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Determination of the equivalent electric circuit parameters of a galvanic cell in the micro-arc oxidation process

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Abstract. A method for determining the thickness of microarc coatings based on the use of electrochemical impedance spectroscopy during the microarc oxidation process is proposed. To obtain the studied oxide coatings, a silicate-alkaline electrolyte was used in the following technological modes: sinusoidal electric current in the anode-cathode mode at a current density of 11 A/dm^2. The frequency range of electrochemical impedance spectroscopy ranges from 20 Hz to 2 MHz. During the study, the structure was revealed and the elements values of the electrical circuit of the galvanic cell were determined, taking into account electrochemical impedances by parametric optimization. The proposed equivalent electrical circuit takes into account the processes of ion diffusion through the oxide layer and the imperfection of the electrical capacitance of the coating, which is due to its porous structure. A regression and correlation analysis of the experimental data obtained was performed, during which the strong inverse correlation of the proportionality factor of the constant phase element of electrical circuit of the galvanic cell with the thickness of the formed coatings was found. The method of indirect measurement of the thickness of oxide coatings has satisfactory accuracy and can be used for laboratory studies. With an increase in the accuracy and speed of measuring operations, industrial application of this method is also possible. The proposed galvanic cell equivalent electrical circuit can be implemented in the decision support subsystem of an intelligent microarc oxidation system.

Keywords: microarc oxidation process, electrochemical impedance spectroscopy, electrical substitution circuit, galvanic cell, parametric identification, digital twin

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Определение параметров схемы замещения гальванической ячейки в процессе микродугового оксидирования

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Аннотация. В работе исследуется возможность применения метода электрохимической импедансной спектроскопии для определения толщины оксидных покрытий в процессе микродугового оксидирования. В ходе исследования выявлена структура и определены значения элементов электрической схемы замещения гальванической ячейки с учетом электрохимических импедансов методом параметрической оптимизации. Предложенная схема замещения учитывает процессы диффузии ионов через оксидный слой и неидеальность электрической емкости покрытия, которая обусловлена его пористой структурой. В результате регрессионного и корреляционного анализа полученных экспериментальных данных обнаружена сильная обратная корреляция фактора пропорциональности элемента постоянной фазы схемы замещения гальванической ячейки с толщиной формируемых покрытий. Метод определения толщины оксидных покрытий имеет удовлетворительную точность и может быть использован для лабораторных исследований. Предложенная схема замещения гальванической ячейки может быть использована для разработки цифрового двойника процесса микродугового оксидирования.

Ключевые слова: процесс микродугового оксидирования, электрохимическая импедансная спектроскопия, электрическая схема замещения, гальваническая ячейка, параметрическая идентификация, цифровой двойник

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Introduction

The task of creating a digital twin is related to the choice of a mathematical model that adequately describes the object of research. For the micro-arc oxidation (MAO) process, the object of the study is a galvanic cell, which is advisable to analyze a metal-oxide-electrolyte type system. For the analysis of electrophysical processes, systems of this type are presented in the form of an electrical replacement circuit. For example, in [1] a model of a galvanic cell based on a substitution circuit is presented, which includes active (resistance) and reactive (capacitance) elements. This substitution circuit does not take into account some features of the research object, as a result of which the model has limited accuracy. As a rule, electrical equivalent circuits for modeling electrochemical systems contain idealized elements characterizing physical and chemical processes in the metal-oxide-electrolyte type system (Warburg impedance *W*, constant phase element *CPE*, etc.) [2–4], while the structure of the electrical equivalent circuit may be different. However, this approach is currently used mainly to study the corrosion resistance of finished samples of oxide coatings. Therefore, it seems urgent to analyze the mathematical model of the microarc oxide coating process and refine it taking into account the electrochemical impedance.

Materials and Methods

To obtain the studied samples of oxide coatings by microarc oxidation, the surface of 10 bars of aluminum alloy AD31 with dimensions of 20×15×2 mm was developed. The processed sample is placed in the galvanic cell as an anode, the cathode is made of stainless steel. The process current source generates a symmetrical sinusoidal current with a density of 11 A/dm^2 in the anode-cathode mode. The following electrolyte was used: 2 g/l NaOH and 9 g/l Na_2SiO_3.

