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EFFECT OF SURFACE MODIFICATION BY NITROGEN AND OXYGEN ON MECHANICAL PERFORMANCE OF Zr-1%Nb ALLOY

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The effect of surface modification by oxygen and nitrogen from a controlled gaseous medium on the fatigue life under cyclic and long-term static loading of Zr-1%Nb alloy thin-sheet samples was studied. Positive effect of gas nitriding and thermal oxidation on mechanical and fatigue performance under cyclic and static loading of Zr-1%Nb alloy was shown: under pure bending – by ~23%; under cyclic stretching – by ~25% and under long-term static loading in air with exposure of 100 h at room temperature – by ~12% and at a temperature of 380 °C – by ~6%. It was established that oxidation and nitriding effectively improve fatigue life and fracture stresses under long-term static loading of Zr-1%Nb alloy thin-sheet.

INTRODUCTION

The key to the development of high-tech industries (aviation, nuclear power, and chemical engineering) is using of the IV group metals (titanium, zirconium, and hafnium, etc.) and their alloys [1–5]. An integral reason for increasing the resource of equipment is the fatigue life of their products under cyclic and static long-term loading, where the surface layer state is an important factor [6–11]. Therefore, the growth of requirements for the surface characteristics leads to the development of novel or improvement of existing treatments of metal parts.

Surface engineering is an effective method for ensuring a wide range of operational performances. The metal surface can be modified, in particular, by deposition of coatings or forming modified layers by thermo-chemical treatment (TCT) [12–16]. Deposition of coatings cannot always be applied due to certain features that are inherent in these methods. Considering that Ti, Zr, and Hf have high reactivity to the interstitial elements (oxygen, nitrogen, carbon), therefore TCT is one of the effective methods of controlling the structure and characteristics of the surface layers of metals. As of today, the main attention is paid to the study of the influence of volumetric saturation with interstitial elements on properties of alloys based on Ti, Zr, and Hf [17–27]. However, there is practically no information about the regularities of surface modification of these materials and establishing a correlation between the characteristics of the formed modified surface layer and fatigue life under different load conditions. In addition, an equally important aspect of ensuring the quality of products is their mechanical processing and the development of machines for their implementation [28–30], because high demands are placed on zirconium products [31–37].

Thus, the study of the effect of surface modification of Zr-1%Nb alloy with interstitial elements (O and N) under thermodiffusion saturation from controlled gaseous mediums on fatigue life under cyclic and static long-term loading is a relevant scientific problem. The work aim is to establish the influence of the modified, surface layer with oxygen- and nitrogen-containing gaseous medium on fatigue life under cyclic and long-term static loading

MATERIALS, SAMPLES, AND RESEARCH METHODS

The studied material was Zr-1%Nb zirconium alloy (98.97 wt.% Zr and 1.03 wt.% Nb), produced in Ukraine. TCT regimes in gaseous medium (oxygen- and nitrogen-containing) were performed with minimal inleakage of air into the reaction chamber of the furnace (Table 1).

Table 1

TCT regimes of Zr-1% Nb alloy

No.	TCT regimes	Symbol
Vacuum annealing		
1	T = 580 °C, P = 0.0133 Pa, τ = 3 h	*R0*
Oxygen-containing medium		
2	T = 580 °C, P = 1.33·Pa, τ = 0.5 h + T = 580 °C, P = 0.013 Pa, τ = 2.5 h	*R1*
Nitrogen-containing medium		
3	T = 580°C, P = 0.00133 Pa, τ = 1 h + T = 580 °C, $P = 1.01\cdot10^5$ Pa, τ = 9 h	*R2*

Long-term strength in air at room temperature and a temperature of 380 °C on a base of 100 h was studied on ring samples with wide – 3 mm (Fig. 1). For the study, a multi-position installation developed at the Karpenko Physico-Mechanical Institute of the NAS of Ukraine

[14] was used, which provides identical test conditions for a series of samples.

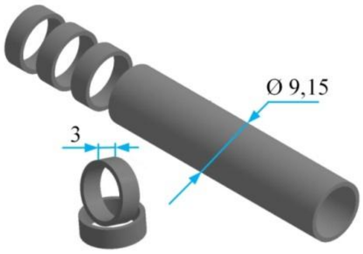

Fig. 1. Schematic of the ring sample made from a fuel rod tube for testing under long-term static and cyclic loading

Samples for pure bending tests were made from thin sheet with a thickness of ~ 1 mm (Fig. 2).

