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MODIFICATION OF SURFACE OF ZIRCONIUM ALLOYS BY PULSED ELECTRON BEAMS

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Abstract

Here the experiment results of pulsed electron beam influence on the structure phase state of alloy Zr1%Nb are represented. It is demonstrated that such treatment leads to forming of complex morphology martensite in the surface layer of the alloy. The processes of hydrogen absorption by zirconium alloy with modified surface have been studied.

Key words: *zirconium alloy, pulsed electron beam, hydrogen*

1. INTRODUCTION

One of the important requirements to the products from zirconium alloys of reactor core is low hydrogen absorption. In most cases, hydrogen saturation leads to decrease of plasticity and fracture strength of alloys, meanwhile brittle hydrides extraction in stress concentration zones can become the cause of product destruction [1, 2]. In order to solve this problem the following directions in research can be identified: composite compound improvement; new alloys development and production; various protecting coatings application and development of new methods of products surface modification. To improve performance characteristics of metals and alloys the methods of modification by concentrated energy flows (electron beams, laser irradiation, ion implantation) of structure phase state of material near-surface layer are considered to be promising. High energy effectiveness and homogeneity of power density in cross-section flux, good impulse reproducibility are the advantageous characteristics of pulsed electron beams (PEB) [3, 4]. While irradiation of metal pulsed electron beam, the conditions for the formation of the surface layer of amorphous, nano- and submicrocrystalline structures are created, which, in turn, can lead to improved physico-mechanical properties of the material [5]. However, in comparison with high-power ion beams, which are also used for surface modification, electron beams are generated with a high efficiency and do not require a special radiation protection due to as well as the accompanying X-ray radiation is screened by the walls of the working vacuum chamber [5]. The physical nature of the interaction between PEB and a solid is that the kinetic energy of accelerated electrons in their inhibition as a result of heat dissipation becomes a component of the internal energy of the target substance (kinetic energy of accelerated electrons dissipates as heat component of internal energy of target substance). At the end of the beam pulse a heated layer quickly is cooled by the process heat in the depth of the material. As a result of changing the properties of the surface layer (changing the microstructure, phase composition changes, etc.) occurs. Since ranges of power and energy concentration in high pulse beam are varied, it is possible to obtain virtually all types of thermal effects on the surface layers of solids: heating to specified temperatures, melting and evaporation at very high speeds. The subsequent sharp cooling is usually accompanied by high-speed melt crystallization and hardening phenomena. Treated material while experiencing heat shock, which leads to the appearance of the powerful waves of mechanical stresses in the bodies. In the works [6] it was demonstrated that pulsed electron beam irradiation with the power density from 15 to 25 J/cm^2, electrons energy – 18 kV, three impulses with duration of 50

μs leads to increase (up to 40 %) of micro- and nanohardness of Zr1%Nb alloy. It was established that modification of zirconium alloy leads to significant decrease (in 2 – 3 times) of hydrogen amount which penetrates the alloy volume in comparison with the bearing alloy, it should be pointed out that the method of hydrogen saturation doesn`t play any role – whether it was electrolytic method or from the vapor phase. Based on thermal design it was shown that high-speed heating ~ 10^9 K/s in the process of pulsed impact and subsequent near-surface layer cooling create conditions for phase and structure transformations. The character of phase transformations and 6different phase formation are related to Nb concentration in zirconium and the speed of material cooling. It is known [7] that under thermal processing the structure transformations with fixed under the indoor temperature conditions metastable structural state in zirconium-niobium alloys are observed. In weakly doped alloys as a result of quenching the lath martensite is being formed. In high-concentration alloys the martensite has the laminated morphology. Increase in cooling speeds leads to the boundary shift of transition from lath martensite to laminated one in favor for lower concentrations. Presence of such structures in near-surface layers of zirconium alloys can provide a considerable influence on the processes of material and hydrogen interaction. In the present paper the structure phase transformations of alloy Zr1%Nb surface as a result of irradiation by pulsed electron beam are discussed, the mechanisms of hydrogen interaction with modified surface are considered.

