteristics of fuel rod cladding Ukrainian-made Zr-1%Nb zirconium alloy.

EXPERIMENTAL PROCEDURES

Ukrainian fabricated Zr-1%Nb zirconium alloy was used in this research. The principal technological schemes for the fabrication of Zr-1%Nb zirconium alloy for nuclear reactors and the production of fuel rod claddings are detailed and shown in [20–22]. A feature of this alloy was the use of calcium-thermal and iodide zirconium as a base with additives of pipe production waste, taken in a weight ratio of 60, 30, and 10%, respectively. The chemical composition of the Zr-1%Nb alloy after two vacuum arc remelting is given in Table 1 [20–22].

Table 1

Chemical composition of Zr-1%Nb alloy ingots

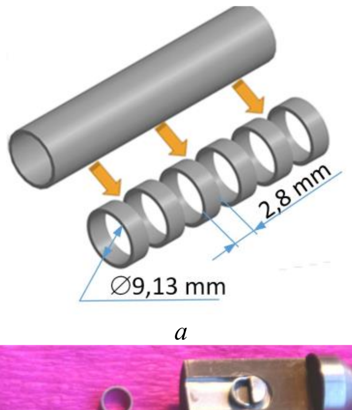
Element content, wt.%					
O_2	N_2	C	Nb	Si	Fe
0.095	0.005	0.005	1.0	0.004	0.014

For TCT was used special equipment developed at the Karpenko Physical-Mechanical Institute of the NAS of Ukraine. Thermodiffusion saturation of the zirconium alloy was carried out in oxygen-, nitrogen- and combined nitrogen-oxygen-containing gaseous media. The treatment regimens are following:

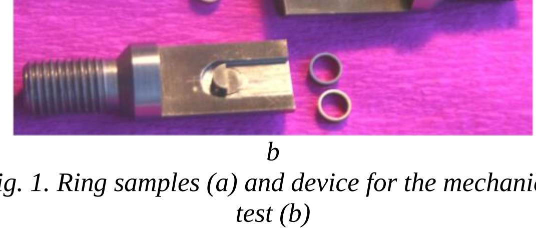
– Oxygen-containing media (***R1*** – T = 580 °C, τ = 3 h, ***P*** = 0.133 Pa; ***R2*** – ***T*** = 580 °C, τ = 0.5 h, P = 1.33 Pa + ***T*** = 580 °C, τ = 2.5 h, $P = 1.33 \cdot 10^{-2}$ Pa);
– Nitrogen-containing media (***R3 – T*** = 580 °C, τ = 10 h; ***R4*** – ***T*** = 650 °C, τ = 10 h);
– Combined nitrogen-oxygen-containing gaseous media (***R5*** – ***T*** = 650 °C, τ = 5 h, with cooling in an oxygen-containing environment).

The tensile mechanical characteristics and microhardness were determined and to explain the change in material properties metallography and structure-sensitive method and acoustic emission were used [23–25].

For studies, ring samples with dimensions 9.13x0.67x2.8 mm were cut from cladding tubes made of Zr-1%Nb alloy (Fig. 1,a). Samples before tests were mechanically polished and ultrasonic cleaned.



a



b

Fig. 1. Ring samples (a) and device for the mechanical test (b)

Surface and matrix hardening before and after TCT of zirconium alloy was determined by PMT-3M device with 0.49 N loads on indenter. To measure microhardness, we have used a Vikers' diamond indenter in the form of a pyramid with a square basis and an angle between opposite faces at the vertex equal to 136°.

During mechanical tests, the samples were stretched in the transverse direction on a 1958 U10-1 universal testing machine using special grippers (see Fig. 1,b) at a strain rate of 0.17 mm/min ($2 \cdot 10^{-4}$ s^{-1}) at room temperature.

Acoustic emission (AE) parameters (activity, total sum of pulses, and amplitude distribution of acoustic emission signals) were recorded synchronously with the mechanical characteristics using the acoustic complex M400 [26, 27], the analysis of which made it possible to determine the features of deformation of the sample material and the surface layer at different stages of deformation. A TsTS-19 piezoceramic transducer with a resonant frequency of 180 kHz was used as an AE sensor. The sensor was fixed to the test sample through a special waveguide, which served as one of the mounting supports for the sample in the test fixture (Fig. 2). To determine the characteristics of the state of surfaces, non-destructive testing can also be used [28].

