Strojnícky časopis – *Journal of* MECHANICAL ENGINEERING,
VOL 72 (2022), NO 2, 211 - 218X

EFFECT OF HEAT TREATMENT IN OXYGEN-CONTAINING MEDIUM ON FATIGUE LIFE OF ZIRCONIUM ALLOY

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Abstract: The effect of heat treatment in oxygen-containing medium on fatigue properties of zirconium alloy samples was shown. This gas treatment improved fatigue life in pure bending and cyclic tensile testing. An increase in fatigue life was explained by the formation of a hardened near-surface layer. According to the data of fractographic studies of destroyed samples, it was found that treatment in an oxygen-containing medium contributes to the formation of a structure with a higher energy intensity of destruction.

KEYWORDS: zirconium alloy, heat treatment, oxygen-containing medium, hardened layers, fatigue life, pure bending, cyclic tensile testing.

1 Introduction

Structural materials for the nuclear reactor core have a special place in the nuclear industry. First of all, such materials include zirconium alloys. Zirconium alloys are widely used in nuclear power engineering due to their attractive combination of mechanical, corrosive and properties, in particular, such as low neutron-capture cross-section, high melting point, corrosive and radiation resistance under normal service conditions [1]. In the nuclear industry, the thin-walled shell tubes for fuel elements shells are manufactured from zirconium alloys. Thin-walled tubes are responsible for productivity since the ingress of fuel into the cooling system due to tube rupture is unacceptable [2].The mechanical properties of zirconium alloys are very sensitive to the content of the interstitial elements [3]. The presence of the interstitial elements (for example, oxygen, nitrogen, carbon) in a solid solution state of metal leads to a change in strength and plasticity. Oxygen is one of the interstitial elements, which strongly affects the properties of zirconium alloys. In industrial zirconium alloys, oxygen is present as an impurity and is sometimes introduced as an alloying element to improve the mechanical properties. The effect of oxygen on the physico-mechanical properties of zirconium and its alloys is ambiguous [4].The influence of impurities on the properties of zirconium alloys and their behaviour upon irradiation is presented in [1, 5]. The segregation of impurities in the metal structure increases the risk of destruction of products from zirconium alloys during exploitation [6]. On the other hand, the interstitial elements contribute to an increase in long-term stability and resistance to creep during irradiation [5]. Therefore, oxygen is included in the composition of the Zr-1%Nb alloy as an alloying element in an amount up to 0.14% [7]. The oxygen content in the Zr-1%Nb alloy is more than 0.16%, which causes its intensive strengthening but does not lead to a significant loss of plasticity [8]. Thus, the effect of oxygen on some characteristics of the Zr-1%Nb alloy is ambiguous and requires additional investigations.

DOI: 10.2478/scjme-2022-0030, Print ISSN 0039-2472, On-line ISSN 2450-5471

Increasing the operational parameters of nuclear power plants simultaneously increases the requirements for their safety. Reliability requires a purposeful change in the properties of products from zirconium alloys used in structural elements of reactors. One way to increase the efficiency of such products is the formation of modified surface layers to improve the properties of the working surfaces. Thus, a new complex of physicochemical properties and surface characteristics of shell pipes will appear, which, as a rule, are not characteristic of the matrix, but will improve the serviceability of near-surface metal layers and elements in general. Therefore, it is important to study the effect of near-surface layers of metal enriched with oxygen on the complex of physico-mechanical properties of zirconium alloys.

Shown to be a positive influence of the functional layer on the performance of Zr–1% Nb alloy at a temperature of 380°C [10]. The results of the hardness estimation of external and internal surfaces of the ring-samples after oxidation and nitriding are presented in research [11].

The purpose of the article is to investigate the effect of heat treatment of a zirconium alloy on the structure, mechanical characteristics and fatigue life under various loading schemes.

2 Experimental techniques

The material used in present study was Zr-1%Nb alloy, the chemical positions is following: Zr – 98.87%, Nb – 1.03% and O – 0.1%.

