Additive manufactured VT6 titanium alloy surface modification by electron-ion-plasma methods

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Abstract. It was shown that alloying of the samples of VT6 titanium alloy made by method of additive manufacturing in a single vacuum cycle on «COMPLEX» installation by deposition of a thin film of zirconium and the subsequent liquid-phase mixing by means of pulse electron beam treatment allows considerably to reduce roughness and porosity of a surface layer and to increase its mechanical properties. In the optimum modes of processing the increase in microhardness at \( \approx 40\% \) in comparison with initial samples has been received. Values of roughness, tensile strength and wear resistance correspond to initial material.

1. Introduction
Purposeful design of the surface of materials and products using modern electron-ion-plasma methods is an urgent task, since its solution allows to create functional layers and coatings that significantly increase the physico-mechanical and performance characteristics of machine parts and mechanisms, as well as a variety of tools, increasing their service life in extreme conditions of operation and thus leading to energy and resource saving [1–4]. A new step in the development of combined electron-ion-plasma technology, which determines its undoubted scientific novelty and practical significance, is the combination of its constituent processes in a single vacuum cycle: (1) the formation of a gradient multiphase surface layer by gas-phase saturation with introducing elements (nitrogen, carbon, oxygen, etc.), (2) synthesis of thin metal films or superhard nanostructured coatings based on nitrides (carbides, borides, etc.) of refractory metals (Ti\textsubscript{Cu}N, Zr\textsubscript{Mo}N, Ti\textsubscript{Si}N, etc.) by ion-plasma methods and (3) formation of surface alloys when mixing a film/substrate system with predicted functional properties or fusion into the substrate of these coatings by a high-intensity pulsed electron beam to increase the adhesion forces of the coating/substrate system [5].

At present, the possibility of using 3D-printers for the manufacture of metal products by the method of fusing a metal powder with a laser or electron beam is growing rapidly [6–8]. A feature of these methods is that the product is built in a thin (50–100 \( \mu \)m) layer of metal powder, where separate particles are fused under the action of laser or electron beam effect. As a result, a porous layer with a large roughness (up to \( R_a = 30 \mu \text{m}, R_z = 150 \mu \text{m} \)) is formed at the product/powder border, due to the adherence of separate powder particles. In most cases, for further use of the product, it is necessary to finish the surface of the material. Earlier [9], using VT6 titanium alloy, it was shown that pulsed electron-beam polishing can be used along with traditional technologies for finishing surface of metal products (mechanical processing, chemical and electrochemical etching).
The purpose of this work is to develop a comprehensive method for finishing surface of metal products manufactured by additive technologies, combining preliminary arc deposition of the coating and subsequent pulsed electron-beam modification of the film/substrate system in a single vacuum cycle. This comprehensive treatment combine the reduction of roughness and alloying the substrate surface with a coating material for modification of surface layer mechanical properties.

2. Materials and research methods

Material of a research were the specimens of BT6 titanium alloy in the form of flat plates of 15 mm × 15 mm × 2 mm in size made by method layer-by-layer selective electron beam fusion in a vacuum («Arcam A2X» setup of Arcam (Sweden) [10]) of metal powder with a size of particles of 40–100 µm. In addition, for mechanical tensile tests the specimens with a narrow part, parallel sides and rectangular ends were cut out.

The combined surface treatment of VT6 titanium alloy specimens created by the method of additive technologies was performed in a single vacuum cycle at «COMPLEX» setup [5] and included two main stages: deposition of a metal Zr-film and surface alloying of the film/substrate system using an electron beam. In addition, the use of preliminary electron-beam smoothing of the surface of the specimens before the deposition of films and the use of finishing after alloying was varied.

The deposition of a metal Zr-film with a thickness of 2 µm was performed by the method of vacuum arc sputtering of a Zr-cathode material. The deposition of the film was preceded by the stage of cleaning the substrate in a low-pressure arc discharge plasma. Using «PINK» plasma source [11], a non-self-sustained arc discharge with a current of 20 A was ignited in a vacuum chamber at a working gas (Ar) pressure of 7.6 × 10⁻² Pa. Pulse negative bias with an amplitude of 900 V, a frequency of 50 kHz, a duty factor of 50% was applied to the specimens. The processing time was 15 minutes.

The Zr-cathode was vacuum-arc sputtered at the discharge current of 80 A and an argon pressure of 7.6 × 10⁻² Pa in the presence of arc discharge plasma of «PINK» plasma source with a current of 20 A. Pulsed negative bias with amplitude of 35 V, a frequency of 50 kHz, a duty factor of 60% was applied to the specimens. The deposition rate of Zr-film was 18.6 µm·h⁻¹.

