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# Influence of different modes of microarc oxidation of titanium on the electrochemical properties and surface morphology of the obtained coatings

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### ABSTRACT

The influence of Microarc Oxidation (MAO) modes of titanium substrate in electrolytes of the original composition is investigated. Used electrolytes no contain sodium silicate but includes nickel sulphate, sodium aluminate and alkali. The morphology and composition of the obtained coatings were studied by electron microscopy. The electrochemical behaviour was studied using polarisation curves and electrochemical impedance spectroscopy (EIS). Proposed Equivalent circuits are adequately corresponded to experimental EIS data with no more 6% error. The dependence between the elements of the Equivalent circuits and the morphological characteristics depending on the processing is considered. It is shown that MAO coatings on titanium have high corrosion resistance in an aggressive sulphuric acid. The electrochemical properties of coatings undergo irreversible changes in the direction of deterioration after anodic polarisation. It has been established that nickel doping of MAO coatings on titanium does not allow them to serve as anode materials.

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### Introduction

Titanium and its alloys are metallic materials widely used due to their comparatively low density and unique combination of properties. Among these characteristics, the most notable one is its relatively high corrosion resistance compared with other metals both at normal and high temperature. Titanium resists corrosion in common environmental conditions, fresh and sea water, chloride-containing media, in various mineral acid salt solutions [1–4].

In most corrosive environments titanium and its alloys exhibit even higher resistance than stainless and acid-resistant steels, as well as aluminium alloys [5–7]. Titanium also exhibits high corrosion resistance in oxidising environments (nitric and chromic acids etc.) and in alkaline solutions, in non-oxidising acids (sulphuric and hydrochloric) at normal temperatures and concentrations of up to 8–10%. With an increase in temperature and concentration of acids and alkalis, the corrosion rate of titanium rises sharply. For example, in the case of sulphuric acid two corrosion rate maxima are observed which correspond to 40% and 75% concentrations [8–10].

High corrosion resistance in different environments makes titanium appealing for the manufacture of critical components, space technology, shipbuilding, chemical equipment, medical devices, and instrumentation. The dimensionally stable anodes (DSA) based on titanium ( $RuO_2$ - $TiO_2$ /Pt-IrO<sub>2</sub>orplatinized) have been widely used in the industry [3, 11].

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However, the development of science and technology creates new ever-increasing demands for the materials used. Their inherent characteristics are no longer sufficient to guarantee the stable and failurefree operation of parts working in harsher exploitation conditions. Considering that modern materials science has virtually reached the limit of the extensive development path, engineering of the surfaces of already existing materials can be considered to be the almost uncontested direction for further research.

Applying of plasma-electrolyte treatment, in particular, the Microarc Oxidation (MAO) technology which provides the formation of titanium dioxide in the form of rutile, anatase and their compositions on the surface allows to radically improve the characteristics of titanium. The authors [12] presented a detailed review of technology and mechanism of the processes that occur during plasma-electrolyte oxidation of titanium substrates, in addition to giving information about the properties, application, and the possible limitations of the use of the modified titanium products. Numerous studies have shown that the ceramic-like MAO coatings formed are able to

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Table 1. The composition of industrial standard VT1-0 (wt.%).

Ti	Si	Ν	C	0
99.66	0.1	0.02	0.07	0.15

significantly increase corrosion resistance, as well as give the surface special properties (catalytic, decorative, optical, etc.) [13–17]. In particular, the authors of [18] describe the application of titanium with MAO coating in medicine, whereas authors of [19] present information on its use in chemical synthesis.

Apart from the oxidation itself, i.e. the formation of surface oxide – ceramic layer, the MAO method permits the doping of synthesised coatings with several additional elements through special additives to the electrolyte. As a result, modification of surface oxide layers is achieved not only by the change in chemical but also by structural-phase state [20,21].

The effect of nickel sulphate additives in a silicatealkaline electrolyte for MAO treatment on the corrosion and electrochemical behaviour of commercially pure titanium grade has been studied in [20]. Sodium silicate silicates Na<sub>2</sub>SiO<sub>3</sub> or potassium silicates K<sub>2</sub>SiO<sub>3</sub> are frequently added to the solution to facilitate the ignition of discharges [15], but this leads to the introduction of silicon into the coating, which is not always justified. Nickel as a rule included in the composition of the MAO coating to give it catalytic properties or for use as an anodic material [22].

Electrochemical studies are the most popular method of assessing the corrosion resistance of materials [23,24]. Since the corrosion and electrochemical properties are in many ways defined by the conductivity of surface layers, the Electrochemical Impedance Spectroscopy (EIS) was chosen as the main method of study. Its application became possible due to the use of computer technologies for the processing of the results in terms of equivalent circuits that adequately describe the experiment. The parameters of these equivalent circuits can be used to estimate the structure and properties of the studied systems. This method, according to many experts, is the most convenient and informative. Therefore, it has found wide application in corrosion studies [25–30].