The heat treatment of zirconium alloy was carried out on laboratory equipment in the reaction chamber of the furnace by the two regimes: $\boldsymbol{R}1$ – $\boldsymbol{T}$ = 580°C, (τ = 0.5 h, $\boldsymbol{P}$ =1.33Pa) + (τ = 2.5 h, $\boldsymbol{P} = 1.33 \cdot 10^{-2}$ Pa) – proposed treatment mode and $\boldsymbol{R}2$ – $\boldsymbol{T}$ = 580°C, τ = 3 h, $\boldsymbol{P} = 1.33 \cdot 10^{-3}$ Pa – finishing standard processing mode [12]. The result of heat treatment in the gas medium of the zirconium alloy according to the ***R1*** and ***R2*** regimes was diffusive dissolution of oxygen and formation of a hardness gradient surface layer.

Samples (10×15×1 mm) were used for metallographic, XRD and durometric measurements. The microstructure of the zirconium alloy before and after the heat treatment was studied on an optical microscope «Epiquant». The phase-structural state of the surface layers was determined by XRD analysis using DRON-3.0 diffractometer in monochromatic Cu Kα radiation with focusing according to the Bragg-Brentano scheme. The anode voltage of the X-ray tube was 30 kV at a current of 20 mA. The scanning step was 0.05°. Surface hardness was determined on PMT-3M microhardness tester with a load of 0.49 N on the Vickers indenter.

Fatigue tests under pure bending of plate samples (fig. 1) were carried out in a rigid load regime in the range of the strain amplitude $\pm\varepsilon_a$ = 0.8...1.0% with a frequency of ν = 0.5 Hz in air at room temperature. Tests under pure bending were performed on UMDU-01 equipment (fig. 2), which was developed and manufactured in Karpenko Physico-Mechanical Institute of the NAS of Ukraine [10]. The results of bending fatigue testing were given in the coordinates "maximum strain amplitude of the cycle – the logarithm of the number of cycles to failure".

Fatigue tests under cyclic loading of ring samples (fig. 3) on were performed on equipment (fig. 4), which was also developed and manufactured in Karpenko Physico-Mechanical Institute of the NAS of Ukraine. The ring samples with a width of 3 mm with V-shaped concentrators of 0.5 mm depth from both sides in the working part were used for fatigue test under cyclic tensile testing (Fig. 3). The samples were tested by cyclic loading at maximum stress σ_{max} = 100 MPa and stress ratio R = 0.2 and frequency f = 46 Hz. The results of the cyclic tensile tests were given in the coordinates "maximum load σ_{max} of the cycle – the logarithm of the number of cycles to failure N_f".

The facility for fatigue testing of materials by cyclic tension consists (Fig. 4). of a force excitation mechanism mounted on a massive base and a control system. The prototype (sample-

ring) 4 is installed in the grips. The upper grip is pivotally attached to the ring dynamometer 3 of the working plate 7. The lower grip is rigidly fixed to the vibrator. A constant load created by the load, which is suspended from the vibrator 4 with the help of a spring 8. The vibrator consists of two horizontally located shafts with unbalanced loads fixed to them, interconnected by textolite gears. One of the shafts is connected by a flexible shaft to an electric motor. The horizontal component of the inertia force of the load is constantly compensated, and the vertical component is the payload applied to the sample.

The working plate 7 with the mechanism of force excitation is rigidly attached to the massive pedestal 10 with the help of pins. This fastening allows you to set the entire system (sample, vibrator, load) strictly vertically. Cabinet 10 is mounted on elastic rubber shock absorbers 11.

The installation allows you to carry out tedious testing of materials on samples of small sizes with an asymmetric cycle of variable tension (with a cycle asymmetry coefficient R = 0.2, maximum load on the sample (P_{max} = 1920 N) both in air, at room temperature, and in liquid corrosive media, using a collapsible glass attached to the vibrator.

The advantage of this setup is the presence of a double vibrator, balanced in the horizontal plane, which does not create additional stresses with any elongation of the sample during research. To fastening the ring samples to the installation, special grippers was designed and made (Fig. 5).

The fractographic analysis of the fracture surfaces of samples after fatigue tests were carried out on an EVO40XVP scanning electron microscope.

