9th INTERNATIONAL SYMPOSIUM ON MEASUREMENT AND QUALITY CONTROL (9th ISMQC)
November 21 – 24, 2007, IIT Madras

MEASUREMENT SYSTEM FOR COATING QUALITY CONTROL DURING HIGH-CURRENT PROCESS IN ELECTROLYTE SOLUTION

Borikov V.N.
Department of Computer-aided Measurement Systems and Metrology
Tomsk Polytechnic University, Tomsk, Russia
E-mail: borikov@camsam.tpu.ru

Abstract: *This paper presents both a tool and a method for control of ceramic coating process by high pulse current in electrolytes. The method is based on the use of symmetric trapezoidal voltage pulse power source for oxidation, running volt-ampere characteristics and defining active and capacitive currents what allows to estimate the coating quality.*
Keywords: *Coating Quality; Measurement System; Volt-Ampere Characteristic.*

1. INTRODUCTION

Electric current through a boundary "electrode-solution" in anodization causes formation of metal oxides on the electrode surface that result in increase of the boundary resistance. Under large polarization voltage, an oxide breakdown happens accompanied with a luminescence. The processes are called the anodic spark electrolyze also known as microplasma oxidation (Kurze at al., 2003). This process is one of electrochemical methods of coating and becomes popular for use in surface modification of alloys and metals with the purpose of ruggedization and providing their necessary anticorrosion, electric, and decorative properties.

It is necessary to keep in mind that when microplasma oxidizing the microplasma coating is formed by only part of all current of electrochemical process. In this relation, the high-current pulse processes are of a great interest. In order to control the technological processes in the electrolyte solutions it is proposed to use the high-voltage pulse of the trapezoidal form and to run the volt-ampere characteristics of the microplasma oxidation by means of a computer-aided measurement system (Mamaev & Mamaeva, 2005).

2. SYSTEM STRUCTURE

For electrochemical measurements a three-electrode electrochemical cell was used that is a ceramic glass 110 mm in diameter and 110 mm in depth (see Fig. 1). The stainless steel electrode 2 mm thick served as auxiliary electrode having the half ring shape and located in the glass. The surface of the auxiliary electrode exceeded a surface of the working electrode. The standard platinum spherical electrode EPL-02 was chosen as a comparison electrode. A working electrode was 10×25 mm rectangular sample of the alloy Al2021. The experiment was carried out in 4 componential electrolyte of the following structure, g/l: $Na_2HPO_4 \times 12H_2O$ – 30; $Na_2B_4O_7 \times 10H_2O$ – 30; H_3BO_3 – 20; NaF – 10.

The measuring setup (Fig. 2) was used for measurement of microplasma currents I and polarized voltage U_p with the purpose of construction of cyclic volt-ampere curves. The experimental installation includes the power supply,

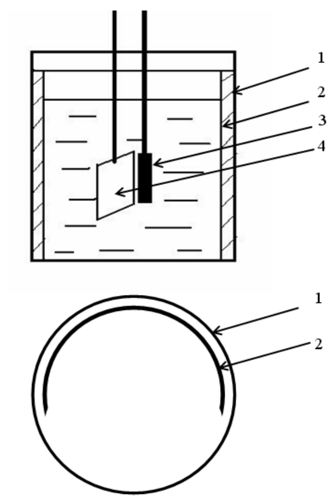

Fig. 1. The circuit of experimental three-electrode electrochemical cell: 1 – ceramic glass; 2 – auxiliary electrode; 3 – comparison electrode; 4 – working electrode.

three-electrode electrochemical system and the measuring equipment for registration and processing of the information (computer-aided measurement system).

The pulse voltage from the power supply to microplasma system is allocated between a working electrode and solution.

The computer measurement system allows to obtain a volt-ampere dependences of microplasma processes in the pulse mode at voltage up to 300 V, voltage rise-time of 10^8 V/s, currents up to 100 A and to registration of the voltage and current signals with discrete 25 mV and 1 mA accordingly.

Measurement of all the electric parameters, *I*, *U*, and U_p, is carried out simultaneously during one pulse (200…250 μs). Fig. 3 shows an example of one of obtained volt-ampere curves at different durations of covering process.