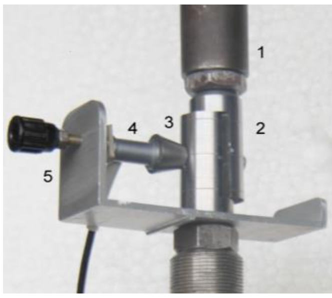


Fig. 2. Devices for testing ring sample for mechanical and AE test: 1 – capture; 2 – mounting unit of the ring sample; 3 – cone waveguide; 4 – sensor AE; 5 – frame device

The collection, processing and analysis of the results, which included information on acoustic emission and deformation parameters, was carried out using a computer and specially developed data processing programs.

RESULTS AND THEIR DISCUSSION

The dissolution of penetration elements (oxygen, nitrogen) in metals (including zirconium alloys) is associated with a distortion of the crystal lattice, resulting in a significant increase in hardness. Therefore, an increase in surface microhardness and depth of the hardened layer indicates that, as a result of TCT, the near-surface layer was enriched with penetration elements (Table 2).

Table 3 shows the mechanical characteristics of Zr1%-Nb alloy ring samples after different TCT regimes. TCT of samples in oxygen, nitrogen and a combined oxygen-nitrogen media (according to regime ***R1–R5***) does not lead to an increase in tensile and yield strength compared to the initial state (***R0***) (see Table 3).

There is a tendency for a slight fluctuation in the values of deformation towards the failure after the TCT.

Table 2

The results of the hardness testing of Zr-1%Nb alloy after TCT

Regime	Surface microhardness HV, GPa	Matrix microhardness HV, GPa	Depth of the hardened layer *l*, μm
R0	2.60±0.25	1.70±0.15	15…19
R1	3.10±0.25	1.70±0.15	19…24
R2	2.75±0.20	1.70±0.15	22…27
R3	3.20±0.15	1.70±0.15	32…37
R4	3.15±0.15	1.70±0.15	34…39
R5	5.20±0.40	1.70±0.15	38…43

Table 3

Mechanical characteristics of Zr-1%Nb alloy samples in the initial state and after TCT in various gaseous media

Regime	Tensile strength, MPa	Yield strength, MPa	Elongation, %
R0	465.0±7.5	387.5±3.6	29.6±1.8
R1	448.9±0.5	370.3±0.5	35.8±0.1
R2	459.0±9.5	390.0±0.8	33.7±0.5
R3	447.6±2.5	374. 8±4.0	30.4±1.5
R4	432.5±7.5	368. 0±5.5	27.3±0.2
R5	432.1±2.5	355.9±2.0	26.8±0.2

To analyse the obtained results, histograms were constructed, which made it possible to visually compare the effect of TCT regimes on mechanical parameter (ultimate strength, yield strength, and deformation to failure). The initial mechanical characteristics were used for fuel rod samples in the state of supply (Fig. 3).

The nature of the deformation curves (Fig. 4) was evaluated, which made it possible to estimate the magnitude of the stress in the sample in any area of deformation and showed the features of the deformation processes in the areas of strengthening and necking. Fig. 4 shows the deformation curves of the tested zirconium alloy samples in the initial state and after different regimes of TCT.

