EFRE 2020

C3-P-047601

Application of impedance spectroscopy for research of the micro-arc oxidation process

Pavel Golubkov, E.A. Pecherskaya, G.V. Kozlov, T.O. Zinchenko, O.A. Melnikov, J.V. Shepeleva

Penza State University, Penza, Russia

Introduction

The impedance spectroscopy method was used to study the processes of charge transfer and the corrosion properties of coatings obtained by micro-arc oxidation (MAO).

The study of changes in the structure and properties of the oxide layer formed during the MAO process, depending on the processing time and technological parameters, is of great interest. The impedance spectroscopy method can be an effective tool for controlling the MAO process and controlling deviations of the formed coatings properties (thickness and porosity) from the required values in real time, which is relevant in view of the difficulties associated with the automation of this technology.

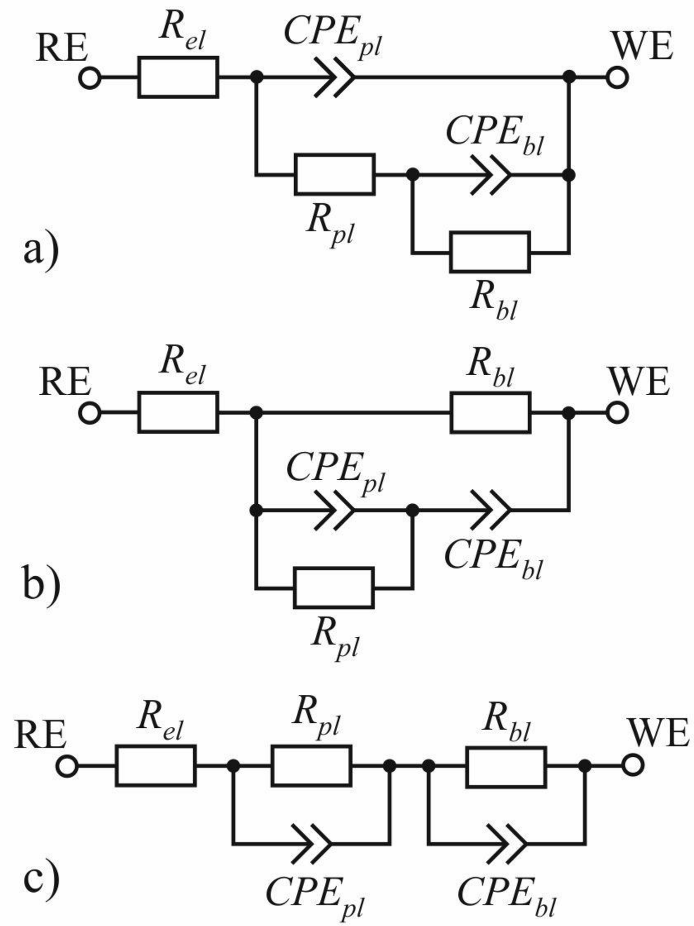

Fig. 1. Equivalent electrical models used for corrosion studies of the MAO process: RE is the reference electrode, WE is the working electrode, R_{el}, R_{bl}, R_{pl} are the resistance of the electrolyte, the barrier and porous layers, respectively; CPE_{bl}, CPE_{pl} – constant phase elements, reflecting the capacity of the barrier and porous layers, respectively.