The surface alloying of the substrate with the deposited film material, carried out as a result of melting of the film/substrate system with a high-intensity pulsed electron beam [12], was performed with the following parameters: working gas (Ar) pressure in the vacuum chamber of 3.6 × 10⁻² Pa; beam pulse duration of 200 µs, energy of electrons of 15 keV, energy density in a pulse of 45 J·cm⁻². Alloying was carried out under the action of 10 pulses with a repetition rate of 0.3 s⁻¹ (mode No.1). The same mode was used for preliminary smoothing and reducing the porosity of the surface layer of the specimens before depositing the coating.

The finishing of the specimens surface with a pulsed electron beam was performed with the following parameters: working gas pressure of 3.6 × 10⁻² Pa; beam current pulse duration of 50 µs; energy of electrons of 15 keV, beam pulse energy density of 20 J·cm⁻². The treatment was performed under the action of 3 pulses with a repetition rate of 0.3 s⁻¹ (mode No.2). Earlier researches [9] showed that mode No.1 can significantly reduce the roughness and porosity of the surface of the initial specimens of the VT6 alloy produced by the layer-by-layer selective electron-beam fusing in vacuum, and the mode No. 2 can modify the mechanical properties and finishing the surface layer.

Experimentally, four modes of surface modification were selected (see table 1), characterized by the presence of preliminary smoothing and reduction of surface layer porosity (mode No. 1) and the use of the finishing mode (mode No.2).

The surface roughness of the specimens was studied using «MNP-1» optical profilometer (basic length of 0.8 mm, at least ten measurements per sample). The study of microhardness of the specimens’ surface was carried out on «PMT-3M» device. The measurement was carried out in not less than ten points on different parts of the surface with a load of 0.5 N. Mechanical tensile testing of the material was carried out with a device «Instron 3369». The initial thickness, width, and length of the working part of the specimens were 2 mm, 2 mm, and 10 mm, respectively; test speed
0.2 mm·min⁻¹; temperature 20°C. Deposition of coating and radiation of specimens was carried out from both flat sides.

### Table 1. Surface treatment modes for VT6 titanium alloy specimens

| Specimen number | Preliminary treatment in mode No. 1: 45 J·cm⁻², 200 µs | Deposition of Zr-coating 2 µm | Subsequent treatment in mode No. 1: 45 J·cm⁻², 200 µs | Finishing in mode No. 2: 20 J·cm⁻², 50 µs |
|-----------------|---------------------------------|-----------------|---------------------------------|-----------------|
| 1               | yes                             | yes             | yes                             | yes             |
| 2               | yes                             | yes             | yes                             | no              |
| 3               | no                              | yes             | yes                             | yes             |
| 4               | no                              | yes             | yes                             | no              |

The tribological properties of the specimens were studied under dry friction according to the disk-ball scheme at «TRIBOtechnic» setup. As the indenter (counterbody) served the ball with a diameter of 6 mm from WC-Co hard alloy. The tests were carried out at room temperature and a relative humidity of 50 % under the following conditions: normal load on the indenter of 3 N, sliding speed of 2.5 cm·s⁻¹, track diameter of 4 mm, distance traveled by the ball of 15 m. The amount of material wear was determined after profilometry of the formed track.

«Philips SEM-515» scanning electron microscope (U_{max} = 30 kV) was used to study the surface structure of the specimens.

### 3. Results and discussion

The images of the specimens’ surface after alloying with zirconium taken by means of the scanning electron microscope are submitted in figure 1. It is shown that use of the mode of a surface finishing (mode No.2) leads to formation of the lamellar structure reminding martensite (figures 1a and 1c). The mode of surface layer alloying (mode No.1) forms structure of cellular crystallization with a size of cells of 0.5–1.5 µm (figures 1b and 1d). The x-ray spectrum analysis of a surface did not reveal difference in element structure for all modes of radiation.

Researches of roughness, microhardness and tribological properties of the specimens are presented in table 2. The modes with use of finishing processing showed optimum improvement of mechanical properties of VT6 samples surface alloyed by zirconium relative to initial specimens (modes No.1+No.2 with preliminary treatment, modes No.1+No.2 without preliminary treatment). Surface microhardness at the same time increased by ≈ 40% relative to initial material. Increase in coefficient of friction at ≈ 24% is followed by growth of wear parameter on ≈ 43% for specimens without preliminary treatment. The specimen with preliminary treatment showed result similar to initial specimen. The roughness of a surface of the specimens alloyed in the optimum modes turned out at the level of R_s = 0.8–1.8 µm that close to the values received on initial specimens at an electron beam processing.