Modified titanium has a wide range of practical applications due to its relatively low density and high corrosion resistance in a wide range of media, especially neutral ones [31–37]. It is especially useful as implantable prostheses in the human body: MAO-

Table 2. MAO processing for titanium samples.

Sample	Electrolyte	MAO duration, min
MAO Ni –3	Nickel Sulphate	3
MAO Ni-5	$(3 \text{ g/L KOH} + 2 \text{ g/L NiSO}_4 \cdot 7H_2O)$	5
MAO Ni-10		10
MAO NaAlO <sub>2</sub>	Aluminate	25
	(1,2rg/L KOH + 15 g/L NaAlO <sub>2</sub> )	
Titanium		-

titanium has high corrosion resistance, including in table salt, which is an imitation of human blood (simulating human blood), unlike magnesium [38], which also has good prospects (engraftment, etc.), but has insufficient corrosion resistance.

MAO treatment of titanium increases the wear resistance of the product, for example, prostheses, implants in the human body, in combination with high corrosion properties of the base. The amazing resistance of MAO coatings to thermal cycling [39] expands the range of practical use of MAO coatings on titanium. Impregnation of various substances into coatings, including with the help of MAO, for example, carbon (graphene) [40–43], makes it possible to search for new areas of practical application of MAO coatings on titanium.

In this work, the electrochemical behaviour of MAO coatings on titanium formed in various electrolytes was studied by scanning microscopy, EIS, polarisation measurements, and corrosion tests. The paper presents the original composition of the electrolyte, which includes nickel sulphate and alkali. Sodium silicate, which is often used as an additive to the electrolyte for MDO, is not used. The influence of various MDO modes in these electrolytes is investigated. Equivalent circuits adequately modelling the experimental frequency dependences of the impedance were proposed.

### **Materials and methods**

Pure titanium grade VT1-0 was chosen for the research. Its chemical composition in accordance with the industrial standard is presented in Table 1.

MAO treatment of titanium samples was carried out for 3, 5, and 10 min in a freshly prepared alkaline solution (3 g/L KOH) containing 2 g/L NiSO<sub>4</sub>7H<sub>2</sub>O (sulphate electrolyte) [44]. The process was carried out in a 3-L bath at the asymmetric alternating current polarisation (U = 500–550 V at a frequency of 50 Hz). We used the ratio between the anodic and cathodic currents as  $I_a/I_c = 1.1$  at the total current density 45 A/dm<sup>2</sup>. After the treatment, the samples were immediately washed in cold running water.

Guided by the fact that many researchers consider the use of aluminate electrolytes the most rational for processing titanium [15,17,45], for comparison, a coating was also obtained in similar conditions. In this case, 15 g/L NaAlO<sub>2</sub> was introduced into the solution (aluminate electrolyte) instead of nickel sulphate at the processing time being 25 min. Table 2 shows samples designations and regimes of MAO processing.

Chemical-grade reagents were used for preparing electrolytes and conducting corrosion and electrochemical studies.

To study the structure of the coating, a scanning electron microscope JSM-6490LV was used in the modes of secondary (SEI) and back-reflected (BEC or COMPO) electrons. For each sample, there were at least three measurements on each surface of the sample. The article presents photographs showing the most characteristic features of the surface. Microanalysis of the coating composition was determined on flat samples using a TESCAN VEGA 3 XMU scanning electron microscope in high vacuum (SE) mode, with an ADVANCED AZTEC Energy microanalysis system based on a nitrogen-free X-MAX 50 STAN-DART energy dispersion detector, the distance from the lens to the sample was 15 mm, the accelerating voltage was 20 kV.

Titanium itself has a high tendency to passivation and a low rate of corrosion in a number of aggressive environments at relatively low temperatures [5]. MAO coatings further increase corrosion resistance by shielding most of the metal surface [17, 20]. Therefore, for electrochemical studies and long-term corrosion tests, sufficiently harsh conditions were chosen in highly concentrated solutions of sulphuric acid (25% and 35% H<sub>2</sub>SO<sub>4</sub>) at room temperature. The samples of the materials studied in the form of rectangular plates with isolated current lead were placed in a three-electrode electrochemical cell with a counter electrode made of platinum mesh. A saturated silver chloride reference electrode was connected to the system via a salt bridge that prevents the penetration of chloride ions into the cell. Measurements were carried out using the potentiostatic complex IPC-FRA (Russia, Volta. SPB.ru) [28]. The EIS measurements of a freshly prepared sample were obtained at the open circuit potential (E<sub>0</sub>) with 10 mV sinusoidal modulation in a frequency range from 0.1 Hz to 50 kHz. After EIS spectrum recording the polarisation curves were obtained from the cathodic region with an anodic sweep rate at 1 mV/s. All potentials were given in a standard hydrogen electrode scale (S. H. E.). The corrosion resistance of samples with MAO coatings and titanium without treatment was evaluated by the potentials and corrosion currents densities in the passive state. Long-term corrosion tests of the coatings in 35% H<sub>2</sub>SO<sub>4</sub> solution were also carried out until they were completely destroyed.