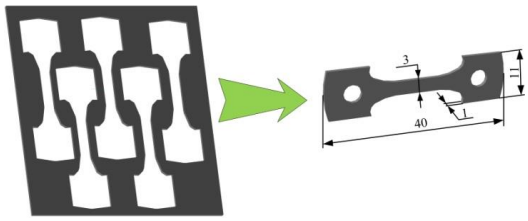
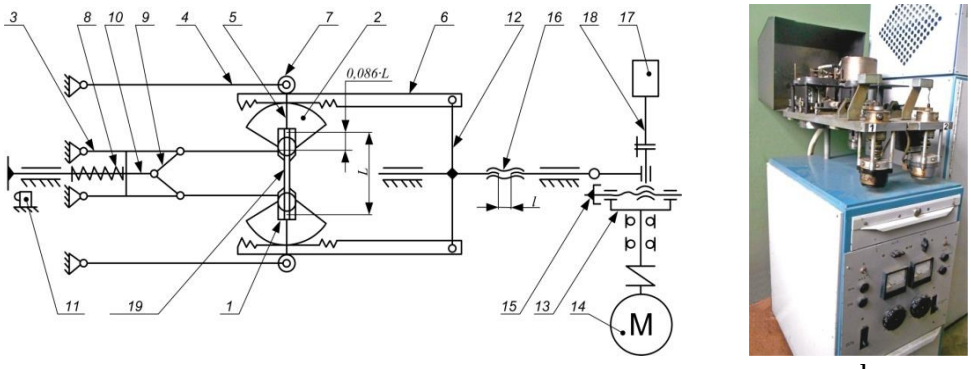


Fig. 1 The scheme of manufactured of plate samples for fatigue testing under pure bending.



a b

Fig. 2 Schematic (a) and general view (b) of equipment for fatigue test under pure bending tests: 1 – capture; 2 – toothed sector; 3, 4 – fork; 5 – link; 6 – gear rack; 7 – roller; 8 – spring; 9, 10 – links; 11 – limit switch; 12 – crossbar; 13 – adjusting crank; 14 – engine; 15 – micrometric crank displacement mechanism; 16 – clutch to create an asymmetric load cycle; 17 – counter; 18 – flexible shaft, 19 – sample.

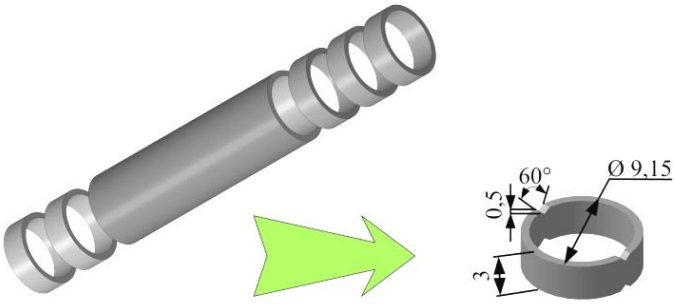
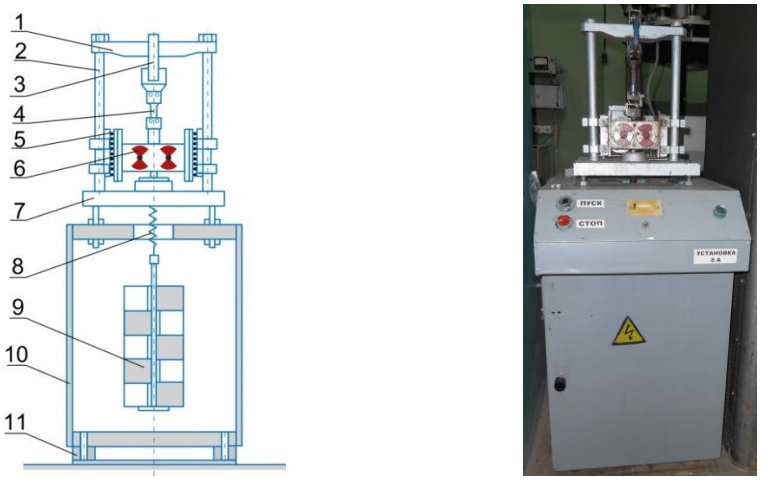


Fig. 3 Scheme of the manufacture of ring-shaped sample for cyclic tensile testing.



a b

Fig. 4 Schematic (a) and general view of device for cyclic tensile testing: 1 – cross bar; 2 – a directing lath; 3 – annular dynamometer; 4 – sample; 5 – double directional vibrator; 6 – cams; 7 – working plate; 8 – the spring; 9 – cargo; 10 – curbstone; 11 – elastic rubber shock absorbers.