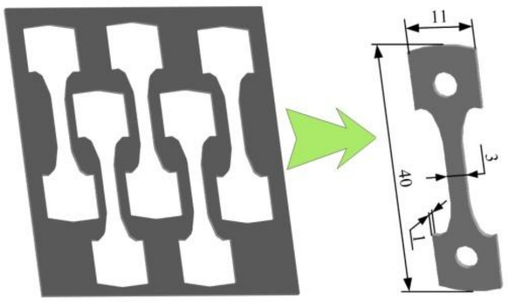

Fig. 2. The schematic of the samples manufacture for pure bending testing

The influence of TCT regimes on the material, the following parameters was used: relative increase in surface hardness $\delta H = ((H^{surf} - H^{core}) / H^{core}) \times 100\%$, where H^{surf} – zirconium surface hardness; H^{core} – hardness of the zirconium core, also investigated the depth of the surface hardened layer (*l*). The surface microhardness and its cross-distribution in the surface layer of samples were determined using a PMT-3M durometer with an indenter load of 0.49 N.

Tensile testing of samples was performed on a 1958 U10-1 universal testing machine with a deformation rate of 0.17 mm/min ($2{\cdot}10^{-4}$ s^{-1}) at room temperature. Parameters of acoustic emission (activity, total sum of pulses, etc.) were recorded using the acoustic complex M400, which allows recording and separating AE signals depending on their amplitude. The amplitude discrimination levels of the channels were 10, 20, 30, 40, 50, 60, 70, and 100 μV relative to this value. A piezo-ceramic transducer made of ceramics TTS-19 with a resonance frequency of 180 kHz was used as an AE sensor-recorder.

RESULTS AND DISCUSSION

The dissolution of interstitial elements (oxygen, nitrogen) in zirconium alloys is associated with distortion of the crystal lattice, as a result of which the hardness increases significantly. Therefore, an increase in the hardness of the surface layer indicates that as a result of TCT, the surface layer was enriched with interstitial elements (see Fig. 2, Table 2).

Based on the analysis of the XRD results, it was established that the modification of the layer with oxygen or nitrogen leads to an increase in crystal lattice strain and the size of crystallites (Fig. 3).

Table 2

The Zr-1%Nb alloy ring samples characteristics after various heat treatments

Regi-mes	Hardness, $HV_{0.49}$			Modified layer depth *l*, μm
	Surface, H^{surf}	Core, $H^{core.}$	Increase, ΔH	
R0	260±25	170±15	90	15…19
R1	275±20	170±15	105	22…27
R2	320±20	170±15	150	32…37

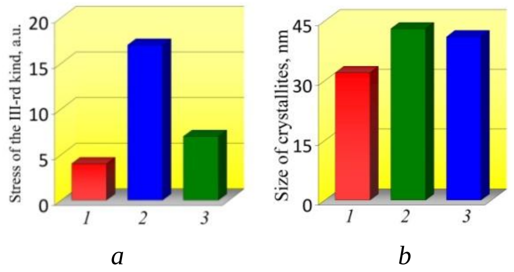

Fig. 3. Crystal lattice strain (a) and the size of crystallite (b) various heat treatments: 1 – R0; 2 – R1; 3 – R2

The modified oxygen-based surface layer had a positive effect on the fatigue life of the Zr-1%Nb alloy under pure bending (Fig. 4,a): the increase in fatigue life at $\pm\varepsilon_a$ = 0.9% is 15%. It is shown that the fracture of the alloy after vacuum annealing occurs according to a mixed type: there are brittle facets with a small number of tearing strips (see Fig. 4,b) in combination with a river pattern. In the samples with modified surface layers, after processing in an oxygen-containing environment, an increase in fatigue life is observed, the surface layer is destroyed mainly brittle, and the core has a large number of tearing strips (see Fig. 4,c). A modified layer with a depth of 20...30 μm with a crushed microrelief of the fracture is visible on the fracture, and there is a significant number of tearing strips, which indicates a ductile type of fracture.