### **Results and discussion**

### Coating structure and composition

The surface structure of the samples subjected to oxidation for 3, 5, and 10 min in a sulphate electrolyte and 25 min in an aluminate electrolyte is shown in Figure 1, and their cross sections in Figure 2.

It can be seen (Figure 1) that the surface of the coating treated in a sulphate electrolyte consists of hemispherical oxide clusters with pores between them. With an increase in the MAO processing duration from 3 min (Figure 1, a) to 10 min (Figure 1(c)), the size of clusters increases and, consequently, the number of pores per unit area decreases.

When treated in the aluminate electrolyte (25 min, Figure 1(d)) a smoothing undulating deposit was formed on the surface. Despite the fact that the scale in Figure 1(d) is 10 times smaller than in Figure 1(a -c) and small pores are not so noticeable, the overall porosity of the coatings is approximately the same, and the size of some large pores is about 1 micron.

Since the kinetics of the process involves the consecutive execution of anodising, luminescence, sparking and ignition of microplasma discharges stages [15,46], in the initial stages of sparking (from the first seconds to 1 min), ending the electrochemical formation of the poreless barrier anodic oxide film. In this film, under the influence of spark and then microarc discharges fragments (clusters) of the MAO-coating are formed. Subsequently, due to the action of the discharges, the number and size of clusters increase. They grow together and over time form a continuous coating. The nature of the coatings surface evidently depends on the quantity and the power of the spark (and later microarc) discharges that form, transform and even melt the coating material. The pores that are visible on the surfaces can correspond to through pores as well as become closed without reaching the base metal.

Three-minute treatment in an alkaline electrolyte with nickel sulphate provides coverage in spark mode. A lot of small pores are formed (Figure 1(a)). However, with an increase in the duration of MAO to 5 min, a proactive transition from spark mode to micro-arc mode is already observed. This is evidenced by a decrease in the number of pores, an increase in their diameter and melting of the surface, which corresponds to an increase in the discharge power. This is accompanied by an increase in the size of the structural elements of the oxide coating. After 10 min of processing, the process completely switches to the micro-arc mode, and the size factor becomes even more noticeable.

Coatings formed for nickel sulphate electrolyte are relatively thin. Nevertheless, the metallographic cross section of these coatings indicates their continuity (Figure 2). There are no noticeable large through pores in the photo. The thickness of the oxide coating, measured metallographically according to the cross sections' photographs, increased from 1 µm (after 3 min, Figure 2(a)) up to 5-7 microns (after10 min, Figure 2(c)). After 25 min processing in the aluminate electrolyte, more thick coatings (about 50 µm) were obtained (Figure 2(d)). On the cross-section of the metallographic specimen, both the through pores and the longitudinal and transverse cracks can be observed. Clearly, the growth of the coating occurs in the microarc mode and at a higher speed than from sulphate electrolyte.



Figure 1. Microphotographs of the surface of titanium samples with MAO-coatings after 3 (a), 5 (b) and 10 (c) minutes of oxidation in sulphate electrolyte and 25 min (d) in aluminate electrolyte.

The calculation of the average pore size and their distribution was carried out using the micrograph of the surface Figure 1 The number of pores and their size distribution using a specially developed programme. Table 3 shows the average pore diameter and standard deviation. The density of the pore per square micron is given in relation to the entire area of the photo (taking into account the individual scale).

The composition of the coatings was studied using X-ray spectral elemental analysis. Despite some discrepancy in the ratio of Ti/O concentrations to stoichiometric for titanium dioxide, it can be argued that TiO<sub>2</sub> is the main component of the coating (Figure 3(a-c)). Some redundancy of titanium in comparison with the stoichiometric composition of the dioxide may be due to the small thickness of the coatings, which enhances the substrate effects on the analysis results. As the coating thickness increases, the X-ray analysis data in mass and atomic terms show a tendency to approach the proportions corresponding to the chemical formula of the dioxide. At the same time, it can be argued with a high probability that the growth of coatings in nickel sulphate electrolyte occurs mainly due to the titanium substrate.

Aluminium oxide predominates in the coating from aluminate electrolytes (Figure 3(d)), which indicates that the growth of the coating occurs mainly due

to the components of the electrolyte, in particular  $(NaAlO_2)$ , and not the metal substrate.