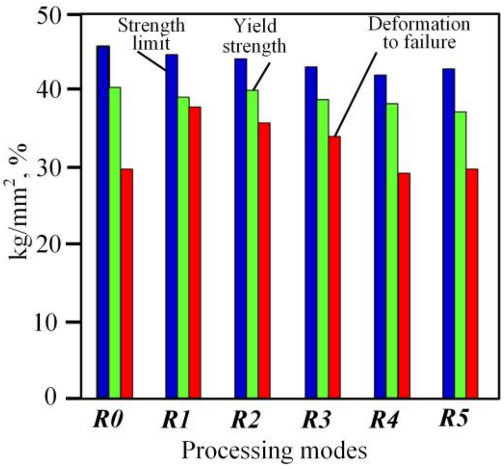


Fig. 3. Mechanical properties of Zr-1%Nb samples after different regimes of TCT

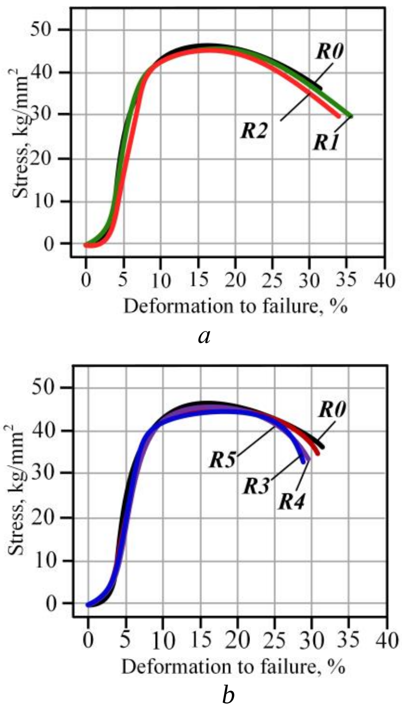


*Fig. 4. Deformation curves (a, b) of Zr-1%Nb alloy samples in the initial state (**R0**) and after TCT in various gaseous media (**R1–R5**)*

According to durometric and mechanical tests, it was established that TCT in different media leads to the formation of a hardened surface layer. However, the TCT regimes have little effect on the mechanical characteristics (elongation, tensile and yield strength) compared to the Zr-1%Nb alloy in the initial state. That is, the TCT modes used in this research do not significantly change the characteristics of the macroscopic deformation of fuel rod elements of claddings made of Zr-1%Nb alloy. The observed fluctuations in mechanical properties are in the range of scatter during testing.

Fig. 5 shows the dependence of the sum of AE pulses on the elongation during the deformation of Zr-1%Nb alloy ring samples.

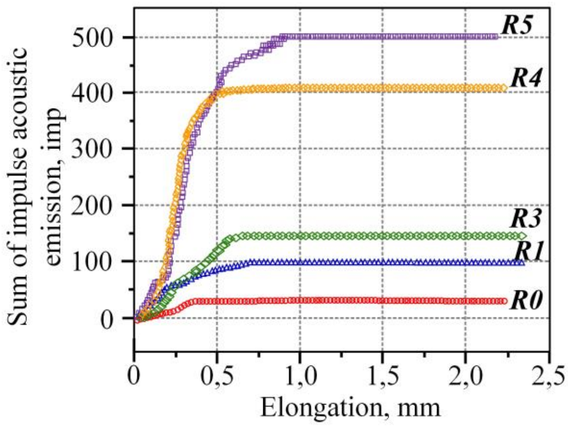


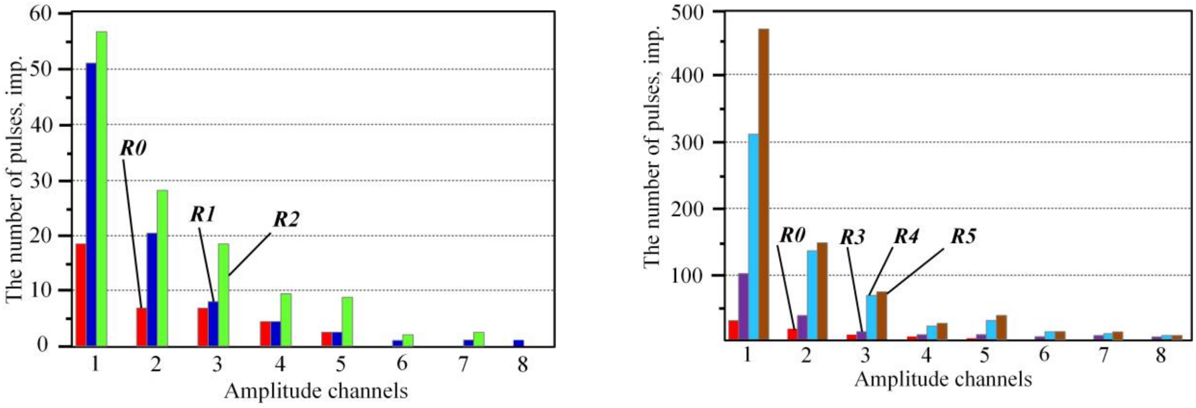
Fig. 5. Dependence of the sum of AE pulses on elongation during deformation of Zr-1%Nb alloy ring samples

The results of the experimental data show that the sum of registered AE pulses depends on the temperature, time exposure and medium of the TCT. From the above data, the following conclusions:

– TCT by different modes leads to an increase in the sum of AE pulses in samples compared to untreated Zi-1%Nb alloy samples;