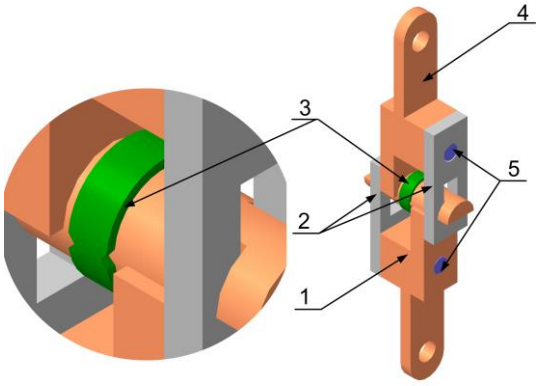


Fig. 5 3D-model of the gripper for fixing of the ring-shaped sample for fatigue testing at the cyclic loading: 1 – lower base, 2 – side bar, 3 – ring-shaped sample, 4 – upper base 5 – pins.

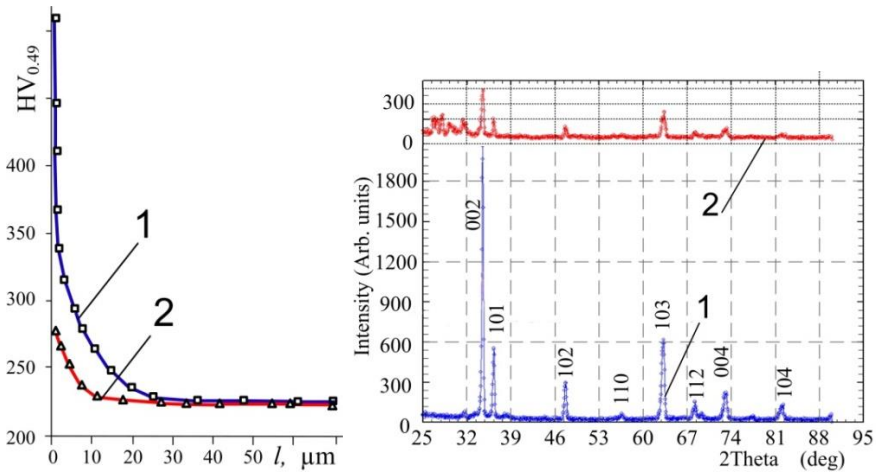
3 Results and discussion

Below are presented and analyzed the results of experimental studies on the effect of heat treatment in gas media on the physico-mechanical and fatigue properties of the zirconium alloy.

3.1 Microhardness and XRD analysis

After heat treatment according to the R1 and R2 modes, as a result of the diffusion of the interstitial elements (oxygen), a gradient in hardness is formed in the near-surface layers of the samples. As a result of diffusion of oxygen in zirconium alloy during heat treatment by regimes R1 and R2, the gradient hardened near-surface layers are formed (fig. 6, a). It was established that surface hardening of Zr-1%Nb alloy after such treatment is dependent on used regime. After heat treatment according to the regime R1 and R2, the surface microhardness increases by 2.7 and 1.3 times and is formed a hardened layer depth of ~15 μm and ~30 μm, respectively (Fig. 6a). It is shown that during heat treatment by regime R1 the oxygen are more intensively absorbed by the zirconium alloy from the rarefied gas atmosphere.