### **Polarisation curves**

The corrosion potential and corrosion current density are thermodynamic characteristics of the materials that indicate their tendency to corrosion. The more positive the open circuit potential (OCP) and less is the current density in a passive state, the better anticorrosive properties the material has [9,24,47].

Figure 4 shows anodic polarisation curves taken from samples with MAO-coatings and unprocessed titanium in 25%  $H_2SO_4$ . Table 4 shows the average OCP and the logarithms of corrosion current densities in the characteristic points of the anodic polarisation curves.

As follows from Table 4, the most positive corrosion potential corresponding to the range of deep passivity potentials has a coating formed after 10 min treatment in an alkaline nickel sulphate electrolyte ( $E_{cor.} = +880 \text{ mV}$ ). The second place takes the coating from aluminate electrolyte ( $E_{cor.} = +818 \text{ mV}$ ). This is followed by coatings formed during 5 and 3 min of treatment ( $E_{cor.} = +723$  and 592 mV, respectively) in nickel sulphate electrolytes. It should be noted that as the processing time of nickel-modified



Figure 2. Microphotographs of the cross sections for titanium samples with MAO-coatings after 3 (a), 5 (b) and 10 (c) minutes of oxidation in sulphate electrolyte and 25 min (d) in aluminate electrolyte.

samples increases, the corrosion potential shifts in a positive direction by almost 300 mV. All the corrosion potentials of samples with coatings are much higher when compared to untreated titanium (200 V). The corrosion potential values indicate that MAO treatment increases corrosion resistance in all cases.

The dependences presented in Figure 4 also confirm that, in 25% H<sub>2</sub>SO<sub>4</sub> solution, all MAO coatings provide deep passivation of the metal in a wide range of potentials. The lowest anodic current density corresponds to MAO Ni-10 and MAO Ni-5 coatings. Less deep passivation was registered for samples MAO Ni-3 and MAO NaAlO<sub>2</sub>. For the last mentioned modes, the logarithms of the current densities are the same.

Comparing the coatings with the highest anodic potentials, it can be seen that for the aluminate solution ( $E_{cor.} = +818 \text{ mV}$ ), the current density was

Table 3. Average pore size and their distribution.

Sample	Average pores diameter, µm	Pores per µm <sup>2</sup>
MAO Ni -3	0,206 ± 0,118	3,960
MAO Ni-5	0,321 ± 0,111	0,631
MAO Ni-10	0,256 ± 0,061	0,750
MAO NaAlO <sub>2</sub>	1,999 ± 1,167	0,049

significantly higher compared to MAO Ni-10 coatings  $(E_{cor.} = +880 \text{ mV})$ . This is noteworthy because the processing time of MAO NaAlO<sub>2</sub> samples is more than twice the duration of MAO Ni-10, which ensures the formation of thicker coatings. Such a discrepancy between the thickness of the coating and the current density in the passive region may indicate less effective protection of the oxide coating based on aluminium oxide compared to titanium oxide coatings, as well as greater defectiveness of this coating. But even these samples when compared to untreated titanium VT1-0 provide passive range current densities that are almost an order of magnitude less. On the whole, the current densities for the modified samples studied turned out to be 1-2 orders of magnitude smaller than for untreated titanium (also see Table 4).

### Electrochemical impedance spectroscopy

The electrochemical impedance spectroscopy method is widely used for electrochemical kinetics studies [25– 27, 30]. Unlike the method of polarisation curves, EIS allows to study the behaviour of samples at small amplitudes of impacts, which preserves the surface. Measuring the impedance of samples at a certain



Figure 3. X-ray spectral elemental analysis of the MAO-coatings formed after 3(a), 5(b), and 10(c) minutes of treatment in sulphate and 25 min (d) in aluminate electrolytes.

frequency makes it possible to compare their resistive and capacitive characteristics, however, based on the values obtained at the only frequency, it is impossible to conclude about the mechanism of electrochemical processes. To do this, need to have an array of measurements at different frequencies (the impedance spectrum) and analyse its nature, for example, in terms of equivalent circuits. Nevertheless, the results obtained at the lowest frequency are of interest because they approach the conditions of DC polarisation, and their interpretation does not depend on the chosen equivalent circuit.

## Low-frequency impedance of samples at open circuit potential

The impedance modulus |Z| and the phase shift  $\beta$  at the lowest modulation frequency (0.39 Hz) were used to compare MAO samples and untreated titanium VT1-0 with their DC properties (according to polarisation curves).

Table 5 shows that the coating from aluminate electrolyte has the largest low-frequency impedance module. Its nominal value is more than 25 times higher than the value of untreated titanium. When modified



Figure 4. Anodic polarisation curves. 1-titanium VT1-0; 2 -MAO Ni -3; 3-MAO Ni-5; 4-MAO Ni-10; 5 - MAO NaAlO<sub>2</sub>.

