ISSN 2070-2051, Protection of Metals and Physical Chemistry of Surfaces, 2017, Vol. 53, No. 1, pp. 100–104. © Pleiades Publishing, Ltd., 2017.
Original Russian Text © I.G. Zhevtun, P.S. Gordienko, S.B. Yarusova, V.E. Silant'ev, A.A. Yudakov, 2017, published in Fizikokhimiya Poverkhnosti i Zashchita Materialov, 2017, Vol. 53, No. 1, pp. 91–95.

NEW SUBSTANCES, MATERIALS AND COATINGS

Producing a Microporous Structure on Titanium Alloys by Means of Plasma Surface Treatment

I. G. Zhevtun[a, b, *], P. S. Gordienko[a], S. B. Yarusova[a, b], V. E. Silant'ev[a], and A. A. Yudakov[a, c]

[a] *Institute of Chemistry, Far East Branch, Russian Academy of Sciences, Vladivostok, 690022 Russia*

[b] *Vladivostok State University of Economics and Service, Vladivostok, 690014 Russia*

[c] *Far Eastern Federal University, Vladivostok, 690950 Russia*

**e-mail: jevtun_ivan@mail.ru*

Received October 30, 2015

Abstract—It has been demonstrated that, with application of plasma methods of treatment of the surface of titanium alloys with subsequent selective chemical etching (on the example of the VT1-0 alloy), a microporous titanium–based structure is formed. The results of laser and electroarc treatment of the surface have been presented, and its composition, size, and pore structure have been determined.

DOI: 10.1134/S2070205117010191

INTRODUCTION

The increased interest of researchers is attracted to the possibility of producing porous structures based on ceramic materials and metals and their carbides, which is caused by the extensive application of porous materials in different fields as filtering elements, lining and thermoinsulating materials, materials with porous cooling, gas separators, catalyst supports, and medical implants [1–5]. The latter is of special importance related to the use of titanium alloys as a base due to the combination of their biocompatibility parameters and corrosion and mechanical properties. A porous structure is an important factor for a surgical implant, since it increases the implant specific surface area, which promotes deeper ingrowth of the bone tissue, thus providing high strength of attachment of bone structures to the implant [6].

To fabricate titanium-based microporous materials, different methods are used [7–9]. The most thoroughly studied and widely used ones are those of powder sintering [10, 11] and self-propagating high-temperature synthesis (**SPS**) [12, 13]. The method of microarc oxidation (**MAO**), which allows formation of porous coatings on the titanium surface, has been already successfully applied for these purposes for 20 years. The former two methods are relatively power-consuming, whereas, with the use of MAO, porosity characterizes not the base itself, but the formed oxide layer, the strength of adhesion of which to the base significantly depends on oxidation conditions and electrolyte composition and is, in many cases, insufficient for practical application [14]. Moreover, the surface treatment may result in a decrease of the fatigue resistance of the titanium alloy by 25–30% [15]. The authors of [16] noted an insignificant decrease of the cyclic strength of α-alloys upon MAO.

The authors of [17] suggested a different approach to producing microporous structures on titanium alloys consisting in plasma treatment of the surface with formation of a composite layer based on Ti–TiC and subsequent chemical etching of titanium carbide grains. The objective of the present work consisted in studies of methods of formation of surface layers on titanium alloys with different pore sizes and structures.

EXPERIMENTAL

Electroarc treatment of samples made of VT1-0 (cathodes) of a size of 40 × 10 × 4 mm was carried out using graphite electrodes (anodes) in a 0.1–0.2% aqueous solution of NaCl. The distance between electrodes was no larger than 1 mm; the current strength in the circuit was 70–90 A. A TiG 200AC/DC welding machine was used as a current source. Thereafter, the samples were polished using a polishing device (a maximum of 0.3 mm of the surface was removed).