It is experimentally investigated that the kind of cyclic

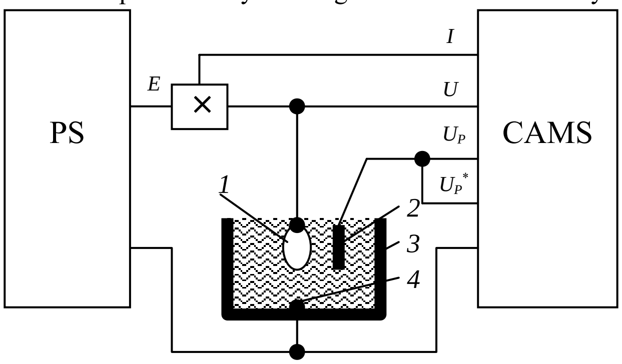

Fig. 2. Diagram of the experimental installation: PS – power supply; CAMS – computer aided measurement system; 1 – coating object; 2 – comparison electrode; 3 – bath; 4 – auxiliary electrode; *U* – voltage of the power supply; *I* – current of microplasma process; U_p – polarizing voltage; U_p^* – polarizing voltage for measurement with increased resolution.

volt-ampere dependencies essentially depends on a material of a working electrode (coating object). Irrespective of the object material the cyclic volt-ampere curves shifts to the range of higher voltages and smaller currents in the course of coating. During the process, the capacitive component of the current and the active one is changing. This is explained by increase of thickness of the formed covering and change of its porosity.

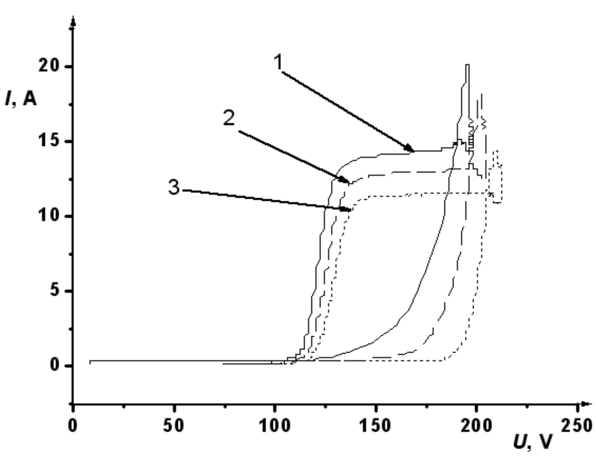

Fig. 3. Volt-ampere characteristics of aluminium alloy 2021 at different durations of covering process: 1 – 3 min; 2 – 4 min; 3 – 5 min.

Table 1 shows results of measuring thickness and porosity of microplasma coating depending on time.

Table 1. Properties of obtained coating.

No	Processing time, s	Thickness, μ	Porosity, %
1	60	4.16	0.92
3	300	9.13	4.11
4	600	11.33	16.89

Therefore, the volt-ampere characteristic can serve as an adequate mapping of physical-mechanical properties of the obtained covering.

3. MODEL OF PROCESS

The elementary equivalent circuit for the microplasma process assumes that two conducting surfaces, electrolyte and metal, between which the dielectric oxide film is situated, produce a condenser.

More complex equivalent circuits take into account capacity of a double layer on border of an electrode-

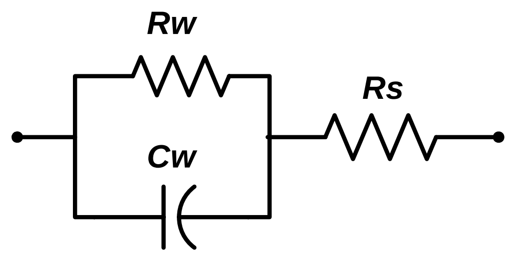

Fig. 4. The equivalent circuit of the microplasma system: C_w – the capacity part of electrode reactance; R_w – the active resistance of electrode; R_s – the solution resistance.

solution (Suminov at al., 2005).

