Structure and hardness of the zirconium surface after laser modification

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Abstract. The change of hardness and structure of the zirconium surface after laser modification in air has been analyzed. The dependences of the hardness parameters and the nature of the surface structure on the laser processing regimes were determined. The hardness of the hard-facing layer of zirconium was increased to 25–34 GPa.

1. Introduction
Due to its physical and chemical properties, zirconium and its alloys have found wide application in machine-building and instrument-making, as well as in the manufacture of medical and technical products. Under the influence of mechanical loads, the ductility and strength characteristics of zirconium products are reduced [1]. To improve performance, zirconium and its alloys are subjected to thermal and chemical-thermal treatment, gas and steam thermal oxidation [2].

Laser hardening of various steels, titanium, tantalum and zirconium alloys [3-10]. In the process of hardening, there is a significant change in the structure of the near-surface layer of the metal and, consequently, of the physical and mechanical properties, such as hardness and wear resistance. Laser processing of various materials is characterized by:

• Versatility - the ability to simultaneously perform thermal and chemical-thermal treatment;
• Locality - the ability to process a specific area of the surface;
• Also, in some cases, laser processing can reduce and sometimes completely eliminate a number of preliminary operations for the preparation of products, such as grinding, polishing, cleaning from process contaminants [11].

The purpose of this work was to determine the dependence of the structure and hardness of the surface layer of zirconium on the conditions of pulsed laser action.

2. Methodology
The processing of zirconium samples was performed using an automated installation for thermophysical coherent surface modification "LRS-50A". The test samples were zirconium plates of E110 grade, the size of which is 10 × 10 × 3 mm. The laser action was carried out at the following voltage parameters $U$, experimentally selected: 350, 375, 400, 425, 450, 475 V. The duration $t$ of the pulse action was set to 0.70, 0.85 and 1.00 ms. The laser ray was focused to a spot diameter of 1 mm.

The scanning of surface was performed at a pulse recurrence frequency of radiating of 15 Hz and an overlap ratio of 0.1. The structure of the paving surface was investigated by optical microscopy using the computer program of graphic processing of microimages "Metallograph". In this case, the coverage areas of 5 mm² were analyzed. The microhardness was measured using a "PMT-3m" hardness tester with a Vickers indentor at an indentor load of 1.96 N (ISO 6507-1: 2005). Statistical processing of the results of the study was carried out using the "DataFit" program.
3. Results
According to the microscopic analysis, the surface of zirconium samples as a result of pulsed laser action acquires a uniformly distributed structure at elevated values of voltage $U = 475$ V and duration $t = 0.70$ ms (Figure 1). With a pulse duration of $t = 1.00$ ms and a voltage of $U = 475$ V, a heterogeneity of the structure and a strong fusion of the laser action zone are observed.

![Figure 1](image1.jpg)

**Figure 1.** Morphology of the surface after pulsed laser action for a duration $t = 0.70$ ms and a voltage $U$: 350 V (a), 475 V (b) and duration $t = 1.00$ ms and a voltage $U$: 350 V (c), 475 V (d)

With a low voltage $U = 350$ V and a short duration of $t = 0.70$ ms, the sample surface was uniform, uniformly distributed. On the prepared microsections there were no microcracks (Figure 2a). With increasing voltage and duration of impulse exposure, the formation of microcracks and their growth into the interior of the metal are visualized (Figure 2b). For example, at a voltage of $U = 475$ V and a duration of $t = 1.00$ ms, the size of the cracks reaches 180 μm.

![Figure 2](image2.jpg)

**Figure 2 (a,b).** Microsections of samples after laser modification: $t = 0.70$ ms and $U = 370$ V (a); $t = 1.00$ ms and $U = 450$ V (b).
The results of hardness measurements showed that the hardness of zirconium samples increases significantly during the laser pulsed operation. The maximum value of \( H = 33.9 \) GPa was obtained at a voltage of 450 V and a pulse duration of 1.00 ms. The hardness value of the original zirconium sample was 2.6 GPa. Based on the obtained results, an empirical model was constructed for the dependence of the hardness of the zirconium surface \( H \) on the modes of laser modification (Figure 3).

\[ H = \ -82.6473 \ + \ 0.689x_1 \ - \ 86.244x_2 \ - \ 4.054x_1^2 \ + \ 77.44x_2^2 \ - \ 0.2427\frac{x_1}{x_2} \]

where \( x_1 \) - voltage (\( U \), V); \( x_2 \) - pulse duration (\( t \), ms).

One of the important characteristics of the coating is porosity \( P \). Based on the measurement results, an empirical model was constructed for the dependence of the open porosity on the voltage and duration of the impulse action (Figure 4). The maximum open porosity is 68% with a duration of 0.95–1.00 ms and a voltage of 440 V, and a minimum value of 43% with a pulse duration of 0.70 ms and a voltage of 340 V.

The constructed empirical model is described by the regression equation:

\[ P = 282064.5 - 3459.98x_1 + 16.91x_1^3 - 0.04x_1^3 + 4.99x_1^4 - 2.42x_1^5 - 170.41x_2 + 81.48x_2^2 \]

where \( x_1 \) - voltage (\( U \), V); \( x_2 \) - pulse duration (\( t \), ms).
Conclusions

It is established that under certain regimes of pulsed laser influence on the zirconium surface a highly hard coating with a homogeneous structure is formed. Laser modification of the surface of zirconium is similar to the chemical-thermal treatment by the results of hardness measurements. Rational regimes for the formation of a highly solid homogeneous structure were recommended.

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Figure 4. Dependence of open porosity on the duration of impulse action and stress.