2. MATERIAL AND RESEARCH METHODS

Samples of zirconium alloy Zr1%Nb (alloy grade E110) with size of 50 × 50 mm and thickness of 0,7 mm served as material for research. Irradiation by pulsed electron beam was performed on the set up «Solo» in the Institute of High Current Electronics of Siberian branch of Russian Academy of Sciences. The influence was performed from both sides of the sample with power density from 15 up to 25 J/cm^2. Current density constituted from 10 up to 50 A/cm^2, electron energy was 18 kV, each sample was irradiated by three impulses with duration of 50 μs. In order to study the structure of the alloy surface the methods of scanning and transmission electron microscopy were implemented. Structure phase composition was investigated by the method of X-ray diffraction analysis on the diffractometer Shimadzu XRD 6000 (CuKα – radiation). Measurements of zirconium alloy hardness were performed on the setup "Nano Hardness Tester" produced by CSEM. Measurements were made with a load of 300 mN to 10 mN. Hydrogen saturation of samples was done on the set up PCI «Gas Reaction Controller». Absolute hydrogen concentration in the sample under study was determined on the RHEN 602 produced by LECO.

3. RESEARCH RESULTS

As research has revealed irradiation by pulsed electron beam causes considerable transformations of Zr1%Nb alloy microstructure. Figure 1 and 2 represent the images of zirconium alloy surface transformations in the central part of pulsed electron beam impact given by raster (Fig.1) and transmission electron microscopy accordingly.

In the central part of pulsed electron beam influence the surface acquires high finish with the traces of melting grain boundaries are being formed and emerge. As a result of high speed cooling (10^7 – 10^8 K/s) of the irradiated samples martensite forming of complex morphology occurs. Detailed study of fine structure with the help of transmission electron microscopy revealed that martensite laminas completely fill the grain. The plate sizes are from 0,1 up to 0,3 micrometer (mainly about 0,1 micrometer). In their turn, martensite laminas have their own morphology. As it is seen (Fig. 2 a) nanoparticles aggregations of the size of about 15 nm are observed in their structure. Peculiarity of formed structure is the presence of twins in some laminas (Fig. 2 b). Results of X-ray diffraction

analysis confirm and complete electron microscopic study. The texture of primarily orientation of 32 % is vividly observed in the initial state. After irradiation the samples are practically isotropous. X-ray pattern development revealed that in Zr1%Nb alloy in the bearing state in the whole interval of angles of incidence the lines of α-phase Zr with hexagonal lattice occur. The lattice parameters constituted a = 3,2357 Å and c = 5,1471 Å. Phase Nb(Zr) was not detected by the method of X-ray diffraction analysis in the virgin samples. Influence by pulsed electron beam leads to evident change in structure phase state of material. The lattice parameters Zr phase after irradiation constitute a = 3,2262 Å and c = 5,1376 Å. The decrease in zirconium lattice parameters after irradiation is related to forming of martensite phase α′Zr.

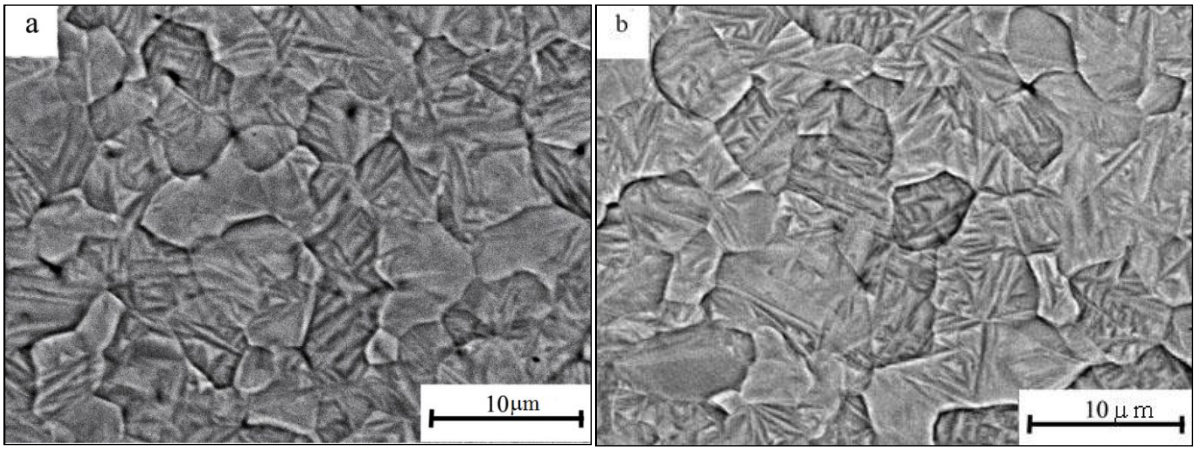


Fig. 1. Microstructure of Zr1%Nb alloy surface irradiated under 15 J/cm^2 (a) and 18 J/cm^2 (b)

