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Nanocrystalline Structure of Surface Layer of Commercially Pure Titanium Subjected to Induction-Thermal Oxidation

A. A. Fomin*, A. B. Shteingauer, I. V. Rodionov, M. A. Fomina, and A. M. Zakharevich
[a] Gagarin Saratov State Technical University, ul. Politekhnicheskaya 77, Saratov, 410054 Russia
[b] Chernyshevskii Saratov State University, ul. Astrakhanskaya 83, Saratov, 410012 Russia
**e-mail: afominalex@rambler.ru*

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Abstract—Metal-oxide coatings on a smooth commercially pure titanium surface were produced that were characterized by lamellar, needled, and prismatic shapes of crystals. Regularities of variations in nanometer morphology characteristics of the titanium surface subjected to induction-thermal oxidation are determined.

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Theoretical and experimental studies that describe in detail mechanisms and kinetics of processes of the oxidation of refractory metals and alloys, including VT1-00 commercially pure titanium, are well known [1]. Current studies deal mainly with kinetics of the formation of metal-oxide compounds under isothermal conditions, as well as with a mass increase for small specimens when thermogravimetric analysis and the oxidative construction of thin-wall ceramic articles are used [2]. Metal materials, e.g., VT1-00, VT1-0, VT6, and VT16 medical titanium alloys are applied to produce frames of intraosteal implants, which serve as artificial supports of the stomato-gnatic and locomotor apparatuses. Clinical experiments carried out in Russia and abroad have shown that bioceramic and metal-oxide coatings of implant surfaces are best suited to stimulating engraftment and are the most efficient solution of the problem of rejecting such structures [3]. The implant surface layer should have a required phase and structural state and possess a definite set of properties, including high hardness and wear resistance. Under these conditions, morphology becomes of special importance, especially that of a nanocrystalline or submicron structure [4]. Morphological conformity with bone tissue elements is determined by both characteristics of coating structure microgeometry and a characteristic nanocrystalline grain size. In connection with this, it is a topical problem to find the dependence of average crystal size of metal-oxide coatings on conditions of the induction-thermal oxidation (ITO) of the titanium base.

The experimental specimens were 2-mm thick plates of VT1-00 commercially pure titanium (in accordance with GOST (State Standard) 19807-91, 99.58–99.9% Ti, as well as Fe, C, Si, N, O, and Al impurities for balance). The preparation of their surfaces involved mechanical grinding and etching in water solution of 1.5 M HF + 1.5 M HNO_3 for no more than 15 s. Metal-oxide compounds were formed on a titanium surface in the form of coatings during ITO in air using a laboratory experimental induction heating setup. In this case, the effect of the basic conditions of the ITO of the titanium substrate on average nanocrystal size in the temperature range from 600 to 1200°C at a treatment duration of 1–300 s was revealed. The coating specimens had double numbering in which the first number corresponded to temperature of the ITO of the titanium substrate and the second one to process duration measured in seconds. Coating morphology, namely, crystal size (diameter or width) D and crystal shape was examined by scanning electron microscopy using a MIRA II LMU electron microscope followed by computer statistical processing.

The surface structure of metal-oxide coatings results from intense oxidation processes that develop during the thermal effect of eddy currents generated in the metal substrate of specimens. Kinetics of coating growth is somewhat similar to known parabolic and linear regularities. A specific feature of considered oxidation processes is high heating rate and short heat-treatment duration. These differences lead to an increased growth of a metal-oxide coating, especially at temperature above the α-Ti $\longleftrightarrow$ β-Ti phase transition. When describing the crystalline structure in the context of geometric characteristics, several morphology types have been revealed (Fig. 1).

The crystal shape mainly depends on ITO temperature; at the minimum value of 600°C, scattered rounded spot oxide structures appear, which begin to transform into a uniformly distributed lamellar structure with increasing process duration and temperature