According to the XRD results, modification of the surface of the Zr-1%Nb alloy with oxygen after treatment according to the R2 and R1 modes does not cause significant phase transformations (Fig. 6b). After heat treatment according to the R1 regime, the intensity of the zirconium line decreases (Fig. 6b, curve 1), which is associated with the protective effect of a thin oxide film. As a result, a line of zirconium oxides appears in the diffraction pattern in the region of small angles [9]. However, after heat treatment according to the R1 regime (treatment in high vacuum), the intensity of zirconium line reflexes is higher (Fig. 9b, curve 2), since almost no oxide film is formed on the sample surface.



a b

Fig. 6 The microhardness distribution on the cross-section (a) and diffraction patterns registered from surface of Zr-1%Nb alloy samples (b) after heat treatments by ***R***1 (1) and ***R***2 (2) regimes.

3.2 Microstructure

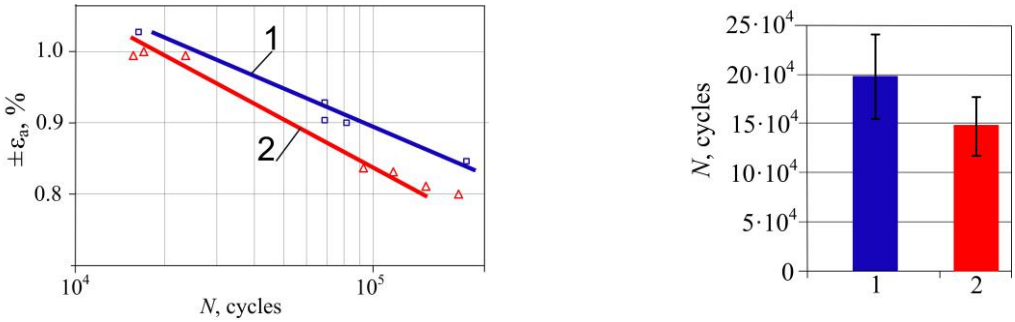
According to the metallography studies, the microstructure of the near-surface layer of zirconium alloy doesn't have significant changes after heat treatment by the regimes R1 and R2: a fine-grained structure without obvious differences was observed in both cases . The reason for the absence of noticeable changes in the near-surface layers of samples are probably the low temperature (T = 580°C) and the time exposure (τ = 3 hours) during their heat treatment.

3.3 Fatigue test

According to the results of tests for pure bending of plate samples, modification according to the R2 mode had a positive effect on the durability of the samples of the analyzed alloy in the range of deformation amplitudes $\pm\varepsilon_a$ = 0.8...1.0% (Fig. 7a). The increase in the fatigue life of the samples is probably associated with the hardening of the near-surface layers (Fig. 2a),

due to which a favorable compressive stress gradient is formed, similar to observed on titanium alloys [13].

Chemical-thermal treatment in an oxygen-containing gaseous medium ensured an increase in the number of cycles to destruction of samples under their cyclic loading. It was believed that this was a consequence of the formation of a hardened layer (Fig. 7b).

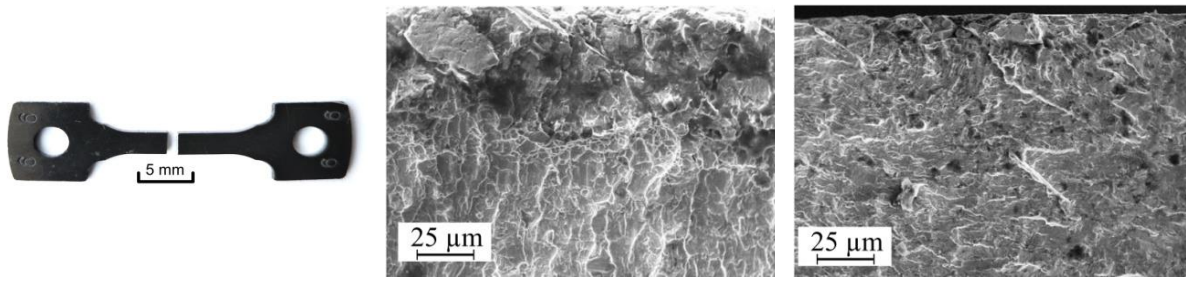


a b

Fig. 7 The fatigue curves for the Zr-1%Nb alloy after treatment by ***R***2 (1) and ***R***1 (2) regimes obtained after fatigue test under pure bending (a) and fatigue life under cyclic tensile testing (b).