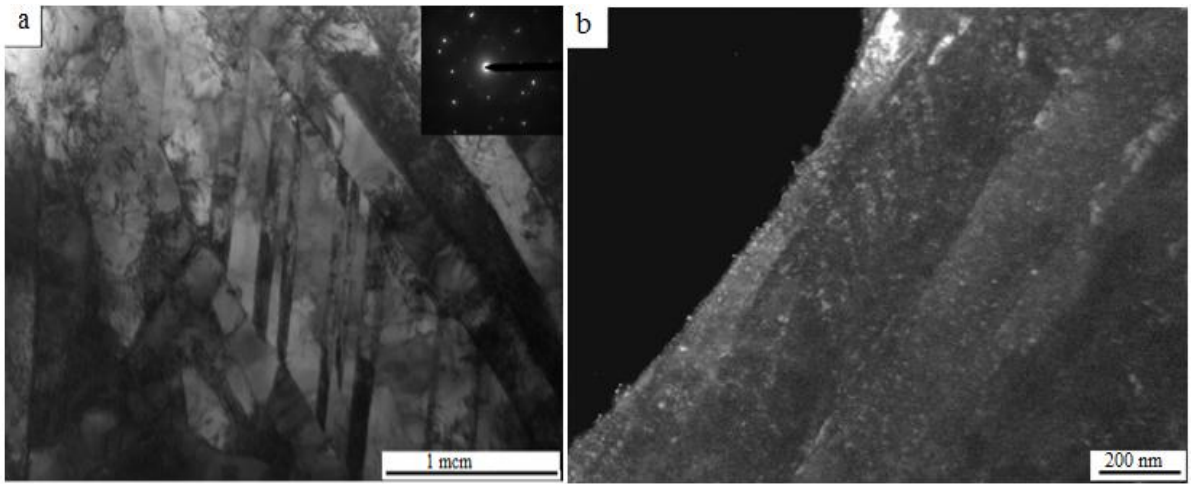


Fig. 2. Electron microscopy image of near-surface layer structure of Zr1%Nb alloy after irradiation

Studies of the dependence of microhardness of the load on the indenter were carried out for the central region of the impact of EPI and the source material. Found at low loads (at a depth of up to 2 μm) have high values of microhardness due to the presence of a thin and durable modified layer. At a depth of 5 - 10 μm microhardness decreases due to structural transformations. Studies of hydrogen

absorption process by zirconium alloy in dependence of the type of surface treatment were held within the temperatures range from 673 up to 823 K. Relation of chamber pressure to hydrogen saturation time for T = 723K and T = 823 K are given in Figure 3 a, b. Hydrogen sorption speed was determined by differentiating the pressure curves in the measuring chamber.