 Table 4. Data from the potentiodynamic curves.

Sample	E <sub>ocp</sub> <sup>1</sup> . (S.H.E),mV	E <sub>cor.</sub> 2 (S.H.E), mV	Lg(i [A/cm <sup>2</sup> ])
MAO Ni -3	+582	+574	-6.0
MAO Ni-5	+723	+743	-6.8
MAO Ni-10	+964	+881	-7.2
MAO NaAlO <sub>2</sub>	+818	+820	-6.0
Titanium	+203	+200	-5.2

<sup>1</sup>The OCP was measured on a fresh sample after exposure for 30 min in solution.

<sup>2</sup>E cor. is obtained from polarisation curves taken from the low cathodic polarisation.

with nickel, the impedance modulus progressively increases with the increase in the duration of the MAO. It is interesting to note that for MAO Ni-3 sample, its Z modulus turns out to be 1.3 times lower than that of untreated titanium. This is probably due to the introduction of nickel oxide and/or nickel metal particles into the surface layers, which have higher conductivity compared to 'pure' TiO<sub>2</sub>.

The phase shift angle for all samples exceeds 60°, i.e. they have a predominantly reactive resistance due to the capacitive factor. The presence of a dielectric oxide layer on the surface causes the formation of a capacitor. After MAO processing, the phase shift angle turns out to be lower than for the untreated titanium. A decrease in the phase shift angle from 78° to ~60° indicates a weakening of the contribution of reactive factors at a low modulation frequency, although MAO processing significantly increases the active resistance of samples  $Z_{Re}$  (with the exception of MAO Ni–3).

The rate of Faraday's processes, which include reactions that cause metal corrosion, as well as reactions with electrolyte components, is inversely proportional to the active resistance  $Z_{Re}$ :

$$Z_{Re} = |Z| \cdot Cos(b) \tag{1}$$

From the results of low-frequency impedance measuring at the corrosion potential, it follows that there is a correlation between an increase in the MAO and an increase in the active resistance of  $Z_{Re}$  of MAO -samples compared to untreated titanium (Table 5). Moreover, the strongest change is observed for MAO-NaAlO<sub>2</sub> mode. In this case, it probably affects both the increase in the treatment duration (and the corresponding increase in the thickness of the coating) and the nature of the doping element. It is also possible to notice some correlation between the increase in the resistance  $Z_{Re}$  with the lengthening of the

**Table 5.** Electrochemical impedance vector parameters at OCP and F = 0.39 Hz.

Sample	Z , kΩ·cm²	β°	Z <sub>Re</sub> , kΩ·cm <sup>2</sup>
MAO Ni-3	3.019	59.4	1.537
MAO Ni-5	14.019	59.1	7.199
MAO Ni-10	19.008	60.2	9.446
MAO NaAlO <sub>2</sub>	109.647	67.9	41.252
Titanium	4.028	78.1	0.831

**Table 6.** Electrochemical impedance vector parameters at the anodic polarisation (E = +1200 mV) and F = 0.39 Hz.

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Sample	Z , kΩ·cm <sup>2</sup>	β°	Z <sub>Re</sub> , kΩ·cm <sup>2</sup>
MAO Ni-3	31.895	72.0	9.856
MAO Ni-5	79.622	71.5	25.264
MAO Ni-10	50.529	72.1	15.530
MAO NaAlO <sub>2</sub>	91.337	73.9	25.329
Titanium	21.885	65.4	9.110

MAO treatment and the shift of the corrosion potential to the anodic direction, which indicates a more oxidised state of the surface. When processed in nickel-sulphate solution, this trend is clearly manifested, and for the solution with aluminate (25 min), the corrosion potential is somewhat more negative (although rather noble) than when processed in a nickel-containing solution (10 min). In this case, the nature of the electrolyte for MAO and, accordingly, the composition of the oxide coating also affects.

## Low-frequency impedance of samples at the anodic polarisation

Table 6 shows the parameters of the low-frequency impedance vectors at F = 0.39 Hz for MAO treated samples and untreated titanium, measured with anodic polarisation in the passive region at E = +1200 mV (S.H.E.). It is taken after the polarisation curve study causing additional oxidation of the surface.

When comparing the data in Tables 5 and 6, it is evident that the anodic oxidation of the samples further increases the phase shift angle for the MAO samples, i.e. the samples exhibit the properties of a capacitor rather than a resistor. For the untreated metal, the phase shift angle decreased, which is probably due to changes in the structure and composition of the surface layers during anodic polarisation. A strong increase in both the impedance modulus and its active component  $Z_{Re}$  is observed for the untreated titanium and during MAO processing in nickel-containing solution. This suggests that the passivation of the metal increases during anodic polarisation. Consequently, MAO coatings doped with nickel do not have properties that allow them to be used as anodic materials. On the contrary, they are promising as corrosion-resistant coatings.