The microarc oxidation process was carried out over the following time: 30, 60, 120, 300, 600, 960 s. Measurements of the real and imaginary components of the complex impedance of the galvanic cell of each test sample were performed before the start of the technological process and at the above-mentioned time points. Measurements were made using the Keysight E4980A LCR meter in the frequency range from 20 Hz to 2 MHz. Before measuring the impedance, the galvanic cell was disconnected from the MAO installation, maintained for 5 minutes and discharged by closing the anode to the cathode for 30 seconds. Based on the results of the experiment, the Nyquist plots of the galvanic cell impedance were plotted for each sample. The structure selection and determination of the elements parameters of the galvanic cell equivalent electrical circuit were performed using the EIS Spectrum Analyser software [5] by parametric optimization using the Powell method. The coatings thickness was determined using a point autofocus probe surface texture measuring instrument Mitaka PF-60. Statistical processing of measurement results, including regression and correlation analysis, was performed using the STATISTICA 10 program.

Results and Discussion

Fig.1, *a* shows the impedance Nyquist plots obtained as a result of experiments. The galvanic cell equivalent electrical circuit, which satisfactorily approximates the impedance Nyquist plots (the model adequacy error does not exceed ± 2%), is shown in Fig. 1, *b*. The elements values of the galvanic cell equivalent electrical circuit are given in Table.

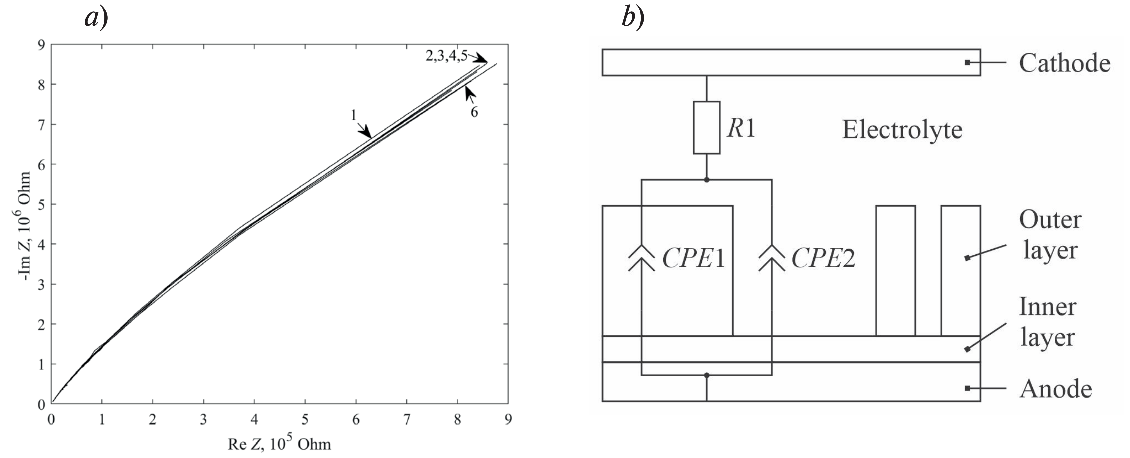

Fig. 1. Nyquist plots of the galvanic cell impedance (*a*) and equivalent electrical circuits of the galvanic cell (*b*): 1 – MAO treatment time of 30 s, 2 – 60 s, 3 – 120 s, 4 – 300 s, 5 – 600 s, 6 – 960 s; *R*1 – electrolyte resistance, *CPE*1 – imperfect capacitance of coating, *CPE*2 – imperfect Warburg impedance

Table

The elements values of the galvanic cell equivalent electrical circuit

Time, s	*R*1, Ohm	P_1	n_1	P_2	n_2
30	504.73	$2.64\cdot10^{-12}$	0.97	$6.20\cdot10^{-11}$	0.46
60	455.82	$2.48\cdot10^{-12}$	0.97	$5.37\cdot10^{-11}$	0.46
120	470.62	$2.44\cdot10^{-12}$	0.97	$4.88\cdot10^{-11}$	0.49
300	551.40	$2.40\cdot10^{-12}$	0.97	$4.40\cdot10^{-11}$	0.49
600	583.66	$2.39\cdot10^{-12}$	0.97	$2.88\cdot10^{-11}$	0.53
960	914.19	$1.73\cdot10^{-12}$	0.99	$6.06\cdot10^{-12}$	0.76

P_1, P_2 are proportionality factors; n_1, n_2 are exponents showing phase deviation. The error in determining the parameters of the galvanic cell equivalent electrical circuit and measuring error of the MAO coating thickness are ± 2% and ± 2.5% respectively.