Impedance Measuring Method

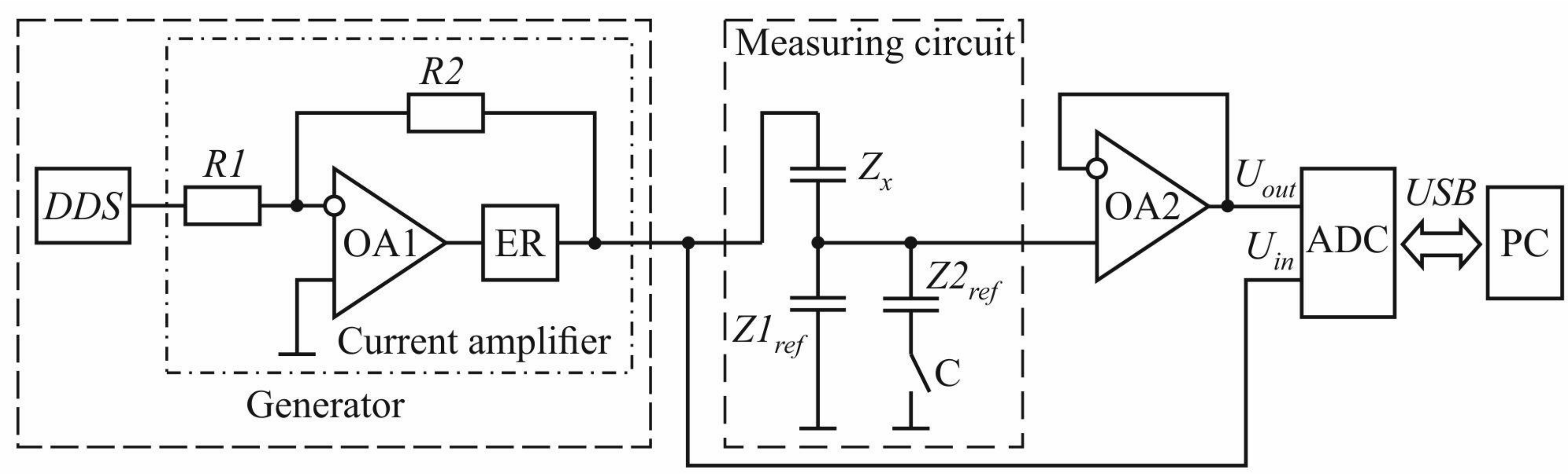

Fig. 2. The design of the MAO coating impedance measuring transducer using the modified I-V method: DDS - digital signal synthesizer; ER - push-pull emitter repeater; Z_x - test sample; Z_{ref} – reference impedance; C – commutator.

This design of the measuring transducer allows to take into account the effect of electrolyte on the measurement result.

Calculation of impedance Z_x

The impedance of the test sample Z_x is calculated by the formula:

$$Z_x = Z_{ref}\left(\frac{U_{in}}{U_{out}} - 1\right) \tag{1}$$

where U_{in} and U_{out} are the input and output voltages of the measuring circuit respectively; Z_{ref} is the impedance of the reference RC circuit:

$$Z_{ref} = \frac{R_{ref} + j\omega C_{ref} R_{ref}^2}{1 + \omega^2 C_{ref}^2 R_{ref}^2} \tag{2}$$

where R_{ref} and C_{ref} are the resistance and capacitance of an reference RC circuit.

The equivalent circuit of the test sample

The test sample can be represented as the equivalent circuit shown on Fig. 3.

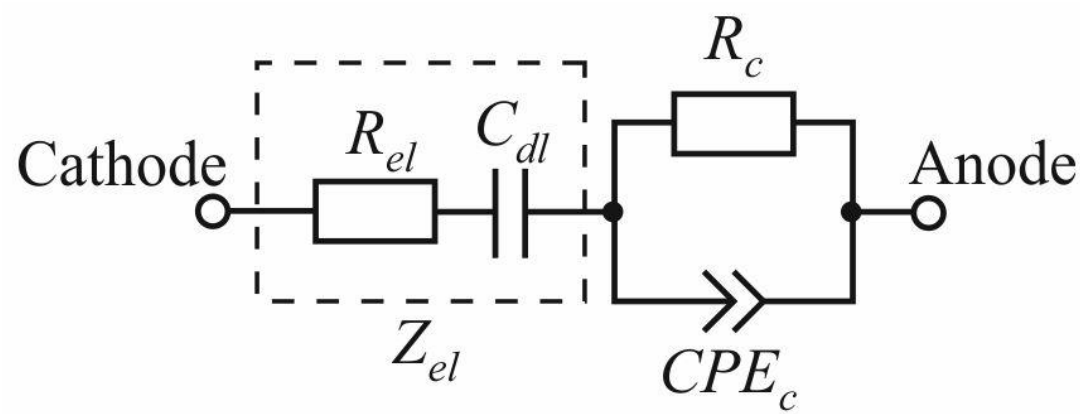

Fig. 3. An equivalent electrical model of the “anode-coating-electrolyte-cathode” system.

