Formation of wear-resistant oxide-carbide coatings on titanium by electrospark alloying

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Abstract. In this paper the peculiarities of formation of wear-resistant coatings on the surface of VT1-00 titanium by electrospark alloying are described. Sequential treatment with titanium and graphite electrodes was used, as a result of which carbide and carbon-nitride coatings were obtained. The chemical composition, surface morphology and microhardness parameters were studied. The surface after electrospark alloying with a titanium electrode had a microhardness of 1270–1300 HV (12.45–12.75 GPa), and after treatment with a graphite electrode it equalled 2040–2080 HV (20.0–20.4 GPa).

1. Introduction
High-strength metals and alloys are used for the production of different items operating under high mechanical loads. Good results are ensured due to the application of titanium alloys, however, they have some disadvantages, namely, a possible contact seizure (during friction) and low wear resistance [1,2]. In order to increase the functional characteristics of metal products, coatings with the required phase composition, structure and mechanical properties are deposited on the surface. The application of electrospark alloying (ESA) allows the formation of coatings with high mechanical properties, in particular adhesion strength and hardness [3-9]. Based on the analysis of the available works on ESA technology, it was established that in order to increase the efficiency of strengthening the surface of products, complex processing is required. In this paper, the results of the study of chemical composition, structural changes in the surface, and microhardness of titanium samples after ESA were presented.

2. Methodology
The formation of coatings by the ESA method was performed on the end surface of cylindrical samples 2–3 mm long with the diameter of 6.5–7 mm and fabricated from VT1-00 titanium alloy. The working electrodes were rods (2.0±0.1 mm in diameter and 20–25 mm long) from VT1-00 titanium alloy and MPG-6 graphite. Current density \( j \) and specific processing time \( t \) were chosen as the controlled factors of the ESA process.

Before coating deposition, titanium samples were cleaned in an aqueous ethanol solution. Scanning electron microscopy (SEM) was used to study the morphology. To study the phase composition, X-ray diffraction analysis (XRD) was performed. When measuring hardness, the Vickers method was applied (the load on the indentor equaled 100 gf).

3. Results
The chemical analysis showed that the main elements in the samples after electrospark alloying with titanium were Ti (43–48 at.%), O (31–43 at.%) and N (13–25 at.%). The subsequent ESA with graphite promoted chemical changes, namely, C (up to 72 at.%) and Ti (20–26 at.%) prevailed in the
coating composition. The composition of the modified coatings also contained Si (up to 4 at.%), which was explained by the initial composition of the alloying electrode.

Due to XRD the spectra showing the peaks of different phases were obtained (Figure 1). In the course of ESA with a titanium electrode, on the surface of the treated product, oxide and nitride compounds of titanium were formed, which were caused by heating and interaction with the surrounding atmosphere. As a result of the subsequent exposure to a graphite electrode, titanium oxide (TiO), titanium disilicide (TiSi₂), titanium carbide (TiC) and silicon carbide (SiC) were found on the surface.

**Figure 1.** The diagram of distribution of chemical elements on the surface of the coatings subjected to ESA.

SEM results of titanium samples showed the presence of structurally heterogeneous surface morphology. During the treatment with a titanium electrode, the main microrelief of the coating surface was formed (Figure 2a), and subsequent treatment with graphite ensured the surface modification (Figure 2b).

The resulting coating was a composite structure. The upper layer of the coating was a film of the anode material modified by the elements of the cathode material and the interelectrode medium. These structures were located on the surface in the form of separate agglomerates, the distribution on the surface of which depended on the treatment conditions, the anode material and the exposure time. There was an area consisting of a mixture of anode and cathode materials under the agglomerates observed. Then was the layer formed due to the diffusion of the chemical elements of the anode material in the cathode material. And beneath the latter layer was the lowest one having the largest thickness, formed as a result of the pulse heat action. It was represented by a granular structure that was formed from the product material. At a bigger depth, this structure gradually changed into the original structure of titanium. Depending on the ESA modes, the significance of the first three layers can be significant or insignificant, and the role of the structure formed under the pulse heat action, is always fundamental.
Figure 2(a, b). Surface morphology of the samples after ESA with titanium (a); and graphite (b).

The thickness of the deposited composite coating depended on the technological modes of ESA (Figure 3). The greatest influence was due to the current density $j$ in the course of treatment with a titanium electrode. With subsequent exposure to a graphite electrode, there was no significant increase in the coating growth, and modification of the deposited titanium layer by the penetration of carbon was observed. Depending on the treatment mode, 8–15 to 40–70 μm thick coatings can be produced. The minimum coating thickness was formed at $j = 11$ A/mm$^2$ and $t = 10$ min/cm$^2$; the maximum thickness was ensured at $j = 18$ A/mm$^2$ and $t = 3.5$ min/cm$^2$.

Figure 3. The microsection of the coating (1) after ESA with titanium and graphite produced on a titanium sample (2) with the greatest current density $j$ and treatment time $t$. 
In the course of treatment with a titanium electrode, the microhardness grew to 1270–1300 HV (12.45–12.75 GPa) at a current density of 14 A/mm$^2$ and a specific processing time of 5 min/cm$^2$. When using a graphite electrode, the microhardness reached 2040–2080 HV (20.0–20.4 GPa) at a current density of 18 A/mm$^2$ and specific processing time of 3.5 min/cm$^2$.

4. Conclusions

Thus, the sequential ESA with titanium and carbon of the surface of titanium products provided the formation of a hard coating (up to 20.0–20.4 GPa), the morphology of which had the required parameters for the effective contact interaction in rubbing elements of various types.

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