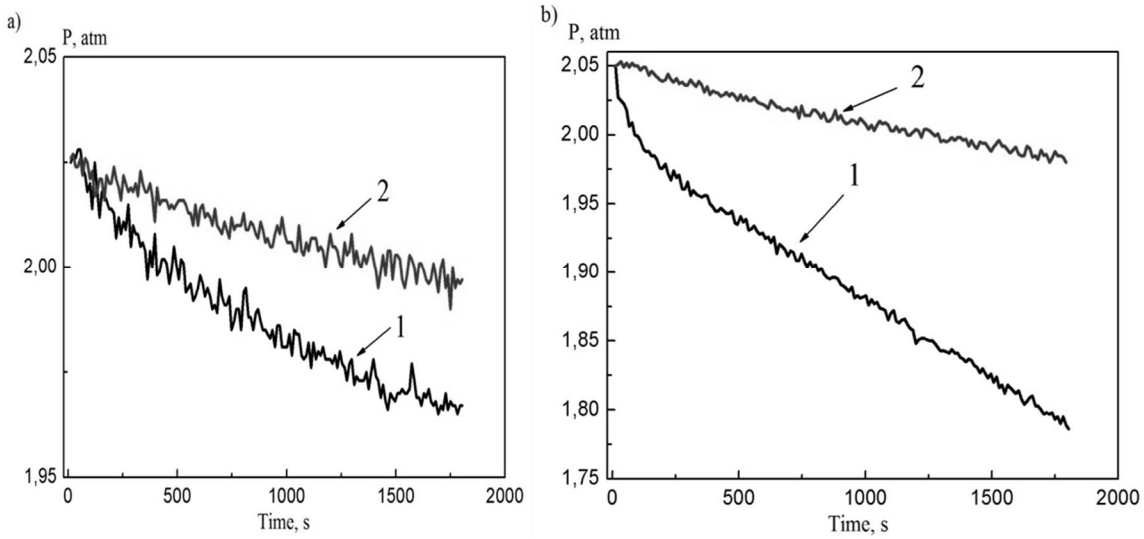


Fig. 3. Changes in hydrogen pressure in measuring chamber during hydrogen saturation: 1 – initial; 2 - samples after pulsed electron beam modification

Pulsed electron beam irradiation leads to changes in kinetics of hydrogen sorption (Table 1). Thus, the rate of hydrogen sorption speed by samples after pulsed electron beam modification under the temperature T = 873 K is three times lower than by the virgin samples. The minimal temperature under which hydrogen absorption for the alloy with bearing state is observed is T = 673 K, after irradiation T = 723 K.

Table 1 – Temperature relation of zirconium alloy sorption speed in the bearing state and after pulsed electron beam irradiation

Hydrogen saturation temperature, K	Hydrogen sorption speed $*10^{-5}$ cm^3 $H_2/(s\cdot cm^2)$	
	initial	pulsed electron beam
673	2,9	-
723	3,1	1,5
773	3,7	2,5
823	12,1	3,8

Analyzer LECO firm studied the effect of electron beam irradiation on the volumetric accumulation of hydrogen in zirconium alloy Zr-1% Nb for the three modes of irradiation. It is established that the hydrogen content in the source material was 0.00102 wt%. After hydrogenation the hydrogen concentration in the specimens of zirconium, not subjected to electronic processing, was 0.0128 wt% (an increase of more than an order of magnitude compared to the original material). In specimens

irradiated with the total contributed by the energy beam 15, 18 and 20 J/cm^2 hydrogen concentration was 0.00733, 0.00465 and 0.00809 wt%, respectively. Thus, the hydrogen concentration in the specimens treated with an electron beam in the regimes of 15 and 20 J/cm2, is less than 1,7 times, and for treatment 18 J / cm ^{2} - 2,5 is less than 3 times compared to the starting material, saturated with hydrogen. These results suggest that irradiation by electron beam forms a surface layer which retards the penetration of hydrogen into the material. After hydrogen saturation from the gaseous phase the surface hardening is observed for initial samples as well as for the samples irradiated by pulsed electron beam (Fig. 4, 5).