In Fig. 3 R_c and CPE_c simulate the resistance and capacitance of the coating, respectively; Z_{el} represents the electrolyte impedance, including the active resistance R_{el} of the electrolyte layer between the anode and cathode and the impedance of double electric layers with a C_{dl} capacity. The constant phase element CPE_c was chosen as a model of the coating capacitance, since the sample under study is a non-ideal capacitor with leakage through the pores.

Measurement technique

Measurement of a coating impedance should include two steps:

1. Preparatory, during which the electrolyte impedance is measured between the anode and the Z_{el} cathode in the frequency range in the absence of coating on the anode.

2. Measurement of the sample impedance Z_x (“anode-coating-electrolyte-electrode” system).

In this case, the impedance Z_{par} of the parallel connection R_c-CPE_c associated with the coating is calculated as the difference of the impedances:

$$Z_{par} = Z_x - Z_{el} \tag{3}$$

On the other hand, this impedance can be represented as followed:

$$Z_{par} = \left(\frac{1}{R_c} + (j\omega)^n \cdot C \right)^{-1} \tag{4}$$

where C is a constant proportional to the coating capacity. The coating thickness can be determined by known formulas.

Experimental Details

To determine the impedance nature of the system “anode-coating-electrolyte-cathode” the following experiment was conducted. A flat sample of aluminum with a size of 15x25x1 mm was polished to a mirror shine with sandpaper with a grain size of 600, 800, 1000 and 2000, then degreased with acetone and pressed onto an insulated current lead from aluminum wire. The current supply was fixed in a clamp on the anode of the galvanic cell of the MAO installation. The MAO process was carried out in the anode-cathode mode at an anode current of 0.25 A and the ratio of the anode and cathode currents $I_K/I_A = 1$ for 30 min in an aqueous electrolyte containing 14 g/l Na_2SiO_3. The impedance was measured in two stages according to the method proposed above.