For laser surface treatment, a YAG–Nd laser device with a maximum average power of 100 W, spot diameter $d = 0.6$ mm at a wavelength of $\lambda = 1.06$ μm, and pulse frequency $\nu = 100$ Hz was used. The treatment was carried out in a chamber with continuous argon feed. The TiC powder (chemically pure grade) was preliminarily deposited on the sample surface. For reliable powder fixation on the surface, the molten rosin was used as a binding component: rosin was heated until melting, the TiC powder was dissolved in

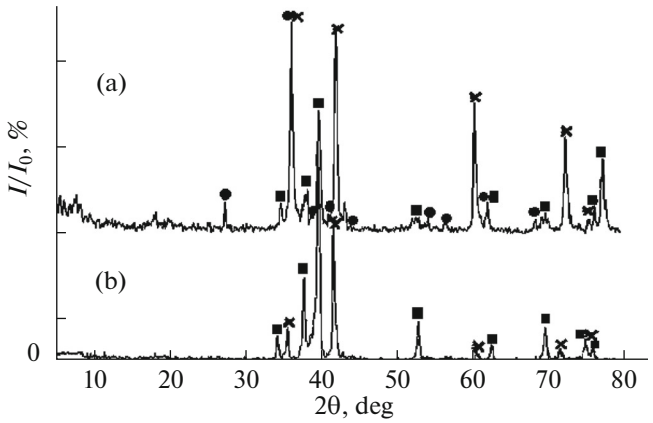

Fig. 1. X-ray images of treated titanium samples: (a) before polishing, (b) after polishing (●—TiO_2 (rutile), ■—Ti, **x**—TiC).

it, and the obtained mixture was deposited on the sample surface. Upon mixture cooling, a glasslike coating formed on the samples surface and, thereafter, underwent laser treatment.

The surface was studied using a Hitachi S5500 high-resolution scanning electron microscope with a Thermo Scientific attachment for energy-dispersive analysis and an EVO-50XVF scanning electron microscope with an INCA 350 Energy accessory. The X-ray diffraction analysis was performed using a Bruker D8 ADVANCE diffractometer in CuK_α radiation: the obtained X-ray images were deconvoluted using an EVA program with a PDF-2 powder database.

Sample etching was carried out in concentrated nitric acid (analytical grade).

RESULTS AND DISCUSSION

According to the data of X-ray diffraction analysis, upon electroarc treatment, on the sample surface prior to polishing (Fig. 1a), one observes, aside from peaks corresponding to titanium and rutile phases, five clearly expressed peaks around $2\theta = 36°$, 42°, 61°, 72°, and 76° corresponding to the (111), (200), (220), (311), and (222) planes of the titanium carbide phase, respectively [18].

Rutile forms on the surface upon sample cooling at the moment of shut-off of the arc impact [19]: in the case of an aqueous electrolyte, local volume tempering occurs automatically. Upon further sample polishing, a thin rutile layer is removed, while Ti and TiC remain (Fig. 1b). Characteristic appearances of the treated surface before and after polishing are shown in Fig. 2.

It is worth mentioning that X-ray images of different samples contain a shift of peaks corresponding to titanium carbide, which is related to changes in the TiC crystal lattice period. Changes in the parameters

