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COMPARISON OF ELECTROLYSIS METHODS OF DIFFUSION COATING OF TITANIUM PARTS WITH BORON

Various regimes of electrolytic diffusion saturation of the surface of titanium parts of BT-0 grade with boron are compared. Electrolysis treatment was carried out in a constant flow of an aqueous electrolyte solution, with a constant current of density up to 4.5A/cm^2 and compared with the same treatment, but in a pulsating electric current mode. As a result of the metallographic analysis, it is established that the change nature of microhardness with the depth in the sample depends on saturation conditions. In different regimes layers with a depth of up to 80 µm with a microhardness of 4 to 14 GPa were obtained, and the pulsed processing showed an improvement in result, inclusions appeared in craters in which a more solid phase was formed that made the surface of component hardened by the principle of composite materials. According to the X-ray diffraction analysis of the processed samples, in the diffusion layer, in addition to TiB, Ti_3B_4, and to a lesser extent TiB_2, titanium oxides Ti_2O_3 and TiO are present. But in this case the oxide phase is insignificant and does not compete with the boride phase. Studies of radiation-absorbing ability of borated titanium treated by various methods show that its absorbing power depends on the method of treatment. It is established that the maximum absorbing ability is observed in samples treated in a pulsed mode. Obtaining wear-resistant coatings on titanium, which include titanium-boron and oxygen-titanium-boron containing phases, is perhaps one of the ways to solve urgent problems of improving the safety and reliability of parts used in aerospace products and nuclear power plants for various purposes.

Keywords: thermochemical treatment, microhardness, diffusion saturation, titanium borides, radiation absorbance, electrolysis, pulsating current, magnetic field, wear resistance, titanium oxides, composites.

1. Introduction

Titanium and its alloys have low density, high mechanical properties and specific strength, and high corrosion resistance, but without hardening, titanium alloys have low abrasion resistance and tendency to sticking, formation of scoring and cavities in the friction units. Electrochemical modification is one of the most common ways to modify metallic surfaces at the nanoscale level [1]; indeed, anodic oxidation was successfully used to transform smooth titanium surfaces into nanotubular structures with diameters lower than 100 nm, and nanostructured layers were created on various metallic surfaces with using electrophoretic deposition [2]. A particular category of physical methods includes technologies that provoke atomic rearrangements such as ion implantation and thermal oxidation; moreover, on the way of nanoscale surface modifications, annealing and thermal oxidation were explored on titanium-based metals to enhance their bioactivity by changing the crystalline structure of the nanometric native oxide layer [3]. To increase the wear resistance of the surface of fabricated titanium products, diffusion saturation with boron can be used too.

The purpose of the study was to determine the most effective method of obtaining a wear-resistant boron-containing coating on the parts of titanium. The research and comparison of various methods of electrolytic diffusion saturation of a surface of titanium samples of grade BT-0 with boron were conducted [4]. Electrolysis treatment was carried out in four ways: 1) using a direct current; 2) with long and multipolar DC pulses; 3) with direct current and under the influence of an alternating magnetic field; 4) with long-term and multi-polar DC pulses, under the influence of an alternating magnetic field.

2. Experimental method

Before the electrolysis treatment, the surface of all samples was cleaned with a file to remove a layer of oxides that could appear during the time spent in the air. The sample attached to the electrode was immersed in a continuous flow of electrolyte, which was well mixed and forcedly cooled. In all four ways, the current density reached the value of 4.5 A/cm^2 over the entire sample area. Voltage was 250 V. And the increase in current density from 2.5 to 4.5 A/cm^2 depended on the electrolyte temperature approaching to the boiling point (Fig. 1). Since the electrolyte was water-based and it was known that the dissociation of water increased near the boiling point, it can be assumed that in the exchange of charges, in addition to the electrolyte ions, hydrogen and oxygen ions took an active part.