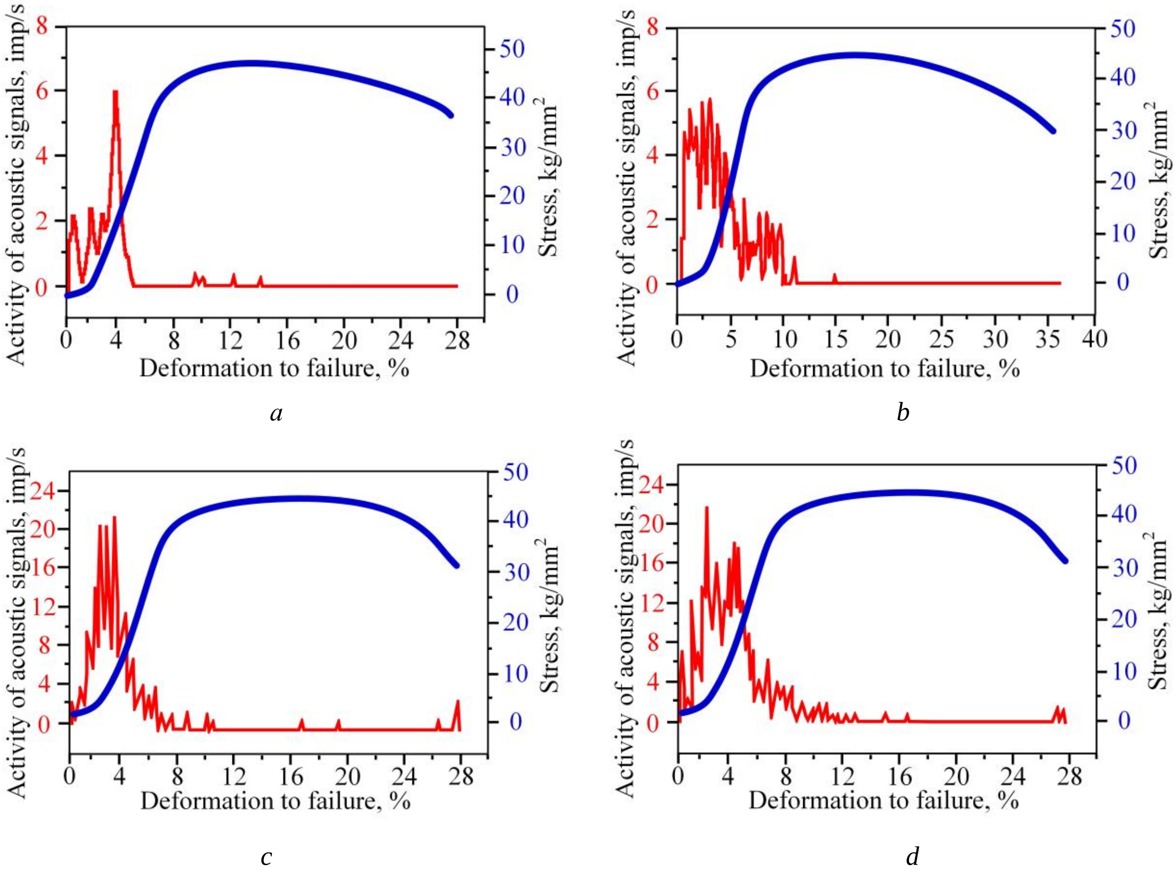
– TCT of samples in a nitrogen-containing (***R4***) and combined nitrogen-oxygen gaseous media (***R5***) leads to a significant difference in the magnitude and nature of the accumulation of AE signals compared to untreated samples.

Fig. 6 shows the amplitude distribution of AE signals when the samples are deformed to failure. An analysis of the data of this distribution showed that the nature of amplitude distribution of the untreated and treated samples of fuel rod claddings tested in this work does not change.



a *b*

*Fig. 6. Amplitude distribution of AE signals during deformation of Zr-1%Nb alloy ring samples in the initial state (**R0**) and after TCT: a – TCT in an oxygen-containing media (**R1, R2**);*
*b – TCT in a nitrogen-containing media (**R3, R4**) and combined nitrogen-oxygen-containing media (**R5**)*



a *b*

c *d*

Fig. 7. AE activity and deformation curves of samples after different TCT regimes:
*a – in the initial state (**R0**); b – **R1**; c – **R4**; d – **R5***

