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Use of the Method of Micro-arc Plasma Oxidation to Increase the Antifriction Properties of the Titanium Alloy Surface

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The analysis of possibilities on phase-structural engineering of titanium-based alloys during micro-arc plasma oxidation (MAO) is carried out. The influence of phase-structural states on the tribotechnical properties of the modified surface of the titanium alloy VT3-1 is also considered. It has been established that in order to achieve high functional properties, it is necessary to use electrolytes of complex composition for MAO. The presence in the electrolyte of $(NaPO_3)_6$ leads to the formation of anatase with a low hardness (about 3 GPa). The formation of crystallites of rutile and aluminum titanate with the use of alkaline-aluminum electrolyte allows to increase hardness significantly (up to 7 GPa). The maximum increase in hardness (up to 12 GPa) is achieved in the coating obtained in alkaline-aluminate-silicate electrolyte. This is due to the formation of crystalline mullite. The friction coefficient of such a material decreases ($f < 0.01$) and as a result, antifriction properties increase. The results of the work indicate the prospects for using the phase-structural engineering method for MAO-processing to optimize the formation of antifriction coatings on titanium alloys.

Keywords: Micro-arc plasma, Titanium, Microstructure, X-ray phase analysis, Phase composition, Hardness, Abrasive wear.

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1. INTRODUCTION

A variety of areas of application of titanium alloys can be explained by the combination of properties such as low density, high specific strength and corrosion resistance [1]. At present, one of the most demanded areas for the use of titanium alloys is their biomedical application [2, 3]. Most of these materials are used for prosthetics (biomaterials) [4, 5]. However, biomaterials must possess not only high mechanical properties, but also good biological compatibility and high corrosion resistance [6].

In addition, when using biomaterials, titanium-based materials should be provided with high antifriction properties of the surface as a rubbing body (steam friction) [7, 8]. However, titanium-based alloys have poor antifriction properties, low wear resistance and a tendency to contact grabbing [9]. In this case, a relatively thin, natural oxide film on titanium is easily destroyed by friction. The coefficient of dry friction for a titanium-titanium pair is ~ 0.6, and is close when tested in oil and water [10].

These peculiarities of titanium-based alloys make it impossible for them to be used in friction units of biomedical and machine-building constructions without special surface treatment [11].

Currently, active development of new technologies for the processing of titanium alloys is underway. These are gas-thermal vacuum spraying [12], anodizing [13], galvanotechnology [14], ion implantation [15], ion-plasma deposition [16], vacuum-arc evaporation [17], thermal and chemical oxidation [18].

One of the prospect modules for the modification of the surface of the ethanol alloy is a method of micro-arc oxidation (MAO) [19]. In the process of MAO, the surface layer of titanium and its alloys is transformed into multifunctional coatings with a unique combination of properties such as high hardness, wear resistance, corrosion resistance, heat resistance, insulation resistance [20].

MAO technology has been well developed for aluminum alloys [21, 22]. For titanium alloys, the focus was on functional characteristics [23, 24], and insufficient attention was paid to the study of the phase composition and the quantitative ratios of the phases included in the MAO-coating under various technological processing conditions, although the phase composition of the coatings determines their tribotechnical properties.

Therefore, the purpose of this work was:

- to investigate the influence of technological parameters of the anode-cathode MAO process on the structure, phase composition and properties of oxide layers obtained on the VT3-1 titanium alloy;
- optimize the composition of the electrolyte and electrical parameters in order to form coatings with a thickness of more than 100 microns and with a hardness of more than 10 GPa.

2. SAMPLES AND METHODS OF RESEARCH

The VT3-1 titanium alloy (foreign analogue Ti-6242S, the alloy composition is given in Table 1) was subjected to micro-arc treatment. The treatment was carried out in alkaline electrolyte with additives of sodium alumina ($NaAlO_2$), sodium hexametaphosphate $(NaPO_3)_6$ and liquid glass (Na_2SiO_3). The composition of the electrolyte and the electrolysis modes varied: current density and processing time.

A 100 liter stainless steel bath was used, bubbling and cooling of the electrolyte were provided. The body of the bathroom served as a counter-electrode. A 40 kW capacitor type power supply was used. Oxidation was

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carried out in the anode-cathode mode.

In the course of the work, the following features of the MAO of the VT3-1 titanium alloy were revealed:

– the complexity of the oxidation organization in the mode of micro-arc discharges (the MAO process quickly stops or goes into arc discharges mode);

– silicate-alkaline electrolytes, which produce good results for aluminum alloys, have shown unsatisfactory results for titanium-based alloys. Coatings obtained in such electrolytes were porous, with low adhesion, poorly resistant to abrasion (not wear-resistant);

– high-density currents (40-50 A/dm2) were needed for the process to pass on the stage of micro-arc discharges.