When treated in an aluminate solution after oxidation at E = +1.2 V, the impedance modulus and  $Z_{Re}$  decreased by about 20%. It can probably be assumed that, unlike MAO coatings in nickel sulphate electrolyte, where the oxide layer is formed mainly by titanium dioxide and undergoes additional oxidation during anodic polarisation, aluminium oxide particles are not subject to further oxidation. On the contrary, at the polarisation in an aggressive acidic environment, a partial destruction of the MAO layer occurs with a partial loss of protective properties. Longterm corrosion tests have confirmed this assumption (see below).

# The choice of an equivalent circuit and the frequency dependence of the electrochemical impedance at open circuit potentials

In the studied frequency range of 0.1 Hz–50 kHz, the Nyquist plots for all samples, including untreated titanium, in complex coordinates represent inclined lines strongly straightened in the low-frequency region. This type of hodographs is typical for systems with significant reactivity due to strong inhibition of electrochemical processes and high insulating properties. In the high–frequency region of 50 Hz - 50 kHz, an arc-shaped section is visible, but it can only be noticed by greatly zooming in for this area. Therefore, the presentation of EIS studies is more revelling in Bode coordinates. Figure 5 shows Bode plots for the original titanium without treatment and with the MAO treatment, obtained at OCP in 25%H<sub>2</sub>SO<sub>4</sub>.

It is obvious from the data, that only for untreated titanium, the EIS spectra can be characterised by a single time constant. Its behaviour can be fitted by the simplest equivalent circuit consisting of a resistor and a capacitance connected in parallel (Figure 6(a)). Taking into account the possible heterogeneity in the structure and properties of the surface, we used a constant phase element (CPE) instead of a capacitance [28–30]. In this case, the exponent phase factor (n) of CPE can serve as a measure of the 'ideality' of the capacitor formed by the electrode surface layers. Therefore, it is possible to evaluate the uniformity of the surface. The results of such equivalent circuit fitting for untreated titanium are presented in Figure 6(a) and in Table 7.

This simplest equivalent circuit adequately describes the EIS spectrum, as can be seen by the coincidence of the dotted line in Figure 5 with experimental points. In this model, R<sub>0</sub> is the ohmic drop in the electrolyte between the sample surface and Luggin capillary. The constant phase element CPE is responsible for the reactance of the system. Its phase coefficient n = 0.943 is close to 1, which makes it possible to consider this element as a completely perfect capacitor formed by an electric double layer (EDL). Formally, the dimension of the CRE modulus is  $\Omega^{-1} \cdot s^{n} \cdot cm^{-2}$ , however, if  $n \approx 1$ , then it can be represented in units of capacity F/cm<sup>2</sup>. The element R is the charge transfer resistance. Thus, this system can be considered as a capacitor with a capacity of  $\sim 100$  $\mu F/cm^2$ and a self-discharge resistance of ~40k $\Omega$ ·cm<sup>2</sup>. Thus, this system can be compared with a capacitor with a capacity.

The simplest equivalent circuits with one time constant Figure 6(a) is no longer sufficient for simulation of the frequency response for the samples with MAOtreatment. For such systems, equivalent circuits providing several time constants have been proposed [48–50] (Figure 6(b)). In this circuit  $R_0$  as previously represents the resistance of the electrolyte. The CPE1 models the general capacitive characteristics of the outer layer at the electrode. Resistor R1 takes into account the ohmic potential drop in the electrolyte filling the pores of the MAO coating. Two parallel chains CPE2/ R2 and CPE3/R3 describe the features of electrochemical processes in the low-frequency region.

We conducted a preliminary simulation of the EIS frequency response for samples with MAO-treatment using this equivalent circuit and it turned out that the lowest fitting errors appear when the values of R2 become higher than  $10^{15}\Omega$ , and the phase factor n  $\approx$ 



Figure 5. Bode plots for samples with and without MAO treatment at OCP. The symbols represent experimental points. The dotted and solid lines represent the results obtained by fitting with equivalent circuits.



Figure 6. Equivalent circuits for simulation the frequency response: a – for untreated titanium; b, c–for samples with MAO-treatment.

0,5. This means that such model can be simplified by replacing the parallel circuit CPE2/R2 with Warburg element (W), see Figure 6(c). In this case, Warburg element W simulates the processes of diffusion ions transfer in pores, as well as semiconductor oxide layers of the coating. According to [51], this element can describe the diffusion of cationic vacancies in semiconductor oxide layers and the release of ions into solution. The parallel chain CPE3/R3 in this case corresponds to the resistive-capacitive characteristics of the electrochemical oxidation process on the internal metal–oxide boarder.