It is obvious that the features of AE that are observed at the beginning of the deformation of the Zr-1%Nb alloy samples are associated with the peculiarity of the behaviour of surface films formed during TCT. The main contribution to the total sum of AE pulses of the samples comes from the failure of surface hardened film. On the surface of untreated samples, the film that forms during the manufacture of the fuel cladding is not very strengthened and is characterized by a weak adhesion strength to the metal. Therefore, even at low loads. the film begins to break down and peel off, TCT at a temperature of 650 °C in nitrogen and combined nitrogen-oxygen gaseous media forms a strengthened film with strengthened adhesion, so we register more signals and a wider range of deformations.

To analyse features of acoustic emission, let us consider the dependences of the AE activity for samples of the initial state (***R0***) and after TCT according to different regimes in different media. Additionally, strain curves for these samples (***R1, R4, R5***) were superimposed on the AE activity dependence graph (Fig. 7).

The assumption about the role surface layer is confirmed by an increase in the sum of registered AE pulses for samples after TCT at a higher temperature and treatment time. Another confirmation of this assumption is the analysis of the fractography of the destroyed samples of the zirconium alloy. On Fig. 8 shows the fracture surface of Zr-1%Nb zirconium alloy ring samples in the initial state (***R0***) and after TCT in a combined nitrogen-oxygen media at 650 °C (***R5***).

Analysis of the obtained data showed:

– registration of AE signals begins immediately after the start of loading;

– the maxima on the activity curves fall in the stress region. below the yield strength;

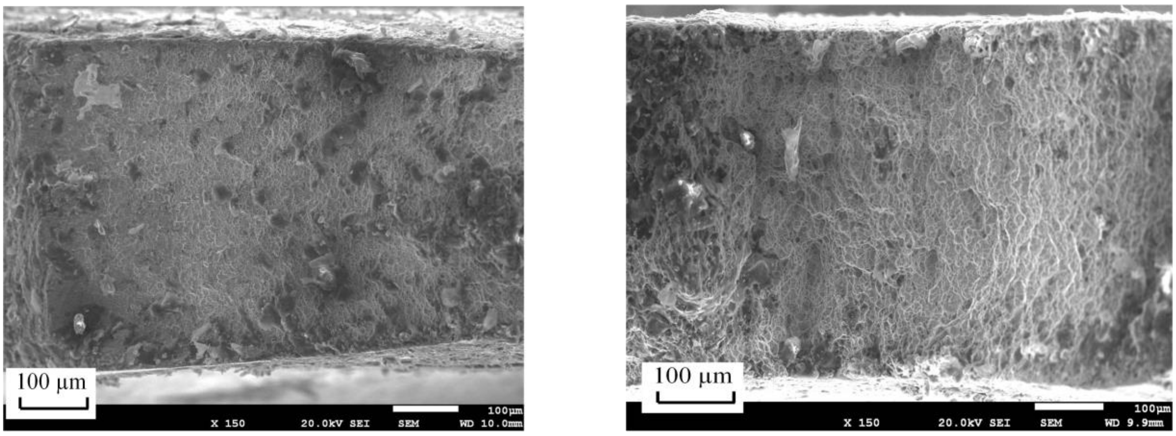
– AE activity in the initial state samples during deformation is low and it increases after in TCT treated samples;

– the generation of AE signals in the treated samples continues up to higher strains;

– after the yield strength, the AE activity drops sharply and remains low until the failure of the material.

Therefore, it can be assumed that, in addition to the gradient layer, an oxide or nitride layer is formed on the surface of the tube during TCT, which is an additional source of AE.

An analysis of the obtained AE parameters showed that the difference in TCT regimes leads to more noticeable changes in the acoustic characteristics than in the mechanical characteristics.



a *b*

Fig. 8. Fracture surface of zirconium alloy samples in the initial state ***R0*** *(a) and after TCT by regime* ***R5*** *(b)*

CONCLUSIONS

1. TCT in oxygen-, nitrogen-, combined oxygen-nitrogen-containing gaseous media significantly increases the surface hardness and depth of the hardened layer Zr-1%Nb alloy samples and does not worsen the mechanical properties of fuel rod samples, including their plasticity.