Significantly higher properties are obtained at MAO-treatment in electrolytes of complex composition. The experimental method determines the conditions of electrolysis (composition of the electrolyte, current density, duration of treatment) in which the anode-cathode oxidation process is steadily implemented in the mode of micro-arc discharges (Fig. 1).

Table 2 shows the composition of the electrolytes, which ensure the formation of coatings in the thickness of more than 100 microns.

Sodium hexamethophosphate $(NaPO_3)_6$, sodium aluminum oxide $NaAlO_2$, KOH, liquid glass Na_2SiO_3 and distilled water were used to prepare the electrolytes.

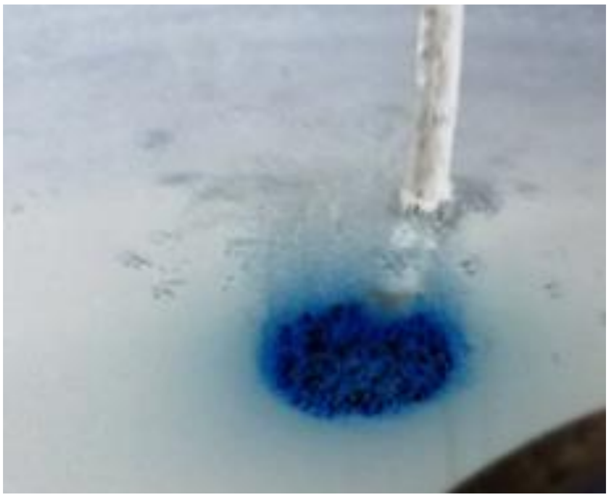


Fig. 1 – The process of anode-cathode oxidation in the mode of micro-arc discharges

Table 1 – Elemental composition of VT3-1 alloy

Fe	C	Si	Cr	Mo	N	Ti	Al	Zr	O	H	Impurities
0.2-0.7	Prior to 0.1	0.15-0.4	0.8-2	2-3	Prior to 0.05	85.95-91.05	5.5-7	Prior to 0.5	Prior to 0.15	Prior to 0.015	Other 0.3

Table 2 – Composition of used electrolytes, g/l

№	$(NaPO_3)_6$	KOH	$NaAlO_2$	Na_2SiO_3
1	8-10	–	–	–
2	–	1-3	10-14	–
3	1-7	1-3	10-14	–
4	–	1-3	1-3	1-3

The thickness of the coatings was measured using the vortex thickness gauge VT-10NTS and on the cross-sections.

X-ray photographs to determine the phase composition and quantification of the phases were carried out on the DRON-3 diffractometer in monochromatic Kα-Cu radiation. Measurement was performed in the angular range of 2θ = 15-60°. All the diffraction peaks from the planes with the highest reticular density of atoms fall into this angle range [25]. Scan step was $2\theta = 0.02°$.

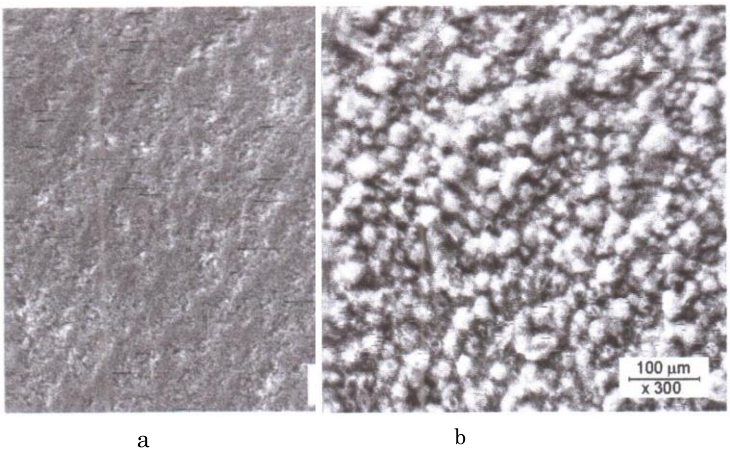
Surface morphology and cross-sectional pavement slabs were analyzed using metallographic microscopes.

Microhardness was determined on the PMT-3 device, tribotechnical characteristics – on the SMC-2 friction machine.