The results of using the equivalent circuit (Figure 6 (c)) for calculations of its elements values for samples with MAO coatings are shown in Table 8. Since the phase coefficient for the element CPE3 turned out to be close to 1, it can be replaced with a simple capacitor C3. A good coincidence of the frequency dependencies obtained from the simulation results according to the equivalent circuit (Figure 6(c)) with the experimental points of the spectrum (Figure 5) allows us to consider this model adequate.

It is evident from Table 8 that with an increase in the duration of MAO treatment the macro-capacitance characteristics of the samples decrease for both types of electrolytes. The modules of CPE1 element are reduced from 26 to 10  $\mu$ F/cm<sup>2</sup> in nickel sulphate solution and up to 2  $\mu$ F/cm<sup>2</sup> in aluminate solution. These data correlate with the results of the oxide layers thickness, since the increase in the thickness of the dielectric coating contributes to a decrease in the capacitance of the capacitor. The phase factor n changes from 0.71–0.85, which may indicate geometric and/or structural heterogeneity of the surface,

**Table 7.** Fitting values for the equivalent circuits for untreated titanium

R0 <sub>,</sub> Ω∙cm²	CPE, Qo $\Omega^{-1} \cdot s^n \cdot cm^{-2}$	CPE, n	R1, M Ω⋅cm <sup>2</sup>	Error of fitting
1.19	108.2·10 <sup>-6</sup>	0.943	0.039821	4.99%

and it decreases with increasing of MAO processing time.

The change in the ohmic pores resistance R1 does not give a direct correlation with MAO duration. On the contrary, the parameters of Warburg diffusion element progressively increase with increasing of MAO duration, the effect of processing time on the resistance R3 is even more noticeable. The values R3 changes by 7 orders of magnitude and formally it can be assumed that after 5 and 10 min of MAO processing, the Faraday's process in the pores practically stops. A significant (by ~50 times) decrease in the capacity of CPE3 with an increase in processing time may indicate the grows of the barrier layer thickness at the pores bottom, through which charge transfer occurs for an electrochemical reaction on the metal surface.

Comparing the behaviour of samples prepared in various electrolytes, it is evident that MAO NaAlO<sub>2</sub> sample demonstrates the most 'passive behavior', especially in the low-frequency region due to blocking of the electrochemical process in a thick oxide layer, where diffusion restrictions are maximum. Also, a decrease in porosity or pore size in the formed layer (an increase in the R1 parameter), due to the nature of the aluminate electrolyte, probably affects.

### EIS of the samples at the anodic polarisation

Table 9 presents the results of modelling EIS data using an equivalent circuit (Figure 6(b)) for samples treated with MAO after additional oxidation E = +1200 mV.

From a comparison of the data in Tables 8 and 9, it can be concluded that as a result of anodic polarisation of nickel-doped samples, their capacitance characteristics (according to the CPE1 Qo parameter) decrease by 1.5–2 times with a slight increase in the phase factor n, which is explained by an increase in the total thickness of the oxide layer. The values of R1 and W increase significantly (by an order of magnitude or

Table 8. Fitting values for the equivalent circuit Fig.6c for samples with MAO coatings at OCP.

		•				•		
Sample	R0, Ω·cm <sup>2</sup>	CPE1, Qo $\Omega^{-1} \cdot s^n \cdot cm^{-2}$	CPE1, n	R1, Ω·cm <sup>2</sup>	W $\Omega \cdot cm^2/n^{0.5}$	C3, µF/cm <sup>2</sup>	R 3, MΩ·cm <sup>2</sup>	Error of fitting
MAO Ni-3	3.31	26·10 <sup>-6</sup>	0.714	312	2300	286.27	0.00814	1.31%
MAO Ni-5	0.42	11·10 <sup>-6</sup>	0.737	2827	13413	58.01	79.264	3.85%
MAO Ni-10	0.69	10·10 <sup>-6</sup>	0.779	528	27706	57.56	714238	2.78%
MAO NaAlO <sub>2</sub>	2.39	2·10 <sup>-6</sup>	0.852	1598	202789	5.42	80990	4.47%

Table 9. Fitting values for the circuit (Figure 6(b)) for samples with MAO coatings after anodic polarisation.