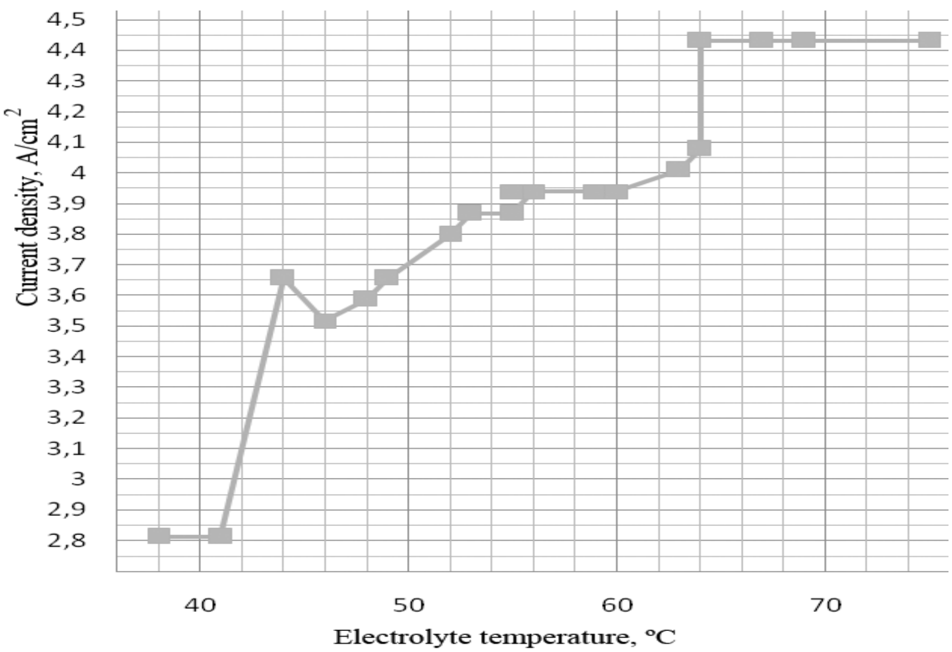

Fig. 1 Dependence of current density on the electrolyte temperature

1) With direct current processing, the sample under test acted as a cathode continuously for 3 minutes, after which, due to the particular installation, the electrolyte began to boil and the resulting vapor sharply reduced the current. After several minutes of forced cooling of electrolyte, the cycle was repeated 7 times. The total processing time was 21 minutes.

2) The method of long pulses was different in the voltage polarity change on the electrodes for 20 seconds immediately before switching to the normal mode for 160 seconds. The total processing time was 21 minutes. The electrolyte temperature increase approximately coincided with the previous method, with the difference that when switching from the reverse, the electrolyte was already heated by the reversal treatment.

3) and 4) analogously, other samples were processed in the forward and reverse modes, but still under the influence of an alternating magnetic field with the induction amplitude of 0.5 T on a sample and the frequency of 50 Hz. A cathode sample and anode edges in the electrolyte stream were placed inside the electromagnetic coil. In this case the current grew at a slightly slower rate than without the use of an alternating magnetic field.

3. Results

The analysis of processed samples was carried out with using metallographic and microhardness testing and X-ray diffraction analysis, on DRON-2, MPT-3, Epiqvant, and Neophot. As a result of electrolytic processing of samples by various methods, a diffusion layer was obtained on their surface, the depth, hardness and phase composition of which depend on the conditions for processing titanium samples. The sets of 6 samples were processed and examined, 100 to 200 measurements of microhardness were made on each of them (Fig. 2). The change of the parameter depends on the penetration depth of the boride phase, on the processing method, and on the remoteness of sample (cathode) area from the anode. The microhardness of diffusion layer obtained with titanium borides varies from 2 GPa to 14 GPa.

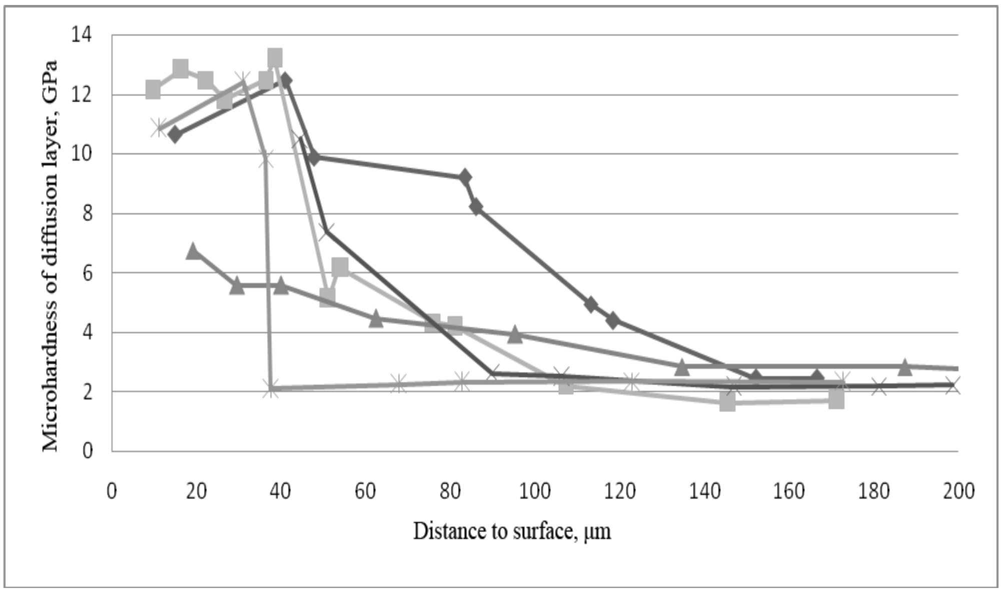

Fig. 2 Measurements of microhardness gradient of samples surface

Fig. 3 clearly shows the layer formed in the shape of differently directed needles. In some places, the directions of needles are staggered.