2. When determining the impact exerted by various time-temperature regimes and the gaseous media of TCT on the properties of the alloy, the acoustic characteristics turned out to be more informative compared to the mechanical ones. Noticeable changes in the acoustic parameters of the samples of the Zr-1%Nb alloy, observed at the beginning of deformation. are associated with the features of the failure of a thin film formed on the surface as a result of TCT.

3. An increase in the surface hardness and depth near-surface hardened gradient layer and the preservation of mechanical properties after the TCT allows us to expect higher efficiency in lowering the rate of hydrogenation and oxidation of fuel rod cladding made of Zr-1%Nb zirconium alloy.

REFERENCES

1. А.С. Займовский, А.В. Никулина, Н.Г. Решетников. *Циркониевые сплавы в атомной энергетике.* М.: «Энергоиздат», 1981, с. 232.
2. Д.Л. Дуглас *Металловедение циркония* / Под ред. А.С. Займовского. М.: «Энергоатомиздат», 1975, с. 360.
3. П.П. Маркелов, А.А. Никулина, М.М. Перегут, Н.Г. Решетников. *Ползучесть оболочек твэлов из циркониевых сплавов:* Препринт ВНИИНМ. М., 1978, с. 135.
4. С.А. Никулин, А.Б. Рожнов, А.В. Бабукин. Структура и сопротивление разрушению циркониевых сплавов для атомной энергетики // *МиТОМ*. 2005, №5, с. 8-17.
5. Б.А. Колачев. *Водородная хрупкость металлов.* М.: «Металлургия», 1985, с. 217.
6. Н.М. Власов, И.И. Федик. Водородное охрупчивание сплавов циркония // *Металловедение и термическая обработка металлов*. 2003, №8, с. 48-51.
7. В.А. Гольцов. Водород в металлах // *ВАНТ. Серия «Атомно-водородная энергетика».* 1977, в. 1, с. 65-101.

8. П.В. Гельд, Р.А. Рябов, Е.С. Кодес. *Водород и несовершенства структуры металла*. М.: «Металлургия», 1979, с. 221.

9. S.V. Ivanova. Effect of hydrogen on serviceability of zirconium items VVER and RBMK-type reactors fuel assemblies // *International Journal of Hydrogen Energy*. 2002, v. 27, N 7-8, p. 819-824.

10. С.А. Никулин, А.Б. Рожнов. Коррозионное растрескивание циркониевых оболочечных труб // *МиТОМ*. 2005, №2, с. 31-39.

11. Б.Г. Парфенов, В.В. Герасимов, Г.И. Бенедиктова. *Коррозия циркония и его сплавов*. М.: «Атомиздат», 1967, с. 258.

12. В.В. Герасимов. *Коррозия реакторных материалов*. М.: «Атомиздат», 1980, с. 253.

13. С.И. Иванова, А.К. Шиков, О.В. Бочаров. Наводороживание циркониевых изделий в процессе изготовления и эксплуатации – фактор, ограничивающий ресурс их работы в реакторах ВВЭР и РБМК // *МиТОМ*. 2003, №8, с. 40-47.

14. V.M. Fedirko, O.H. Luk'yanenko, V.S Trush. Influence of the Diffusion Saturation with Oxygen on the Durability and Long-Term Static Strength of Titanium Alloys // *Materials Science*. 2014, v. 50, p. 415-420.

15. I.M. Pohrelyuk, J. Padgurskas, O.V. Tkachuk, A.G. Luk'yanenko, V.S. Trush, S.M. Lavrys. Influence of oxynitriding on antifriction properties of Ti–6Al–4V titanium alloy // *Journal of friction and wear*. 2020, v. 4(41), p. 333-337.

16. I.M. Pohrelyuk, V.N. Fedirko, S.M. Lavrys, T.M. Kravchyshyn. Regularities of thermal diffusion saturation with nitrogen combined with standard heat treatment of VT22 titanium alloy // *Mater Sci*. 2017, v. 52, p. 841-847.

17. V.N. Fedirko, A.G. Luk'yanenko, V.S. Trush. Solid-Solution Hardening of the Surface Layer of Titanium Alloys. Part 2. Effect on Metallophysical Properties // *Metal Science and Heat Treatment*. 2015, v. 18, N 56, issue 11, p. 661-664.

18. V.S. Trush, A.G. Lukianenko, P.I. Stoev. Influence of Modification of the Surface Layer by Penetrating Impurities on the Long-Term Strength of Zr-1%Nb Alloy // *Materials Science*. 2020, v. 55, p. 585-589.