3.4 Fractography analysis

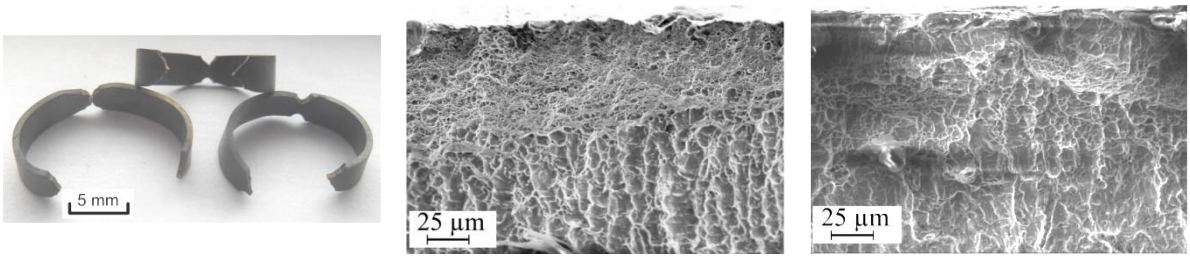
The features of fracture of Zr-1%Nb alloy samples with modified surface layer after fatigue testing under pure bending with strain amplitude $\pm\varepsilon_a = 0.9\%$ are revealed. In particular, it is shown that after vacuum treatment by regime R2 and a mixed fracture type occurs: there are fragile chips with a small number of deformation crests (Fig. 8c) in combination with a river pattern, corresponding to a ductile fracture. For samples hardened by the R1 regime the near-surface layer is failured by a brittle type with a small number of deformation crests [14]. After the hardened layer, at a distance of 20...30 μm from the surface, there is a characteristic crushing of the microrelief of the fracture surface and there is a significant amount of deformation crests, which indicates a ductile type of fracture [14, 15]. In the core of the samples, after treatment in two regimes, a ductile type of fracture is observed (Fig. 8b). Similar results of fractography were also obtained on the fracture surface of specimens after cyclic loading (Fig. 9).



a b c

Fig. 8 General view of a fatigue-damaged plate sample (a) and fractograms of near surface layers of Zr-1%Nb alloy samples heat-treated by R1 (b) and R2 (c) modes after fatigue tests in pure bending with a deformation amplitude of $\pm\varepsilon_a = 0.9$ %.

The results of the work can be used in the development of technologies for the chemical-thermal treatment of zirconium alloys to improve the serviceability of thin-walled elements for nuclear power engineering.



a b c

Fig. 9 General view of damaged annular samples after cyclic tensile tests (a) and fractograms of surface layers of Zr-1%Nb alloy samples after processing according to R1 (b) and R2 (c) modes, failured during cyclic tensile tests.

CONCLUSION

Experimental studies have confirmed the positive effect of the modification of near-surface layers by an interstitial element (oxygen) on a complex of properties of samples from the Zr-1%Nb alloy (in particular, on microhardness and phase composition). It has been established that the modification of near-surface metal layers under the proposed temperature-time and gas-dynamic parameters provides an increase in the fatigue characteristics of ring specimens from the Zr-1%Nb alloy during cyclic tensile tests. The obtained properties satisfy the requirements for the final heat treatment of fuel rod claddings made of Zr-1%Nb alloy. Differences in the mechanisms of destruction of samples after various treatments are shown. In particular, it has been shown that the fatigue failure of samples after treatment in practically vacuum during pure bending tests occurs according to the ductile mechanism. For samples after treatment in an oxygen-containing gas medium, the fatigue life of which turned out to be higher than when processed in vacuum, the failure of the near-surface layers occurred according to a mixed brittle-ductile mechanism.