Fig. 3 Structure of titanium borides phase

Some samples were reflowed for research purposes, which contributed to the appearance of phases with a high microhardness of 10 – 15 GPa. It coincides with the microhardness of the TiB phase. The fusion of samples occurred from the near to the anode and when the current density achieved and maintained at 4.5 A/cm^2.

The use of long-term, multipolar DC pulses led to a more uniform distribution of areas with an increased boron content over the sample surface. A denser cathodic crust was formed on the surface, which, in part, prevented the ion current, provided a more even the electric current distribution across the surface of sample. Ions, penetrating through the pores in the near-cathode crust, formed the local microdischarges that led to melting and formation of the boride phase in the depth of a breakdown crater (Fig. 4). The averaged density of such craters is 9 ± 2 per mm^2, this parameter depends on the processing mode. The diameter of craters is from 20 to 200 μm, the boride phase is clearly visible only in large craters.

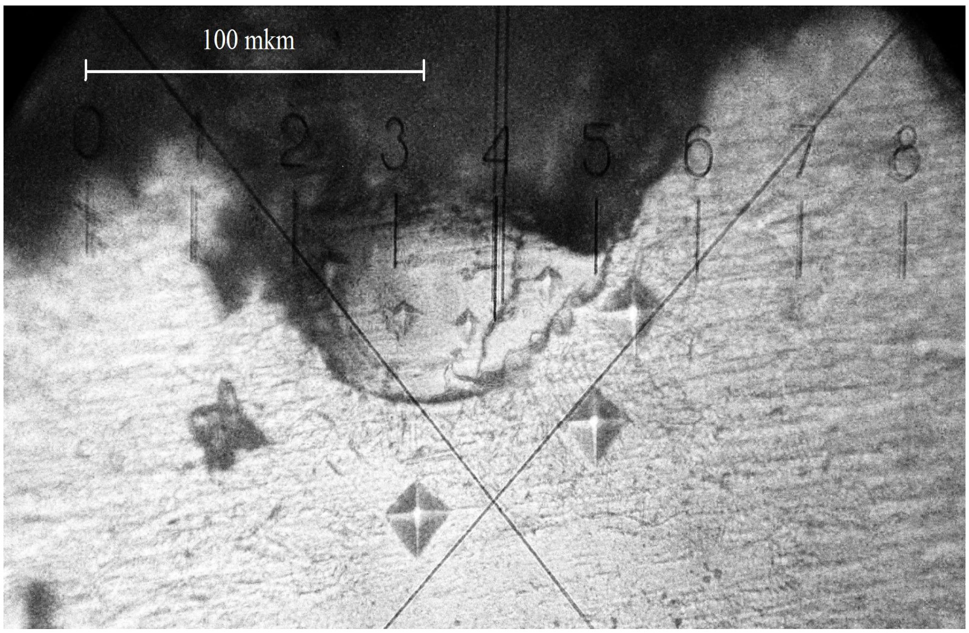

Fig. 4 Phases of titanium borides are appearing in the "craters"

The alternating magnetic field has some influence on the current in the electrolysis process, but no significant effect on the diffusion saturation with boron was observed.

According to the X-ray diffraction analysis of the processed samples, in addition to TiB, Ti_3B_4 phases, and to a lesser extent TiB_2, titanium oxides – Ti_2O_3, TiO – are present in the diffusion layer, but in this case the oxide phase is insignificant and does not compete with the boride phase.

4. Conclusions

The conducted study of the methods of electrolysis treatment shows the difference between the pulsed mode and the ramjet one. In the pulsed mode, a dense cathodic crust is formed on the entire surface of a sample, regardless of proximity to the anode, which partially prevents the direct electrolyte contact with the metal surface. As a result, a more uniform distribution of breakdown areas through the pores in the near-cathode crust occurs. The surface of the sample becomes covered with craters with the phases of borides formed in them. Such a surface can be resistant to mechanical wear, according to the principle of composite materials.

In the forward current mode, it is convenient to harden the local section on the workpiece while maintaining the unchanged microstructure on the rest of the workpiece surface.

Titanium, as a material for this work, is chosen because of its propensity for strong oxidation and surface destruction at thermochemical treatment. This can be avoided by electrolysis in aqueous solutions.

This method of diffusion saturation, also allows the production of borides of other metals, for example, aluminum alloys, steels, etc. [5]

The electrolysis method of diffusion saturation makes it possible to obtain a boron-saturated phase at the part of surface and to maintain an unchanged structure at the depth of the part, which is especially important in high-alloyed hardened alloys. The production of wear-resistant coatings on titanium, that include titanium-boron and oxygen-titanium-boron-containing phases, is one of the possible ways of solving urgent problems of safety and reliability of nuclear power systems for various purposes.

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