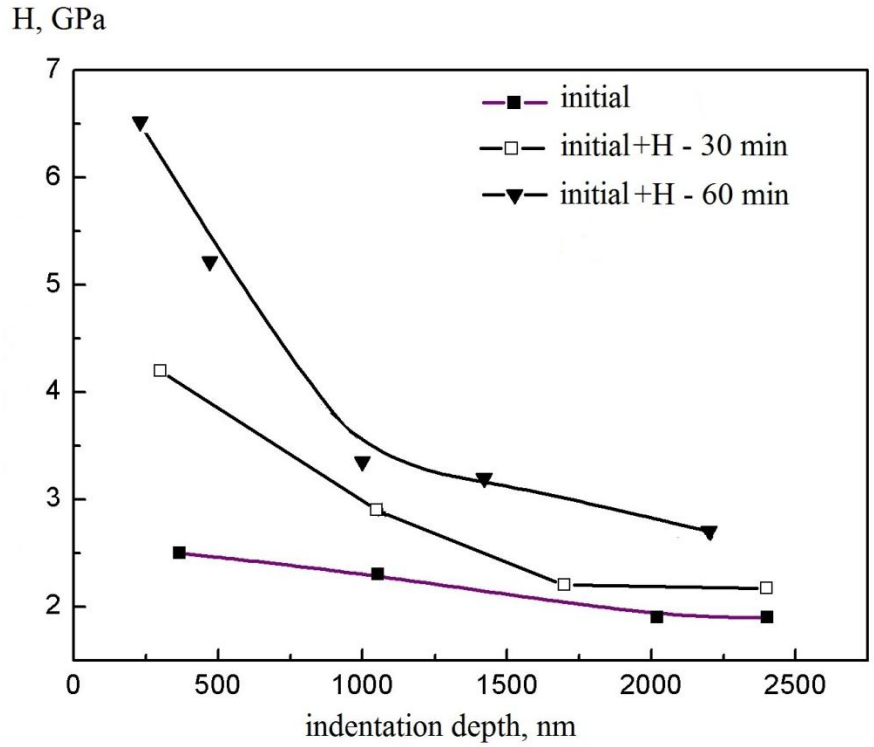


Fig.4. Distribution of zirconium alloy hardness in the bearing state after hydrogen saturation

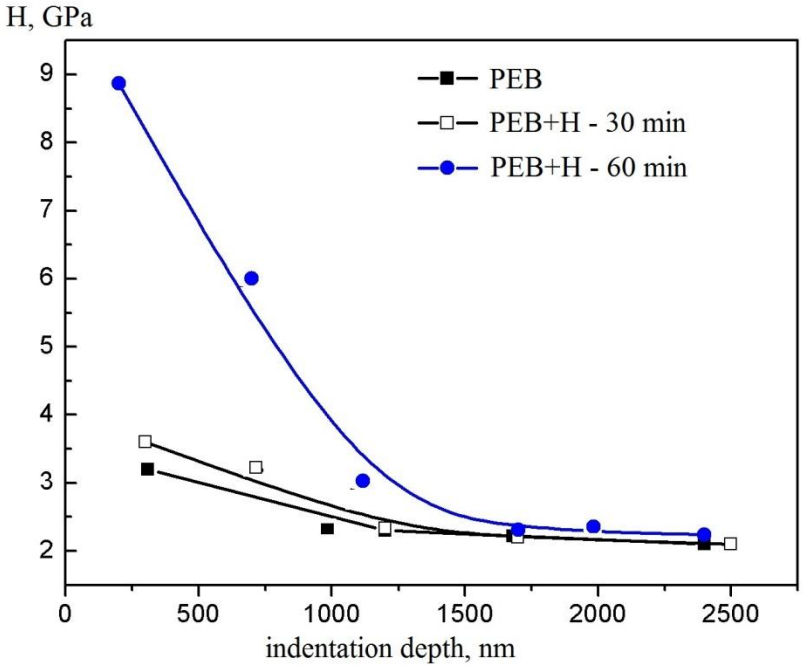


Fig.5. Distribution of zirconium alloy hardness in the bearing state after modification and hydrogen saturation

The peculiar feature for the modified samples is that increase of hardening is observed for the depths about 1,7 micrometer, at the same time the zirconium alloy in the bearing state after hydrogen saturation is characterized by high hardness also in the depths of more than 3 micrometer. Increase in hardness in this case is related to forming hydrides during the hydrogen saturation process. Thus, the effect of decrease of hydrogen sorption by modified surface of zirconium alloy Zr1%Nb is determined by forming specific quenching structure under the irradiation impact up to the temperatures that exceed the melting temperature and subsequent high speed surface cooling. Such layer becomes the barrier layer for hydrogen penetration into material volume. By concentrating in modified surface hydrogen causes surface hardening of samples.

CONCLUSIONS

The held complex of research activities allows to make the following conclusions: 1) Specifics of irradiated samples structure is the presence of martensite texture with single twins in surface layer. The size of martensite laminas are from 0,1 to 0,3 micrometer. 2) Modification of Zr1%Nb alloy surface by pulsed electron beam considerably decreases hydrogen absorption speed. Sorption of modified alloy under the temperature of 723 K constitutes 1,5 cm^3 $H_2/(c \cdot cm_2)$ and 6,0 cm^3 $H_2/(c \cdot cm^2)$ under the temperature T = 873 K accordingly, this is respectively in three times lower that in comparison with the initial material. 3) Formed as a result of pulsed electron beam irradiation surface layer prevents hydrogen penetration into material volume.

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