3. RESULTS OF COATING STRUCTURE AND STUDY OF PROPERTIES

At the beginning of the process, a light-gray coating with a low roughness forms on a surface of VT3-1 titanium alloy (Fig. 2a). With increasing process duration (τ), the surface morphology is changed – the roughness and dimensions of asperities increase, and the melting point is clearly visible (Fig. 2b).

The change in surface morphology in the oxidation process is due to changes in the density and power of microcircuits. The initial stages of the process are characterized by a high density of low power discharges; with an increase in the coating thickness, the density of discharges decreases, their power increases.



a b

Fig. 2 – Morphology of the surface of the oxide coating on the VT3-1 alloy: a – $\tau = 0.5$ h; b – $\tau = 3$ hours. (Electrolyte: 2 g/l KOH + 2 g/l $NaAlO_2$ + 3 g/l Na_2SiO_3, current density $J = 50$ A/dm²)

The microstructural feature of the coating on a titanium alloy is a layered structure – the technological and main layer (Fig. 3) are clearly identified. The technological layer is porous, non-wear resistant, is easily removed by stripping on abrasive paper. The share of the technological layer is 30-40 % of the total thickness of the coating.

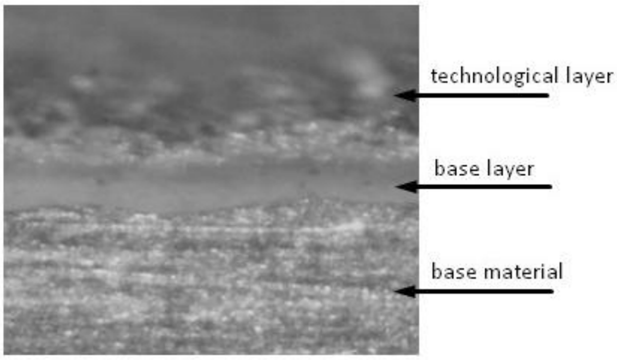


Fig. 3 – Microstructure of transverse section of the coating on the VT3-1 alloy

The results given below will refer to the base layer, which is not less than 100 microns thick (Fig. 3).

It is known that the properties of coatings, in the first place, are determined by their phase composition. The X-ray diffraction analysis carried out in the work allowed to determine the effect of the electrolyte composition on the phase composition of the coatings (Table 3). Diffraction patterns of coatings obtained in electrolytes of different composition are shown in Fig. 4.

Thus, it was found that the coating formed in a phosphate electrolyte consists of an X-ray and amorphous phase and a titanium dioxide in anatase modification (Fig. 4, spectrum 1). The X-ray absorptive titanium dioxide included in the coating can be used as a dry lubricant, which reduces the coefficient of friction. However, its low hardness does not provide durability.

The use of alkaline-aluminate electrolyte provides a significant increase in the hardness of the coating (see Table 3). The coating consists of titanium dioxide in the modification of rutile and complex $TiAl_2O_5$ oxide (aluminum titanate). The main phase is aluminum titanate (Fig. 4, spectrum 2).

Introduction to the electrolyte hexamethophosphate contributes to the formation of anatase (Fig. 4, spectrum 3), reduction of the content of aluminum titanate and increase of the content of rutile.

The maximum increase in the hardness of the coating is achieved in alkaline-aluminate-silicate electrolyte (see Table 3). The presence of mullite $3Al_2O_3 \cdot 2SiO_2$ in the coating determines the hardness of the coating.

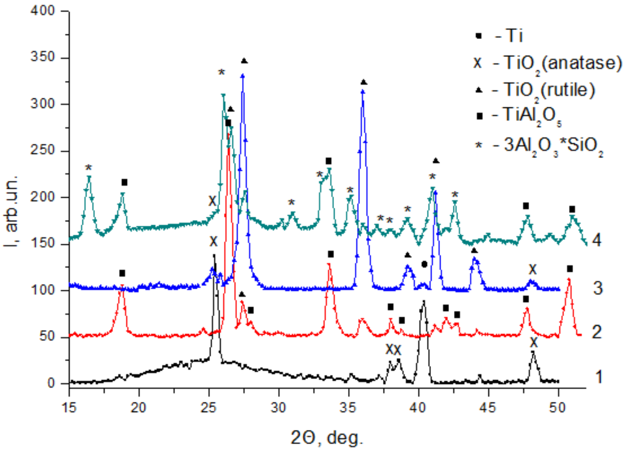


Fig. 4 – Diffractogram of the coatings formed in electrolytes of different composition: 1 – phosphate electrolyte; 2 – alkaline-aluminate electrolyte; 3 – alkaline-aluminate-phosphate electrolyte; 4 – alkaline-aluminate-silicate electrolyte