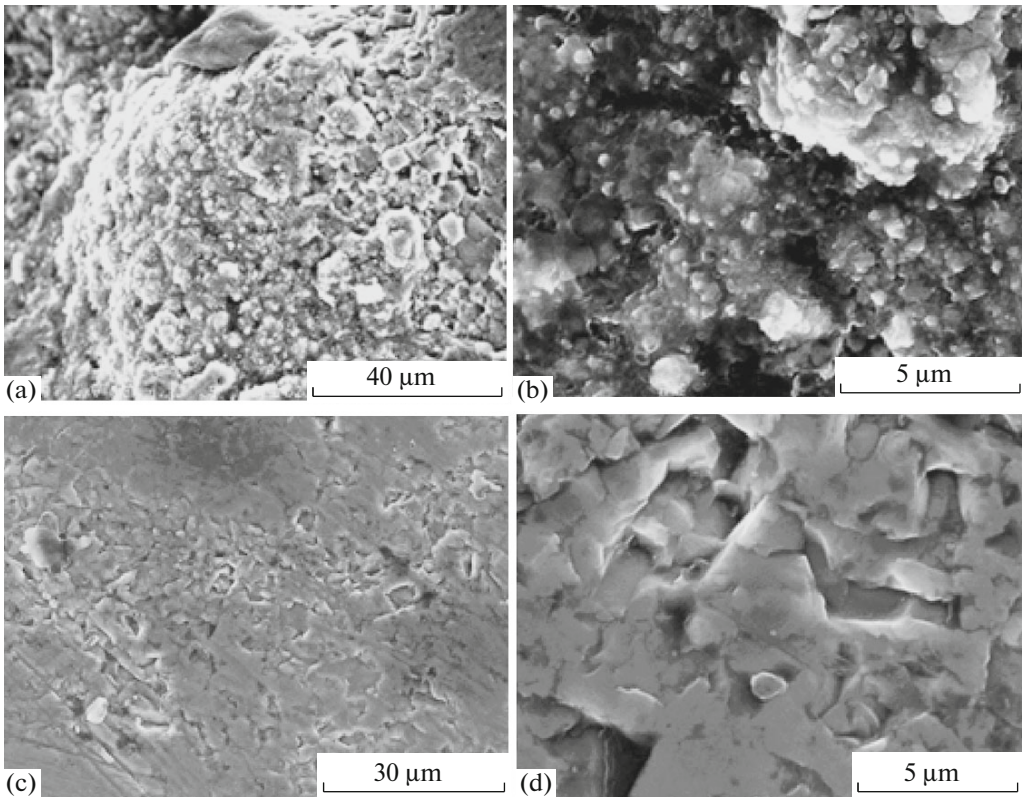

Fig. 2. Microphotographs of the surface of treated samples: (a, b) before polishing; (c, d) after polishing.

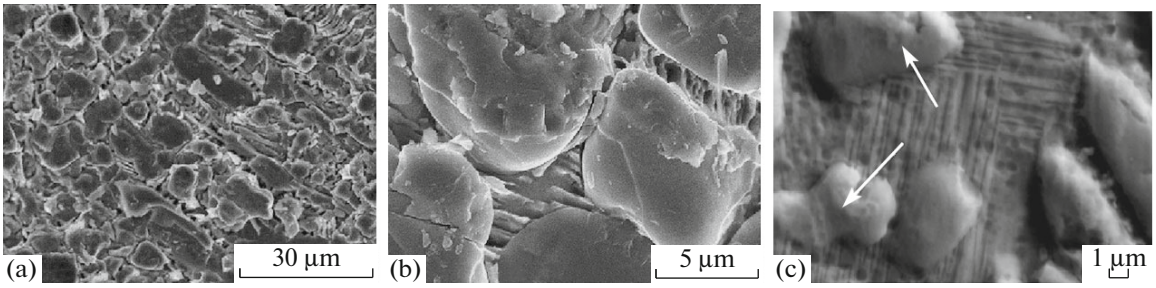

Fig. 3. Treated surface of the alloy after removal of titanium matrix (TiC grains of sizes from 1 to 10 μm are distinguishable) [22].