The results of tensile testing of alloyed specimens are presented in figure 2. The maximum values of tensile stress were also shown by specimens alloyed in modes No.1+No.2 (with and without preliminary treatment). Their values are comparable with the tests of the initial specimens without electron-beam processing (± 7%). All samples showed similar plasticity values despite the difference in ultimate strength (table 3).
Figure 1. The surface structure of the «Zr (coating)/VT6 (substrate)» system irradiated by pulsed electron beam in different modes: a – mode No.1+No.2 with preliminary treatment; b – mode No.1 with preliminary treatment; c – mode No.1+No.2 without preliminary treatment; d – mode No.1 without preliminary treatment.

Table 2. Roughness, microhardness, and tribological properties of VT6 specimens surface alloyed with zirconium.

| Mode                        | Microhardness, HV50 | Coefficient of friction | Wear parameter (mm³·N⁻¹·m⁻¹) | Roughness (µm) |
|-----------------------------|---------------------|-------------------------|--------------------------------|----------------|
| No.1 (without preliminary treatment) | 462                 | 0.46                    | 6.6×10⁻⁴                      | 2.3±0.5        | 9.6±1.5       |
| No.1+No.2 (without preliminary treatment) | 437                 | 0.45                    | 6.6×10⁻⁴                      | 0.8±0.5        | 5.2±1.5       |
| No.1 (with preliminary treatment) | 364                 | 0.47                    | 7.7×10⁻⁴                      | 1.8±0.5        | 11.6±1.5      |
| No.1+No.2 (with preliminary treatment) | 420                 | 0.44                    | 4.7×10⁻⁴                      | 1.6±0.5        | 8.1±1.5       |
| Initial                     | 306                 | 0.36                    | 4.6×10⁻⁴                      | 20.2±1.5       | 93.8±10       |
| No.1+No.2                   | 303                 | 0.32                    | 5.2×10⁻⁴                      | 1±0.5          | 5±1.5         |
Figure 2. Tensile test results for «Zr (coating)/VT6 (substrate)» system irradiated by pulsed electron beam in different modes.

Table 3. Tensile tests of VT6 titanium alloy specimens manufactured by additive technologies.

| Mode                  | Tensile stress (MPa) | Tensile strain (in %) |
|-----------------------|----------------------|-----------------------|
| No.1+No.2 (with PT)   | 999.3                | 17.3                  |
| No.1+No.2 (without PT)| 874.5                | 17.6                  |
| No.1 (with PT)        | 755.7                | 16.6                  |
| No.1 (without PT)     | 840.6                | 16.2                  |
| Initial               | 933.2                | 17.2                  |
| No.1+No.2             | 1047.2               | 19                    |

The structure of a surface of destruction of the best and the worst (on tensile stress) alloyed specimens is presented in figure 3. Pictures of a surface of destruction show existence of cavities and pores in volume of initial material that demonstrates insufficiently quality fusion of metal powder particles during the growth of specimens. In general, the destruction of structure of the specimens has similar character. Besides, the alloyed layer which thickness is about 20 μm is distinguishable on both specimens.
Figure 3. Pictures of specimens surface of destruction of «Zr (coating)/VT6 (substrate)» system irradiated by pulsed electron beam: a, c – mode No.1+No.2 with preliminary treatment; b, d – mode No.1 with preliminary treatment.

4. Conclusion
Thus, as a result of the studies, it was shown that the combined technology of alloying with zirconium in single vacuum cycle of the surface of VT6 titanium alloy specimens manufactured by the additive technologies method allows to carry out a simultaneous smoothing and modification of the strength properties of the surface layer. In optimal processing modes, an increase in microhardness by \( \approx 40\% \) in comparison with not alloyed specimens was received. The values of roughness, tensile stress and wear resistance in this case correspond to the initial material.

The developed way of reduction of roughness (initial \( R_a \approx 20 \mu m \)) and improvements of strength properties of a surface of the materials and products made by means of additive technologies consists in alloying of a surface with other material or a composite by creation in a single vacuum cycle of the «film/substrate» system (thickness of a film of 2–4 \( \mu m \)) and the subsequent radiation by a pulse electron beam in the surface smoothing mode (energy density in a pulse > 30 J·cm\(^{-2}\), duration of a pulse of 150–200 \( \mu s \)), and then in the mode of finishing processing (energy density in a pulse \( \leq 20 \) J·cm\(^{-2}\), duration of a pulse of 50–100 \( \mu s \)). The degree of influence of both modes is defined by quantity of pulses which are selected individually for each material and shape of the product. In addition, the mode of preliminary treatment which corresponds to the smoothing mode can be used before coating deposition.
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