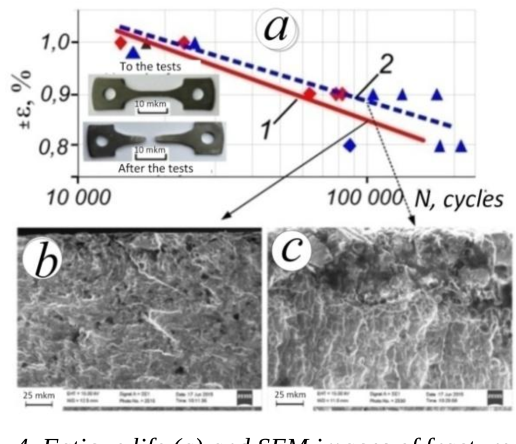

Fig. 4. Fatigue life (a) and SEM images of fracture surfaces (b, c) of the Zr-1%Nb alloy after tests under pure bending ($\pm\varepsilon_a$ = 0.9%) and heat treatment: 1 – in vacuum; 2 – in oxygen-containing medium

A positive effect of gas nitriding of Zr-1%Nb alloy ring samples on fatigue life under cyclic loading at room temperature was revealed. Thermal oxidation provides an increase in fatigue life by 15…20% (σ_{max}=100 MPa) compared to processing in a vacuum.

It is shown that after modification with oxygen, a layer with a thickness of 20...30 µm with a large number of fatigue grooves and tearing strips is released in the surface layer, which indicates a viscous type of failure (Fig. 5).

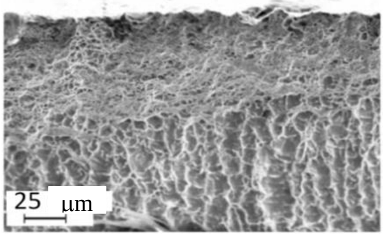

Fig. 5. Fracture surface of the Zr-1%Nb alloy treated by R1 regime after tests under cyclic loading

It was found that thermal oxidation and gas nitriding have a positive effect on fracture stresses during long-term static exposure to air. The fracture stresses of the oxidized and nitrided ring samples treated for 100 h are 10...15% higher than untreated ones (Fig. 6).

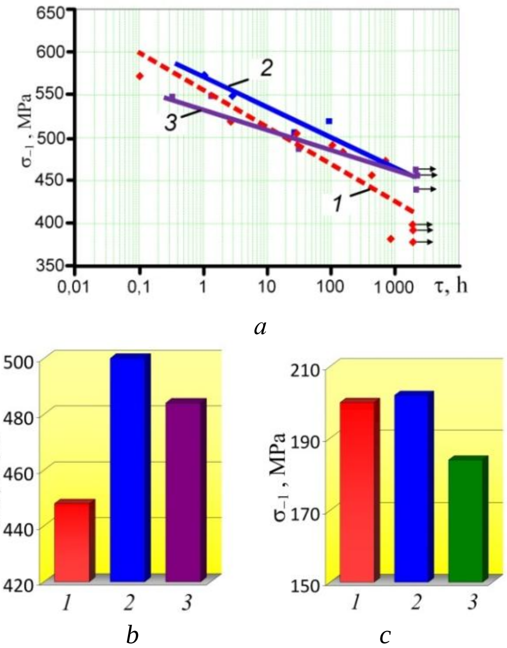

Fig. 6. Long-term strength (a) and fracture stresses based on 100 h (b, c) of Zr-1%Nb alloy in air at 20 °C (a, b) and 380 °C (c) by R0 (1), R1 (2), and R2 (3) regimes

It was found that the activity of the acoustic emission of the treated samples is an order of magnitude higher compared to the untreated ones (Fig. 7,a,b). This allows us to assume that the presence of a hardened layer leads to an increase in the activity of acoustic emission in the areas of elastic and plastic deformation. Such a significant increase in acoustic emission activity is due to several factors at the same time. Firstly, the interstitial elements (oxygen) present in the near-surface layer fix some of the dislocations and after a certain stress level is reached, the dislocations break away from the fixations, which lead to an increase in the number of mobile dislocations and, accordingly, the number of registered acoustic emission signals (see Fig. 7,b). Secondly, this may be related to twinning, because in the initial stages (up to 10%) of tensile deformation in zirconium, twins appear and the changes in the location of the elementary prisms of the lattice directly depend on the stress state.