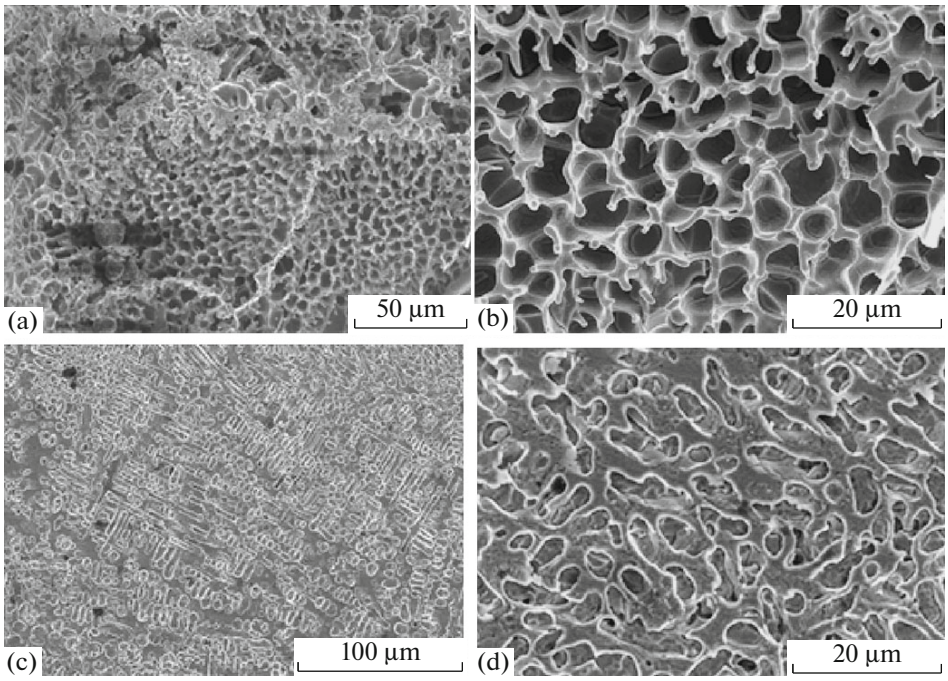

Fig. 4. Porous microstructure of the titanium alloy surface upon treatment.

of the titanium carbide lattice can be explained both by its carbon-related defects and by the presence of admixtures [20]. The period of the lattice of the formed TiC phase corresponds, in different cases, both to stoichiometric titanium carbide not containing oxygen and other admixtures (a_0 = 4.326 Å) and to a nonstoichiometric one or one containing admixtures (a_0 = 4.3300, 4.317 Å). However, since only Ti and C without foreign admixtures are identified by energy-dispersive analysis of the surface, this inconsistency must be explained by the varying stoichiometry of the formed TiC phase.

Studies of the microstructure of the treated surface [21] enabled us to establish that a heterogeneous microstructure consisting of TiC grains randomly distributed in the titanium matrix is formed in the alloy surface layer at a depth of down to 2 mm during electroarc treatment of titanium alloys by a graphite anode (Fig. 3). The grain sizes vary from dozens of nanometers to dozens of microns, but the most characteristic grain sizes are in the range of 1–10 μm. Such a microstructure promotes a significant increase of the alloy antifriction properties, as well as its resistance to oxidation [22].

To study the produced microstructure, works on selection of an optimal composition of the etching solution were performed [23]. As a result, it was established that, in the course of etching, for a Ti–TiC-based composite layer titanium carbide grains were completely etched from the surface by nitric acid solution, whereas the titanium matrix remained in the intact state due to its capability for passivation in such a solution. Therefore, the above treatment yields the formation of a microporous structure with the most characteristic pore sizes of 1–10 μm on the surface of titanium alloy (Fig. 4).