Table 3 – Phase composition and hardness of coatings

Electrolyte	Crystalline phases, %				Microhardness kg/mm^2
	TiO_2 Anatase	TiO_2 Rutile	$TiAl_2O_5$ Aluminum Titanate	$3Al_2O_3 \cdot 2SiO_2$ Mullite	
Phosphate $(NaPO_3)_6$	100 + amorphous phase	–	–	–	200-300
Alkaline Aluminate $KOH+NaAlO_2$	> 3	5-15	85-95	–	550-700
Alkali Aluminate Phosphate $KOH+NaAlO_2+(NaPO_3)_6$	20-25	40-50	30-35	–	300-400
Alkaline Aluminate Silicate $KOH+NaAlO_2+Na_2SiO_3$	> 3	10-20	50-60	20-40	1000-1200

Frictional tests were performed in order to determine the antifriction characteristics of oxide coatings on the VT3-1 titanium alloy. The test was carried out on a SMC-2 friction machine according to the disk-block diagram. For comparison, tests of an electrolytic chrome coating applied to the VT3-1 alloy have been conducted. The coatings were applied to the pads and treated with grinding to roughness, corresponding to the 7-8 grade of surface cleanliness. The counter was a disk of 50 mm in diameter made of gray iron.

The antifriction characteristics of the coatings were evaluated by the coefficient of friction at a step load in the range of loads of 0.12-2 kN. The research results are shown in Fig. 5.

The antifriction characteristics of the coatings were evaluated by the coefficient of friction at a step load in the range of loads of 0.12-2 kN. The research results are shown in Fig. 5.

Analysis of the obtained results shows a high level of antifriction properties of the oxide coating (Fig. 5,

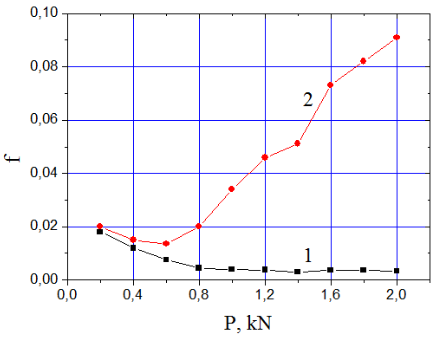


Fig. 5 – Dependence of the coefficient of friction (f) on the load (P) for VT3-1 alloy: 1 – oxide coating; 2 – chromium coating;

curve 1). In the whole range of loads, the coefficient of friction (f) is lower than the coefficient of friction of the chromium coating (Fig. 5, curve 2). With an increase in load, the difference significantly increases.

4. CONCLUSIONS

1. The electrolysis conditions were optimized to ensure the formation of oxide-coated titanium alloy VT3-1 in the micro-arc discharge mode.
2. It is shown that in electrolyte containing KOH, sodium aluminate, and liquid glass, coatings of heterophase composition (rutile, aluminum titanate and mullite) are formed, which provides their high hardness (10-12 GPa) and antifriction ($f < 0.01$).
3. The results of the work indicate the prospects for using the phase-structural engineering method for MAO treatment to optimize the formation of antifriction coatings on titanium alloys.