At impact of the large voltage, the boundary metal-oxide-electrolyte behaves as a nonlinear element. This effect is explained by theory using representations about semi-conductor properties of oxides and *p*-*i*-*n* layer on the boundary. Occurrence of *p*-*i*-*n* layer is defined by a various degree of deviation of microplasma process boundary structure. Surplus of positive ions near metal-oxide partition promotes the electronic impurity conductivity (formation of a *n*-layer) while surplus of oxygen ions causes the hole conductivity of layers near electrolyte. Thus average layer is considered as a dielectric with only ion conductivity.

In the general case the equivalent circuit for the metal-oxide electrode is depicted by the parallel connected capacity C_w and the active resistance R_w with series connected active resistance of the solution R_s (Fig. 4) (Dyer, 1974).

To investigate how the capacitive and active current components vary in time there was created a MATLAB model of microplasma process (Fig. 5) using the equivalent circuit presented in Fig. 4.

In this model, a DC voltage source switched by a breaker was used as the power supply.

Parameters of output impedance of the modeled power supply (*RL* Source) were in correspondence to parameters of the power supply of experimental installation and were defined experimentally. The experiment was implemented using an electric circuit with the following element values: $R_1 = 10\ \Omega$, $R_2 = 100\ \Omega$ and $C = 0.94\ \mu F$ (Fig. 5).

The experimental and modeled data are shown in Fig. 6. It is clear from the Fig. 6 that modeled results coincide with experimental data. Output impedance of the source was characterized by the following parameters: $L = 43\ \mu H$ and $R = 1.3\ \Omega$.

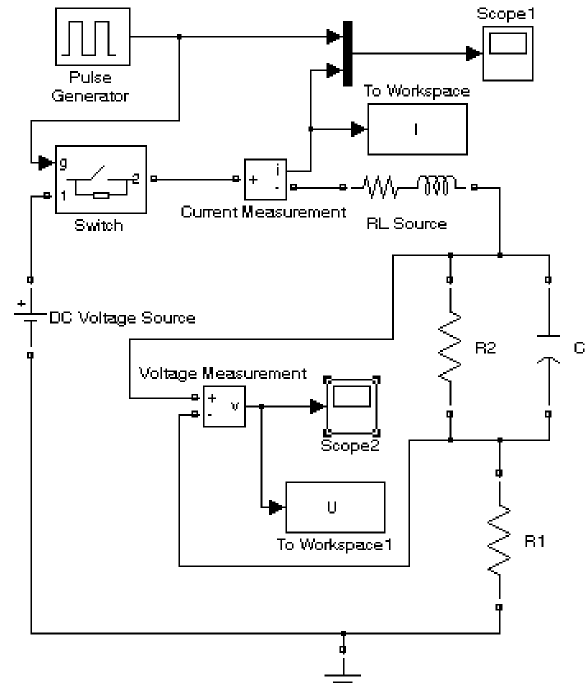

Fig. 5. The coating process model in MATLAB.

Upon determination of parameters of the power supply, microplasma process modeling was realized. Element parameters of the equivalent circuit were calculated from experimental volt-ampere curves for Al2021 (Fig. 3). They are presented in Table 2. Solution resistance value R_s was equal to 5 Ω.

Table 2. Equivalent circuit parameters.

Processing time, s	R_w, Ω	C_w, μF
180	10.5	0.6
240	12.4	0.4
300	15.3	0.2

The obtained data have been verified by the model presented in Fig. 5, where $R_2 = R_w$, $C = C_w$, $R_1 = R_s$ are taken from the Table 2.

Compliance of the experimental and modeled (Fig. 7) currents at different durations of covering process confirms adequacy of the equivalent circuit of process for input pulse voltages. Thus, by variations of resistance and capacity one can make conclusions of parameters of a microplasma coating.

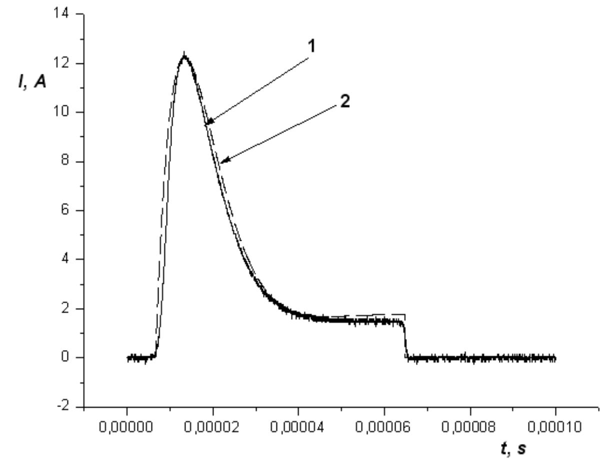

Fig. 6. The R_1 current pulse: 1 – from experiment; 2 – from model.