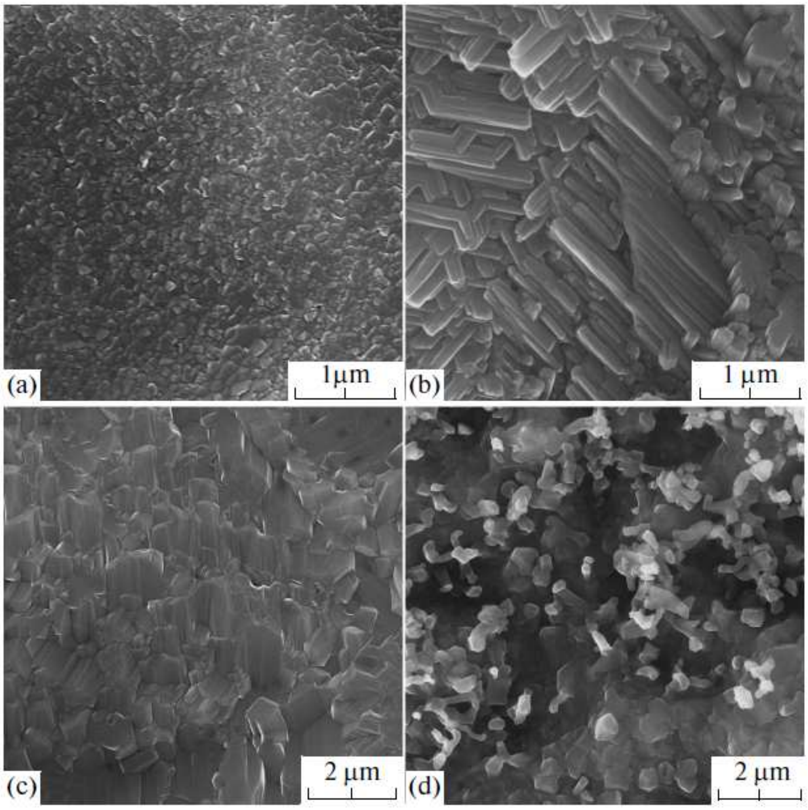

Fig. 1. SEM images of nanostructure morphology of metal-oxide coatings produced under different ITO conditions: (a) 800–30, (b) 800–120, (c) 1000–30 (thick outer layer), and (d) 1200–30 (sublayer).

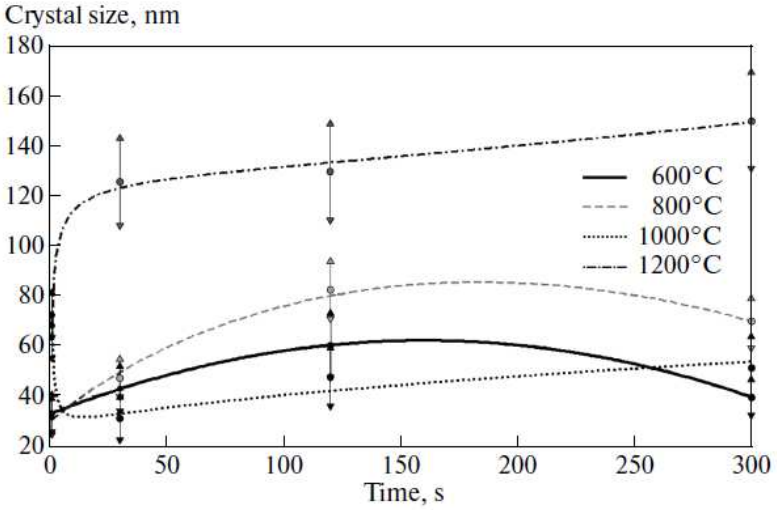

Fig. 2. Dependences of average oxide-coating nanocrystal size on temperature and ITO process duration.

(Fig. 1a). This morphology type is best revealed at ITO temperature of 800°C; in this case, size D of nanocrystals themselves substantially decreases (from 30 to 60–80 nm) (Fig. 2). An increase in ITO duration to 250–300 s leads to a growth of small structural defects in the coating due to the formation of needled, split lamellar, and prismatic crystals (Fig. 1b). This regularity is described by the following parabolic law:

$$D_{600} = 32.67 + 0.37t - 0.0012t^2, \quad (1)$$

$$D_{800} = 29.33 + 0.91t - 0.045t^{1.5}, \quad (2)$$

where t is the ITO duration process in seconds and D_{600} and D_{800}, are the oxide-coating nanocrystal size in nanometers at ITO temperatures of 600 and 800°C, respectively.

A different state of affairs arises at an ITO temperature of 1000°C, when oxide-coating crystal size D reaches 70 nm as a specified temperature is achieved (Fig. 2). With an increase in process duration over 3–5 s, intense disintegration occurs of structure elements into more than two parts and lamellar crystals are formed (Fig. 1c). The kinetics of nanocrystal growth obeys a more complex law, which unites the inversely proportional and quasi-linear dependences as follows:

$$D_{1000} = 20.78 + 1.88t^{0.5} + 49.41t^{-1}, \qquad (3)$$

where D_{1000} is the coating-crystal size in nanometers at an ITO temperature of 1000°C.

This change in the pattern of the dependence of average crystal size D at temperature of 1000°C can apparently be due to the repeated crystallization of the metal substrate, which affects the formation of a large number of crack defects and finally results in the spontaneous separation of thick-layer oxides. The structure of the underlayer formed consists of prismatic crystals firmly fixed to the titanium surface (Fig. 1d). At a maximum temperature from the considered ITO temperature range equal to 1200°C, the dependence of crystal size D is quasi-parabolic:

$$D_{1200} = 134.12 + 0.0036t^{1.5} - 65.94t^{-0.5}, \qquad (4)$$

where D_{1200} is coating crystal size in nanometers at ITO temperature of 1200°C.

Analysis of the effect of ITO on processes of structure formation on the commercially pure titanium surface has allowed us to find a regularity of variations in nanocrystal size and the nanocrystal shape in metal-oxide coatings depending on basic process parameters, i.e., temperature and heat-treatment duration. Characteristic kinetic dependences of the growth of these crystals have been determined in different temperature ranges, i.e., parabolic dependences in the range 600–800°C, the inversely proportional and quasi-linear portions that characterize transient processes at 1000°C, and the quasi-parabolic portion at 1200°C. The best parameters of the structure of metal-oxide coatings, in particular, the lamellar and needled nanocrystal shapes were obtained on the VT1-00 commercially pure titanium surface by the ITO method at temperature of 800°C and thermal-effect duration of 30–120 s. This biocompatible material possesses improved morphological heterogeneity and geometrical bioactivity factor.

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