REFERENCES

1. X. Liua, P.K. Chub, C. Ding, *Mater. Sci. Eng.* **R47**, 49 (2004).
2. H.J. Rack, J.I. Qazi, *Mater. Sci. Eng.: C* **26** No8, 1269 (2006).
3. C.N. Elias, J.H.C. Lima, R. Valiev, M. A. Meyers, *J. Metals* **60** No3, 46 (2008).
4. L.S. Morais, G.G. Serra, C.A. Muller, L.R. Andrade, E.F.A. Palermo, C.N. Elias, M. Meyers, *Acta Biomater.* **3** No3, 331 (2007),
5. R.Z. Valiev, R.K. Islamgaliev, I.V. Alexandrov, *Prog. Mater. Sci.* **45**, 103 (2000).
6. C.M. Cotrut , A.C. Parau, A.I. Gherghilescu, I. Titorencu, I. Pana, D.V. Cojocaru, V. Pruna, L. Constantin, I. Dan, D.M. Vranceanu, A. Vladescu, *Metals* **7**, 86 (2017).
7. B.G. Wendler, W. Pawlak, *J. Achiev. Mater. Manuf. Eng.*, **26** No2, 207 (2008).
8. M. Lepicka, M. Gradzka-Dahlke, *Rev. Adv. Mater. Sci.* **46**, 86 (2016),
9. M. Kindrachuk, O. Radionenko, A. Kryzhanovskyi, V. Marchuk, *Aviation* **18** No2, 64 (2014),
10. U.H.Doshi, W.A. Bhad-Patil, *Am. J. Orthodont. Dentofacial Orthopedics* **139** No1, 74 (2011).
11. N.S. Radhi, Z. Al-Khafaji, *Int. J. Mec. Prod. Eng. Res. Dev.* **8** No4, 247 (2018).
12. H. Zhou, F. Li, B. He, J. Wang, B. Sun, *Surf. Coat. Tech.* **201**, 7360 (2007).
13. H. Sarvamangala, J. Gopal, P. Muraleedharan, R. P. George, R. K. Dayal, K. A. Natarajan, *Min. Metal. Exp.* **25** No3, 149 (2008).
14. C. Sola, A. Amorim, A. Espias, S. Capelo, J. Fernandes, L. Proenca, L. Sanchez, I. Fonseca. *Int. J. Electrochem. Sci.* **8**, 406 (2013).
15. T. Rautray, T.-Y. Kwon, R. Narayanan, K.-H. Kim. *J. Biomed. Mater. Res. Part B Appl. Biomater.* **93** No2, 581 (2010)
16. O.V. Sobol', *Phys. Solid State* **49** No6, 1161 (2007).
17. R. Krause-Rehberg, A.D. Pogrebnyak, V.N. Borisyuk, M.V. Kaverin, A.G. Ponomarev, M.A. Bilokur, K. Oyoshi, Y. Takeda, V.M. Beresnev, O.V. Sobol', *Phys. Metal. Metallogr.* **114** No8, 672 (2013),
18. R.D. Radman, J.R.P. Djuansjah, M.R.A. Kadir, H. Nur, E. Hamzah, *Adv. Mater. Res.* **650**, 12 (2013),
19. Yi. Wang. H. Yu.C. Chen Z. Zhao, *Mater. Design.* **85**, 640 (2015).
20. K. Rokosz, T. Hryniewicz, S. Raaen, *Int. J. Adv Manuf Technol.* **85**, 2425 (2016).
21. V. Belozerov, O. Sobol′, A. Mahatilova, V. Subbotina, T.A. Tabaza, U.F. Al-Qawabeha, , S.M. Al-Qawabah, *East.-Eur. J. Enterpr. Technol.* **5**, 52 (2017),
22. V. Belozerov, O. Sobol′, A. Mahatilova, V. Subbotina, T.A. Tabaza, U.F. Al-Qawabeha, S.M. Al-Qawabah. *East.-Eur. J. Enterpr. Technol.* **1**, 43 (2018),
23. P. Santiago-Medina, P. A. Sundaram,N. Diffoot-Carlo. *J. Mater. Sci. Mater. Med.* **25** No6, 1577 (2014).
24. Su Cheng, D. Wei, Yu Zhou, *Procedia Eng.* **27**, 713 (2012).
25. O.V. Sobol′, A.A. Postelnyk, A.A. Meylekhov, A.A. Andreev, V.A. Stolbovoy, V.F. Gorban, *J. Nano- Electron. Phys.* 9 No3, 03003 (2017).

Використання методу мікродугового плазмового оксидування для підвищення антифрикційних властивостей поверхні титанового сплаву

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У статті проведено аналіз можливостей по фазово-структурній інженерії сплавів на основі титану при мікродуговому плазмовому оксидуванні (МДО). Також розглянуто вплив фазово-структурних станів на триботехнічні властивості модифікованої поверхні титанового сплаву ВТ3-1. Встановлено, що для досягнення високих функціональних властивостей необхідно при МДО використовувати електроліти різного складу. Наявність $(NaPO_3)_6$ в електроліті призводить до утворення анатазу з невеликою твердістю (близько 3 ГПа). Значно підвищити твердість (до 7 ГПа) сприяє формуванню кристалітів рутилу і титанату алюмінію при використанні лужно-алюмінієвого електроліту. Максимальне збільшення твердості (до 12 ГПа) досягається у покритті, отриманому в лужно-алюмінато-силікатному електроліті. Це відбувається через утворення кристалічного мулліту. Коефіцієнт тертя такого матеріалу знижується ($f < 0.01$) і в результаті цього підвищуються антифрикційні властивості. Результати роботи свідчать про перспективність використання методу фазово-структурної інженерії при МДО-обробці для оптимізації режимів формування антифрикційних покриттів на титанових сплавах.

Ключові слова: Мікродугова плазма, Титан, Мікроструктура, Рентгено-фазовий аналіз, Фазовий склад, Твердість, Абразивний знос.