Experimental results. Stage 1

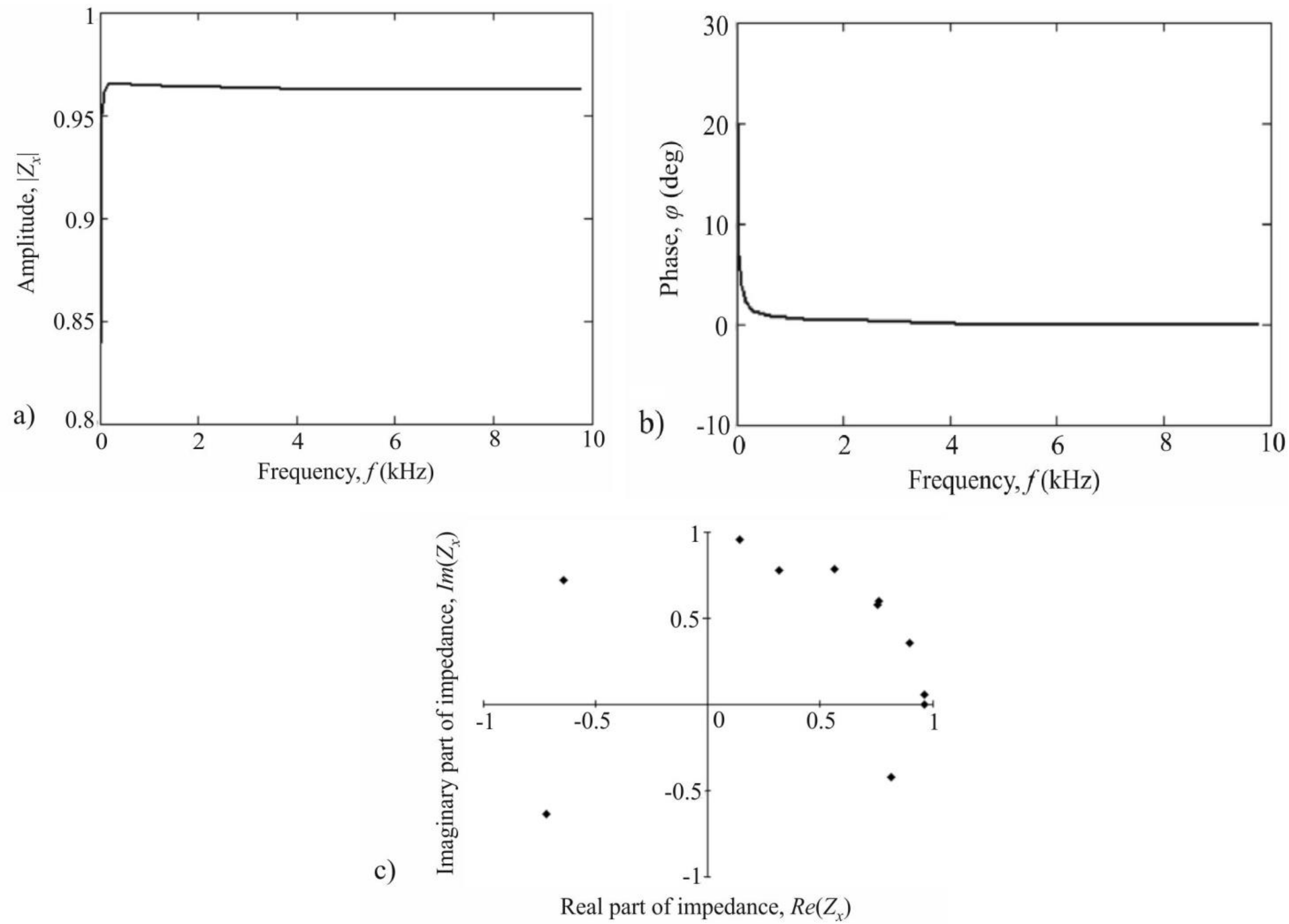

Fig. 4. Characteristics of the “anode-electrolyte-oxide-cathode” system at the first stage of impedance measurement: (a) and (b) are the amplitude-frequency and phase-frequency characteristics (on a linear scale); (c) is the impedance hodograph.