REFERENCES

[1] Banerjee, S., Banerjee, M. K. "Nuclear applications: zirconium alloys", Reference module in materials science and materials engineering, Oxford, pp. 1 – 15, **2016**. DOI: 10.1016/B978-0-12-803581-8.02576-5

[2] Azevedo, C.R.F "Selection of fuel cladding material for nuclear fission reactors", Engineering Failure Analysis 18, pp. 1943 – 1962, **2011**. DOI: 10.1016/j.engfailanal.2011.06.010

[3] Lee, D., Hill, P. "Effect of oxygen on the fatigue behavior of zircaloy", J. of Nuclear Materials 60(2), pp. 227 – 230, **1967**. DOI: 10.1016/0022-3115(76)90170-7

[4] Chosson, R., Gourgues-Lorenzon, A. F., Vandenberghe, V., Brachet, J. C., Crépin, J. "Creep flow and fracture behavior of the oxygen-enriched alpha phase in zirconium alloys", Scripta Materialia 117, pp. 20 – 23, **2016**. DOI: 10.1016/j.scriptamat.2016.02.021

[5] Adamson, R. B., Rudling, P. "Properties of zirconium alloys and their applications in light water reactors (LWRs)", Materials ageing and degradation in light water reactors, pp. 151 – 245, **2013**. DOI: 10.1533/9780857097453.2.151

[6] Aitchison, I., Davies, P. H. "Role of microsegregation in fracture of cold-worked Zr-2.5Nb pressure tubes" J. of Nuclear Materials 203 (3), pp. 206 – 220, **1993**. DOI: 10.1016/0022-3115(93)90377-B

[7] Steinbrück, M. "Oxidation of Advanced Zirconium Alloys in Oxygen in the Temperature Range 600-1600°C", Proceedings of the 16th International Conference on Nuclear Engineering ICONE16, pp. 567 – 577, **2008**. DOI: 10.1115/ICONE16-48054

[8] Griger, A., Hozer, Z., Matus, L., Vasaros, L., Horvath, M. "Reports of International conference on WWER fuel performance, modelling and experimental support", 19 – 23 September 2005, Congress Center Albena, Bulgaria, **2005**.

[9] Selmi, N., Sari, A. "Study of oxidation kinetics in air of Zircaloy-4 by in situ X-Ray diffraction", Advances in materials physics and chemistry 03 (02), pp. 168 – 173, **2013**. DOI: 10.4236/ampc.2013.32023

[10] Trush, V. S., Fedirko, V. N., Luk'Yanenko, A. G., Tikhonovsky, M. A., Stoev, P. I. "Influence of thermochemical treatment on properties of tubes from Zr-1%Nb alloy", Problems of Atomic Science and Technology 114 (2), pp. 70 – 75, **2018**.

[11] Trush, V. S., Fedirko, V. M., Voyevodin, V. M., Stoev, P. I., Panov, V. A. "Influence of the functional layer on the operating characteristics of Zr – 1% Nb alloy at a temperature of 380°C", Materials Science 57 (2), pp. 234 – 239, **2021**. DOI: 10.1007/s11003-021-00537-y

[12] Vakhrusheva, V. S., Dergach, T. A., Sukhomlin, G. D., Zamoshchikov, V. Ya., Medvedevm, M. I. "Development of a basic technological scheme for the industrial production of Zr1Nb fuel cladding pipes in Ukraine", Problems of atomic science and technology, Series Physics of Radiation Damage and Radiation Materials Science 6 (82), pp. 84 – 87, **2003**.

[13] Fedirko, V. N., Luk'yanenko, A. G., Trush, V.S. "Solid-solution hardening of the surface layer of titanium alloys. Part 2. Effect on metallophysical properties", Metal Science and Heat Treatment 56 (11-12), pp. 661 – 664, **2015**. DOI: 10.1007/s11041-015-9818-1

[14] Maruschak, P. O., Panin, S. V., Stachowicz, F., Danyliuk, I. M., Vlasov, I. V., Bishchak, R. T. "Structural levels of fatigue failure and damage estimation in 17Mn1Si steel on the basis of a multilevel approach of physical mesomechanics", Acta Mech 227, pp. 151 – 157, **2016**. DOI: 10.1007/s00707-015-1420-5

[15] Maruschak, P. O., Panin, S. V., Ignatovich, S. R., Zakiev, I. M., Konovalenko, I. V., Lytvynenko, I. V., Sergeev, V. P. "Influence of deformation process in material at multiple cracking and fragmentation of nanocoating", Theoretical and Applied Fracture Mechanics 57(1), pp. 43 – 48, **2012**. DOI: 10.1016/j.tafmec.2011.12.007