The analysis of the data in Table, taking into account the available data on the MAO coatings structure [6, 7], allows us to interpret the physical meaning of the elements of the galvanic cell equivalent electrical circuit as follows. The resistor *R*1 represents the electrolyte resistance; the constant phase element *CPE*1 is an almost ideal capacitor ($n_1 \approx 1$) and represents the capacitance of the coating (barrier layer, working layer and porous layer, except for the pore area). The constant phase element *CPE*2 is the Warburg impedance ($n_2 \approx 0.5$), which in this case simulates the diffusion of oxygen and aluminum ions through the oxide layer; in this case, the parameter P_2 makes sense of the diffusion coefficient. The structure of the galvanic cell equivalent electrical circuit has some similarities with the one presented in [8].

The effect of the technological process time on the thickness of the oxide coating is shown in Fig. 2, *a*. It can be seen that this dependence is linear in nature, which is consistent with the results of [9–11]. The scattering diagram (Fig. 2, *b*) allows to analyze the relationship between the thickness of the synthesized coating and the coefficient P_1, which characterizes the electrical capacitance of the coating. It can be seen that with a confidence probability of 95%, the points in Fig. 2, *b* are within the confidence interval (curve *2* corresponds to the approximating curve, curves *1* and *3* correspond to the upper and lower boundaries of the confidence interval). The results of statistical processing confirmed the presence of an inverse correlation between the coating thickness and the coefficient P_1 (correlation coefficient $\rho = -0.89$). The above conclusions confirm the possibility of indirectly determining the thickness of the oxide coating using the parameter P_1.

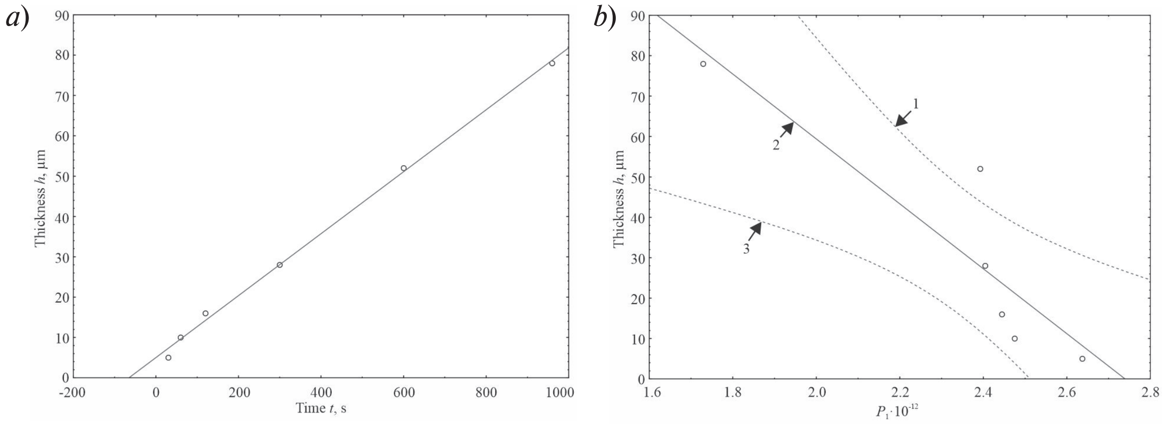

Fig. 2. Functional dependence showing the effect of the duration of the technological process *t* on the thickness of the coating *h* (*a*) and a scattering diagram reflecting the correlation between the coating thickness *h* and the coefficient *P*1 (*b*). Solid lines show approximating curves, dashed lines show the boundaries of the confidence interval

Conclusion

Thus, the revealed structure of the equivalent electrical circuit and the values of its elements obtained by parametric optimization adequately describe the behavior of the galvanic cell in the MAO process, taking into account the ions diffusion through the oxide layer and the imperfect capacitance of the coating having leakage through the pores. The model makes it possible to predict the change in coating thickness during the MAO process using the parameter *P*1 of the constant phase element *CPE*1, which has a physical meaning of electrical capacitance. The proposed thickness measurement method can be used for laboratory studies, since obtaining electrochemical impedance spectra suitable for analysis requires careful experimental preparation and takes a long time. In addition, the methods of parametric optimization used are not ideal and may give different results depending on the initial conditions, as a result of which the correct interpretation of the electrochemical impedance spectra is possible only with a deep understanding of the physical processes underlying the phenomena under consideration. Automation of measurement operations and improvement of parametric optimization methods will partially eliminate these disadvantages, which will make it possible for industrial use of the proposed method for determining the MAO coatings thickness.

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