Experimental results. Stage 2

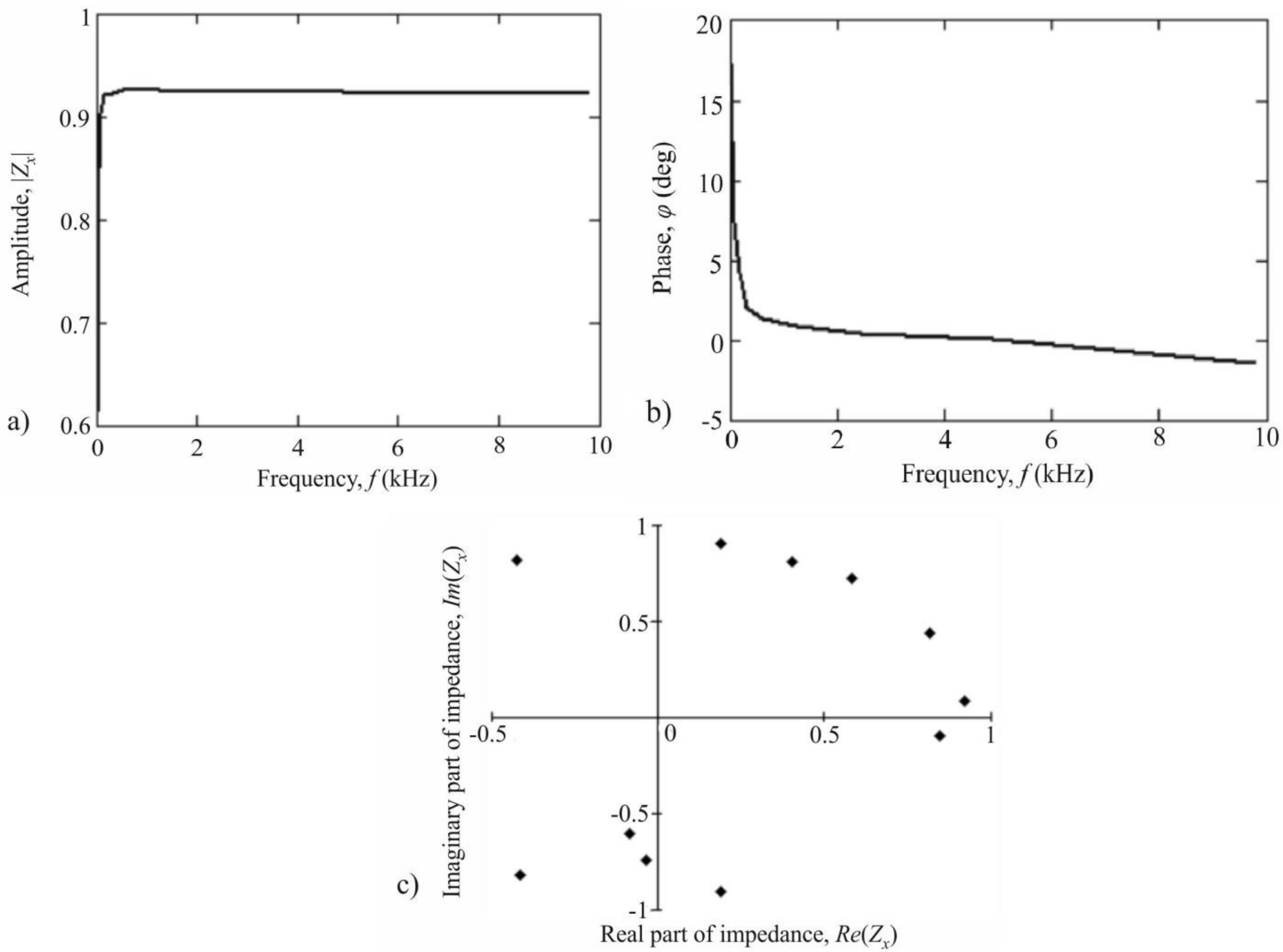

Fig. 5. Characteristics of the "anode-electrolyte-oxide-cathode" system at the second stage of measuring impedance: a and b are the amplitude-frequency and phase-frequency characteristics (on a linear scale); c is the impedance hodograph.

The further work

Selection of the structure and ratings of the equivalent electrical model components for satisfactory approximation and interpretation of experimental data, it is necessary to carry out numerical methods using optimization algorithms. The disadvantage of this approach is that experimentally determined impedance values can correspond to different equivalent electrical models, the values of the same elements of which may not coincide with each other.

Thus, calculating the coating thickness based on the results of impedance measurements is a complex task, the solution of which requires:

- Eliminate measurement errors;
- Improve the design of the measuring transducer;
- Find a convenient way to unambiguously approximation of the measurement results;

To develop an analytical method for calculating the impedance of models that include idealized elements, for example, a constant-phase element, with the possibility of determining the thickness and porosity of coatings.

Conclusion

The study confirms the possibility of the impedance spectroscopy method application to study the MAO coatings properties in the process of their formation. The proposed measurement method allows realizing the measurement of the oxide layers impedance in real time and can be used to control the properties of multifunctional coatings obtained by the MAO process.

However, the proposed method for measuring impedance has disadvantages associated with both the hardware implementation of the measuring transducer and the difficulty in interpreting the results of the experiment. The elimination of these disadvantages will make it possible to fully realize the advantages of the impedance spectroscopy method and apply it to control the MAO coatings properties in the process of their controlled synthesis.

Thank you for your attention!