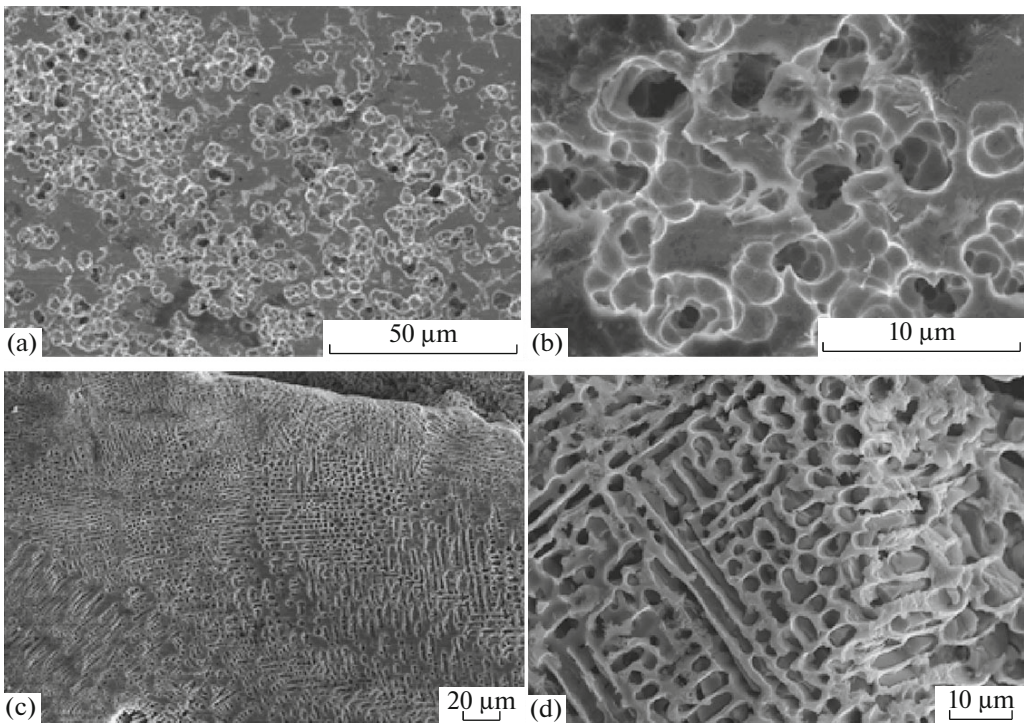

Fig. 5. Microstructure of the surface of samples produced using (a, b) laser and (c, d) electroarc treatment in an aqueous electrolyte.

The element composition of the surface upon treatment is represented by titanium with an insignificant quantity of the residual carbon (up to 3 wt %).

To implement the above approach to producing a microporous structure of a titanium alloy surface, laser surface treatment in an argon-filled chamber using the TiC powder was applied as well. During such treatment, particles of a refractory powder are known to penetrate into the support surface layer that has been melted by a laser beam. The layer depth can vary from dozens of microns to a few millimeters, depending on the radiation power, beam diameter and displacement velocity, and support material physical properties [24]. In our case, at a laser power of 90 W and beam diameter of 0.6 mm, the molten layer depth did not exceed 300 μm.

Upon surface treatment of the titanium alloy with subsequent etching of TiC grains, a surface microstructure that was similar, according to a visual assessment, to that obtained by the electroarc treatment was produced (Figs. 5a, 5b). However, as seen from SEM images, in the case of laser treatment, the distribution of pores over the sample surface is less homogeneous than in the case of electroarc treatment. Moreover, application of an arc discharge yields more complex pore shapes of a dendrite structure (Figs. 5c, 5d), which is important for surgical implants [6].

The advantages of laser treatment include the possibility of adjusting the thickness of the molten layer by varying the laser power and the variation of pore sizes using powders of different fractions.

CONCLUSIONS

To sum up, plasma treatment of titanium alloy with subsequent etching on the alloy surface produces a titanium-based microporous structure. The characteristic pore size under electroarc treatment by a graphite anode in an aqueous electrolyte is in the range of 1–10 μm, whereas sizes are determined by the fraction of the used powder in the case of laser treatment.

The advantages of the above approach include its power consumption efficiency in comparison with powder methods and the possibility to produce a microporous structure on a pure titanium surface. Moreover, in the case of an arc discharge, a complex configuration of pores with developed internal surfaces is provided due to etching of dendrites of different shapes, which serves as an important factor for osteointegration. However, further systematic studies are required to assess the efficiency of producing porous structures on titanium alloys by means of plasma treatment.

ACKNOWLEDGMENTS

The work was financially supported by the Ministry of Education and science of Russian Federation (agree-

ment no. 14.578.21.0015 of June 5, 2014, ID RFMEFI57814X0015) and the Program of Basic Research of FEBRAS "Far East" (project no. 15-I-3-017).