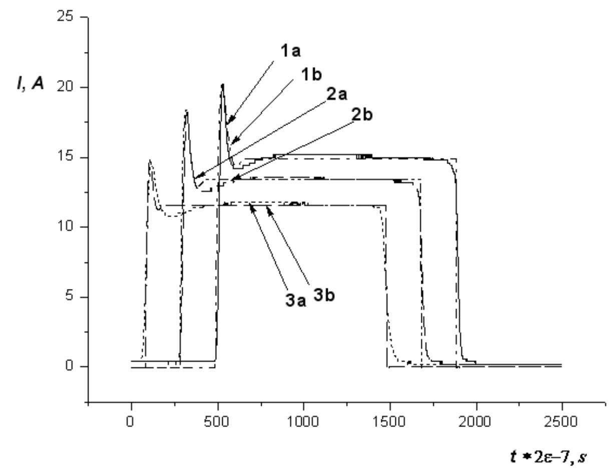

Fig. 7. Compare of the microplasma currents from experiment and from model: 1a, 1b – 3 min; 2a, 2b – 4 min; 3a, 3b – 5 min; where a – from experiment; b – from model.

4. PROCESSING ALGORITHM

Results of modeling microplasma process prove a possibility to control coating quality by means of estimating capacitive and active components of the microplasma current.

The current can be represented as a sum of active component I_a and capacitive component I_c:

$$I = I_a + I_c\ . \quad (1)$$

The speed of change of potential dU/dt and the capacity C can be defined by the volt-ampere characteristic as follows:

$$C = I_c / (S \cdot dU / dt) \quad (2)$$

where S is covering surface area.

The measurement system allows to define an active and capacitive components of the current depending on the voltage during one pulse.

Definition of active and capacitive currents is based on a trapezoidal voltage pulse (Fig. 8).

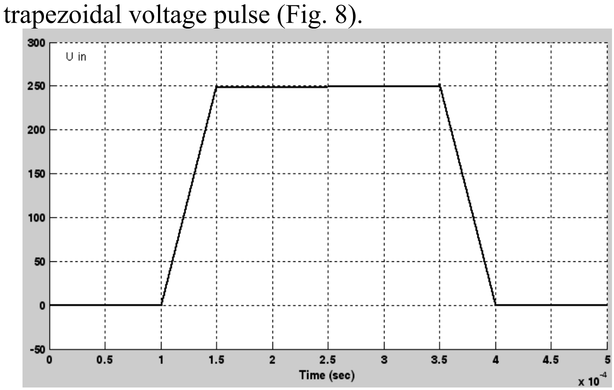

Fig. 8. Input voltage signal for microplasma process.

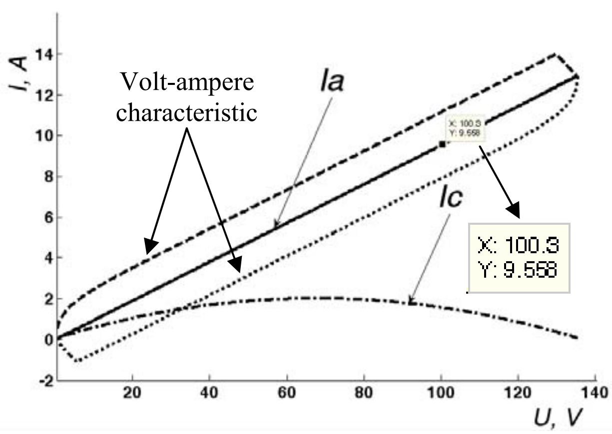

Fig. 9. Graphical form of algorithm

The pulse leading edge current is determined by ratio

$$\vec{I}_{\Sigma} = \vec{I}_a + C \cdot S \cdot d\vec{U} / dt \qquad (3)$$

and the pulse droop current

$$\overleftarrow{I}_{\Sigma} = \overleftarrow{I} + C \cdot S \cdot d\overleftarrow{U} / dt \; . \qquad (4)$$