19. V.S. Trush, V.N. Fedirko, A.G. Luk'yanenko, M.A. Tikhonovsky, P.I. Stoev. Influence of thermochemical treatment on properties of tubes from Zr-1%Nb alloy // *Problems of Atomic Science and Technology*. 2018, N 2(114), p. 70-75.

20. В.С. Вахрушева, Т.А. Дергач, Г.Д. Сухомлин, В.Я. Замощиков, М.И. Медведев. Разработка принципиальной технологической схемы промышленного производства труб-оболочек твэл из сплава Zr1Nb в Украине // *ВАНТ. Серия «Физика радиационных повреждений и радиационное материаловедение»*. 2002, №6(82), с. 84-87.

21. В.М. Ажажа, В.С. Вахрушева, М.Л. Коцарь, В.С. Красноруцкий, С.В. Ладохин, В.И. Лапшин, К.А. Линдт, А.П. Мухачев, И.М. Неклюдов, И.А. Петельгузов, М.П. Уманец, А.П. Чернов, В.Н. Шишкин. Кальциетермический цирконий для атомной энергетики Украины // *ВАНТ. Серия «Физика радиационных повреждений и радиационное материаловедение»*. 2002, №3(81), с. 74-82.

22. В.М. Ажажа, А.Ф. Болков, Б.В. Борц, И.Н. Бутенко, А.Ф. Ванжа, В.Н. Воеводин, Н.П. Вьюгов, П.Н. Вьюгов, Л.В. Горожанкина, И.Б. Доля, О.Е. Кожевников, С.Д. Лавриненко, В.В. Левенец, К.А. Линдт, И.М. Неклюдов, Н.Н. Пилипенко, В.Н. Пелых, В.И. Попов, Г.Р. Семенов, В.А. Щетинин. Вакуумно-дуговой способ получения трубной заготовки из сплава Zr1%Nb // *ВАНТ. Серия «Физика радиационных повреждений и радиационное материаловедение»*. 2005, №5(88), с. 110-114.

23. В.А. Стрижало, Ю.В. Добровольский, В.А. Стрельченко. *Прочность и акустическая эмиссия материалов и элементов конструкций*. Киев: «Наукова думка», 1990, с. 232.

24. И.Э. Власова. *Акустическая эмиссия*. М: «Спектр», 2011, с. 224.

25. И.И. Папиров, М.Б. Милешкин, П.И. Стоев, М.И. Палатник. Акустическая эмиссия при деформации бериллия // *ФММ*. 1984, т. 57, в. 5, с. 1037-1040.

26. В.А. Грешников, Ю.Б. Дробот. *Акустическая эмиссия*. М.: Изд-во стандартов, 1976, с. 272.

27. Н.А. Бунина. *Исследование пластической деформации металлов методом акустической эмиссии.* Л.: Изд-во Ленинградского университета, 1990, с. 155.

28. B.P. Rusyn, N.P. Anufrieva, Hrabovs'ka, et al. Nondestructive testing of the state of surfaces damaged by corrosion sitting // *Materials Science.* 2014, v. 49, p. 516-524.

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МЕХАНІЧНІ ТА АКУСТИЧНІ ХАРАКТЕРИСТИКИ ОКСИДОВАНОГО, АЗОТОВАНОГО ТА ОКСИНІТРОВАНОГО ЦИРКОНІЄВОГО СПЛАВУ Zr-1%Nb

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Наведено дані щодо впливу складу газового середовища, в якому проводили хіміко-термічну обробку (ХТО), на механічні властивості та акустичні параметри зразків із сплаву цирконію Zr-1%Nb. Показано, що ХТО за вибраними режимами в кисневмісному, азотовмісному та азотокисневмісному газових середовищах суттєво збільшує твердість поверхневого шару зразків сплаву цирконію та не погіршує механічні характеристики зразків твельних оболонок, у тому числі їх пластичність. Показано, що за впливом середовища ХТО на характеристики сплаву акустичні параметри виявилися більш інформативними порівняно з механічними властивостями. Зроблено припущення, що помітні зміни акустичних параметрів, що спостерігаються на початковій стадії деформування, пов'язані з особливостями руйнування тонкої плівки, що утворюється на поверхні трубки в результаті ХТО.