					2			
Sample	R0 <sub>,</sub> Ω⋅cm <sup>2</sup>	CPE1, Qo $\Omega^{-1} \cdot s^n \cdot cm^{-2}$	CPE1 n	R1, Ω∙cm²	W $\Omega \cdot cm^2/n^{0.5}$	C3, µF/cm <sup>2</sup>	R3, MΩ∙cm²	Error of fitting
MAO Ni – 3	3.02	10·10 <sup>-6</sup>	0.794	3269.8	40843	6.40	78.9	1.36%
MAO Ni – 5	2.17	4·10 <sup>-6</sup>	0.854	134019.0	270114	4.12	1.66	3.53%
MAO Ni - 10	1.97	7·10 <sup>-6</sup>	0.854	1944.5	322818	127.82	7748.6	4.96%
MAO NaAlO <sub>2</sub>	3.37	4·10 <sup>-6</sup>	0.835	35351	696170	-	-	5.67%

more), which indicates that the charge transfer through the pores is blocked. At the same time, by changing the capacity of C3 for samples MAO Ni-3 and MAO Ni-5, we can assume an increase in the thickness of the barrier layer at the bottom of the pores, and its thinning for the sample MAO Ni-10. Nevertheless, in the latter case, the total charge transfer through the pores in the oxidised state will eventually be lower due to strong blocking of diffusion transfer (the value of W) and ohmic pore resistance (the value of R1).

For a coating obtained from the aluminate solution, it can be seen that after anodic polarisation, the macro-capacitance (CPE1), the pore resistance (R1) and especially the diffusion restrictions (W) also increase. The value of W increased by an order of magnitude! As a result of almost complete pore blocking, the values of the C3/R3 elements turned out to be practically insignificant, and this chain was excluded from the model.

### **Continuous corrosion tests**

The results of continuous corrosion resistance tests are presented in Table 10. The corrosion resistance of the coatings was determined as the time until their destruction in 35% sulphuric acid at the temperature of  $25^{\circ}$ C.

As follows from the test results, the corrosion resistance of the coatings obtained in nickel sulphate electrolyte has somewhat increased as a result of the increase of the MAO treatment duration from 3 to 5 min. When treated for 10 min the coating remained undestroyed for 1.5 years.

The oxide layer on the titanium sample with MAO treatment in the aluminate electrolyte was destroyed after 12 days of corrosion tests. Despite the significant increase (approximately 5 times) in the thickness of the oxide layer on this sample when compared to MAO Ni-10, its corrosion characteristics turned out to be significantly worse. As can be seen from Table 9, the value of Warburg impedance for the coating

 Table 10. Time until the destruction of the coating at longitudinal corrosion tests.

Sample	Time until destruction
MAO Ni-3	5 days
MAO Ni-5	7 days
MAO Ni-10	Not destroyed in 1.5 years
MAO NaAlO <sub>2</sub>	12 days

obtained in the aluminate solution is significantly higher than that for MAO Ni-10, but the value of resistance R3 (barrier layer resistance) on the contrary is higher for the latter sample by an order of magnitude. It is likely that in this case, the resistance of the barrier layer at the boundary: the metal substrate – MAO coating had a predominant effect on the high protective properties, and not just on the thickness of the oxide layers.

It should also be noted that the destruction of the coating does not occur immediately and, most likely, during the first days the metal remains in a passive state. Over time, the substrate undergoes 'activation', and as a result, the coating begins to peel off due to the high rate of corrosion.

### Conclusions

- Based on the results of EIS and potentiodynamic curves the electrochemical behaviour of titanium samples with MAO coatings in 25% H<sub>2</sub>SO<sub>4</sub>, a significant increase (up to 10 times) in the impedance modulus at low frequency and 1–2 orders of magnitude lower current densities in the anodic region compared with untreated titanium was found. The corrosion potentials of the samples with MAO coatings are 600–900 mV noble than for untreated titanium, which indicates the predominantly oxidative nature of the processes occurring during MAO processing.
- 2. No clear correlation was found between the current densities' levels on the anodic polarisation curves and the values of the impedance modulus at low frequency, obtained both at open circuit potentials and at the anodic polarisation at (+1200 mV). However, for coatings modified with nickel, both measurement methods showed a direct relationship between the duration of MAO treatment and the inhibitory effect.
- 3. The anodic polarisation of samples (+1200 mV) leads to a significant increase in the impedance modulus.
- 4. Several equivalent circuits are proposed that adequately simulate the experimental EIS data with fitting error no more than 6%. The influence of the stages of sample formation and their subsequent electrochemical treatments on the nominal values of the equivalent circuit elements is considered.

- 5. It is shown that the studied MAO coatings on titanium have high corrosion resistance in an aggressive sulphuric acid environment.
- 6. It is shown that there is no direct correlation between the duration of the MAO treatment, the thickness of the formed oxide layers and electrochemical and corrosion characteristics. The composition of the formed oxide, its continuity and the properties of the barrier layer at the boundary with the matrix metal play a decisive role.
- 7. It has been established that nickel doping of MAO coatings on titanium using this technology does not allow them to serve as anode materials.

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