REFERENCES

1. Belov, S.B., *Poristye materialy v mashinostroenii* (Porous Materials in Machinery Manufacture), Moscow: Mashinostroenie, 1976.
2. Sevost'yanova, I.N., Anisimov, V.Zh., Gnyusov, S.F., and Kul'kov, S.N., *Fiz. Mezomekh.,* 2004, vol. 2, no. 7, p. 89.
3. Kul'kov, S.N., Gnyusov, S.F., Sevost'yanova, I.N., and Molchunova, L.M., *Vopr. Materialoved.,* 2004, vol. 37, no. 1, p. 64.
4. Alymov, M.I., Zelenskii, V.A., and Ankudinov, A.B., *Perspekt. Mater.,* 2009, no. 4, p. 75.
5. Shi, L., Zhao, H., Yan, Y., et al., *Scr. Mater.,* 2006, vol. 55, p. 763.
6. Savich, V.V., Saroka, D.I., Kiselev, M.G., and Makarenko, M.V., *Modifikatsiya poverkhnosti titanovykh implantatov i ee vliyanie na ikh fiziko-khimicheskie i biomekhanicheskie parametry v biologicheskikh sredakh* (Modification of Titanium Implants Surface and its Effect onto their Physical, Chemical and Biomechanical Parameters in Biological Media), Minsk: Belarusskaya Navuka, 2012.
7. Wang Zhoucheng, Chen Yanwen, and Lin Zhixiong, CN Patent 102921037, 2013.
8. He Fuming, Shen Jianwei, and Wang Huiming, CN Patent 104027839, 2014.
9. Wang, S.-F., Yang, T., Lee, S.-Y., et al., TW Patent 201420137, 2014.
10. Babkin, A.V., *Zh. Grodn. Gos. Med. Univ.,* 2008, no. 2, p. 102.
11. Astanin, V.V., Kayumova, E.Z., Nikitin, V.V., and Farkhetdinov, A.I., *Ross. Zh. Biomekh.,* 2015, vol. 19, no. 1, p. 116.
12. Khodorenko, V.R., Anikeev, S.G., and Gyunter, V.E., *Izv. Vyssh. Uchebn. Zaved., Fiz.,* 2014, vol. 57, no. 6, p. 17.
13. Amosov, A.P., Bairikov, I.M., Shcherbovskikh, A.E., et al., RF Patent 2459686, 2012.
14. Sharkeev, Yu.P., Psakh'e, S.G., Legostaeva, E.V., et al., *Biokompozity na osnove kal'tsiifosfatnykh pokrytii, nanostrukturnykh i ul'tramelkozernistykh bioinertnykh metallov, ikh biosovmestimost' i biodegradatsiya* (Biocomposites on the Base of Calcium-Phosphate Coatings, Nanostructure and Ultra-Fine Grain Bioinert Metals, their Biocomparability and Biodegradation), Tomsk: Tomsk State Univ., 2014.
15. Erubaev, E.A., Kolobov, Yu.R., Kuz'menko, I.N., et al., *Fundam. Issled.,* 2014, no. 12, p. 2575.
16. Gordienko, P.S. and Gnedenkov, S.V., *Mikrodugovoe oksidirovanie titana i ego splavov* (Micro-Arc Oxidation of Titanium and its Alloys), Vladivostok: Dal'nauka, 1997.
17. Zhevtun, I.G. and Gordienko, P.S., *Materialy IV mezhdunarodnoi konferntsii po khimii i khimicheskoi tekhnologii* (Proc. 4th Int. Conf. on Chemistry and Chemical Technology), Yerevan, Sept. 14–18, 2015, p. 186.
18. Storms, E.K., *The Refractory Carbides, Los Alamos*: *Los Alamos* Scientific Laboratory, Univ. of California, 1967.
19. Zhevtun, I.G., Gordienko, P.S., and Dostovalov, V.A., *Khim. Tekhnol.,* 2011, no. 11, p. 663.
20. Kiparisov, S.S., Levinskii, Yu.V., and Petrov, A.P., *Karbid titana. Poluchenie, svoistva, primenenie* (Titanium Carbide. Synthesizing, Properties, Application), Moscow: Metallurgiya, 1987.
21. Gordienko, P.S., Zhevtun, I.G., Dostovalov, V.A., et al., *Vestn. Mashinostr.,* 2012, no. 2, p. 52.
22. Zhevtun, I.G., Gordienko, P.S., Kukhlevskaya, T.S., and Mashtalyar, D.V., *Vestn. Mashinostr.,* 2013, no. 3, p. 23.
23. Zhevtun, I.G., Gordienko, P.S., and Kaidalova, T.A., *Materialovedenie,* 2014, vol. 206, no. 5, p. 41.
24. Grigor'yants, A.G., Shiganov, I.N., and Misyurov, A.I., *Tekhnologicheskie protsessy lazernoi obrabotki* (Technological Processes of Laser Processing), Moscow: Bauman Moscow State Technical Univ., 2006.

Translated by D. Marinin