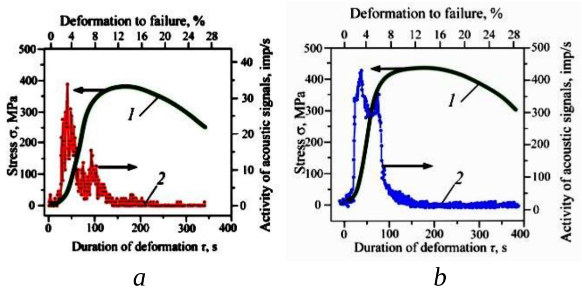

Fig. 7. Dependence of tensile strength (1) and AE activity (2) on the loading time of treated samples by R0 (a) and R1 (b) regimes

According to the results of the analysis of AE signals, differences in the activity of low-amplitude acoustic signals were detected, which were recorded in the process of testing ring samples from the Zr-1%Nb alloy (Fig. 8). It is shown that for samples after treatment according to *R0* regime that is, after processing in a vacuum, a gradual increase in low-amplitude signals is observed, and then their sharp decline already 50 s after the beginning of the tests. Whereas for oxidized samples, their gradual growth and their presence during the entire test were recorded. The significant presence of low-amplitude acoustic emission signals for the oxidized sample indicates the high energy intensity of destruction, which correlates with fatigue tests.

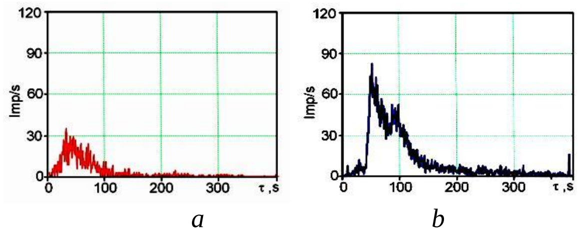

Fig. 8 Activity of low-amplitude AE signals during sample testing by R0 (a) and R1 (b) regimes

Therefore, the results of fatigue tests and acoustic emission signals correlate with each other and confirm the effectiveness of using TCT to increase fatigue life and fracture stresses under long-term static loading of Zr-1%Nb thin-sheet.

CONCLUSIONS

1. TCT in oxygen- and nitrogen-containing gaseous medium provides the formation of a modified surface layer. The surface microhardness compared to the core one is greater by 105...150 units and the thickness of the modified layer after oxidation or nitriding is 22...27 and 32...37 µm, respectively.

2. It was established that the presence of a surface layer modified with oxygen or nitrogen provides an

increase in fatigue life and strength under long-term static loading.

3. The increase in fatigue life of the Zr-1%Nb alloy under various load conditions with a regulated modified surface layer is: in pure bending – by ~ 23%; during cyclic stretching – by ~ 25% and during long-term static loading in air with exposure of 100 h at room temperature – by ~ 12% and at a temperature of 380 °C – by ~ 6%.

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ВПЛИВ ПОВЕРХНЕВОГО МОДИФІКУВАННЯ АЗОТОМ ТА КИСНЕМ НА МЕХАНІЧНІ ВЛАСТИВОСТІ СПЛАВУ Zr-1%Nb

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Представлені результати впливу модифікування поверхневого шару елементами кисню та азоту з контрольованого газового середовища на втомну довговічність за циклічного та тривалого статичного навантажень тонколистових зразків зі сплаву Zr-1%Nb. Встановлено ефект підвищення довговічності цирконієвого сплаву Zr-1%Nb з регламентованим модифікованим поверхневим шаром, сформованим за дифузійного насичення з кисне- та азотовмісного газових середовищ за циклічних та статичних умов навантаження: чистого згину – на ~ 23%; циклічного розтягу – на ~ 25% і тривалого статичного навантаження на повітрі на базі 100 год за кімнатної температури – на ~ 12% та температури 380 °C – на ~ 6%. Зроблено висновок, що застосування оксидування та азотування є ефективним методом для підвищення втомної довговічності та руйнівних напружень за тривалого статичного навантаження тонколистового матеріалу зі сплаву Zr-1%Nb.