Values of $d\vec{U}/dt$ and $d\overleftarrow{U}/dt$ are the same under symmetric trapezoidal pulse of polarizing voltage but have different signs:

$$d\vec{U} / dt = -d\overleftarrow{U} / dt \; . \qquad (5)$$

Summing of the volt-ampere dependencies (3) and (4)

$$\vec{I}_{\Sigma} + \overleftarrow{I}_{\Sigma} = 2I_a \qquad (6)$$

allows to have a dependency of active current vs

Subtraction of the volt-ampere dependencies (4) from (3)

$$\vec{I}_{\Sigma} - \overleftarrow{I}_{\Sigma} = 2 \cdot C \cdot S \cdot dU / dt = 2I_c \; (7)$$

allows to have dependency of the capacity current vs voltage.

In order to verify the method, it was modeled in MATLAB for the case of the alloy AL2021 at 180 s durations of covering process. Graphic dependences of capacitive and active currents (Fig. 9, 10) were received. Results obtained confirm the method adequacy.

Thus, received cyclic volt-ampere dependency under a symmetric trapezoid polarizing pulse of the voltage enables to define dependency of an active current and capacity C on voltage. It is necessary to note that measured polarizing voltage for volt-ampere dependencies allows excluding influence of the electrolyte properties on measurement results.

5. CONCLUSION

The pulse power supply for oxidation supplemented of computer measurement system allows to define the active and capacitive part of microplasma process resistance and to supervise quality of coating: thickness, change of thickness and porosity (Mamaev et al., 2006).

The technological process is controlled by stabilization of the active current or polarizing voltage. In this process by values of active and reactive resistances one can judge of expediency of the process continuation or termination.

It is necessary also to notice that for a proper use of the method one should know how the capacitive and active current components depend on the coating physical properties.

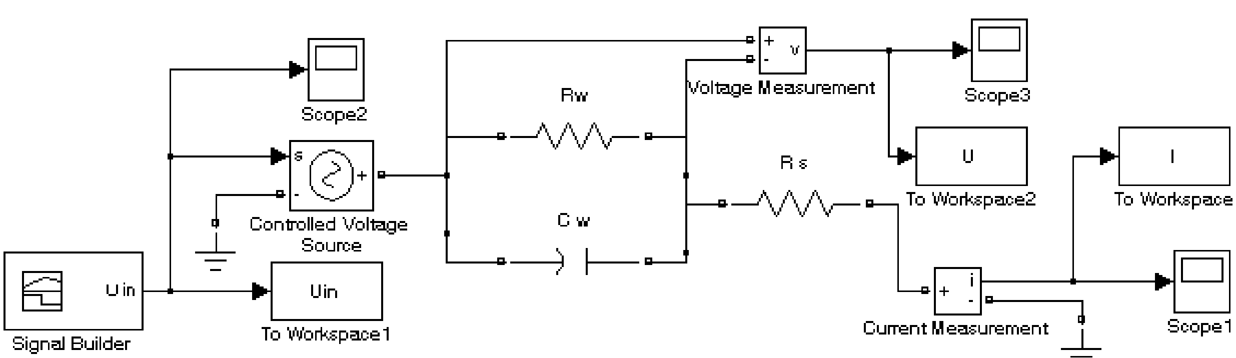

Fig. 10. Modeling of the method in MATLAB

6. ACNOWLEDGMENT

This work was supported in part by the Grant NP 2.1.2.5273 on basic researches in engineering sciences from Analytical Program of the Ministry of Education of Russian Federation.

7. REFERENCES

Dyer C.K. (1974). Electrolytic rectification and catholic charge reversibility of some valve metals. Electrocomponent Science and Technology, Vol. 1, pp. 121-127

Kurze P. et all. (2003). Micro Arc/ Spark Anodizing – was ist das? Micro Arc/ Spark Anodizing – what is that? Galvanotechnik, No. 8, pp. 1850 – 1863

Mamaev A.I., Mamaeva V.A. (2005). The High Current Processes in the Electrolyte Solutions, Siberian Branch of the Russian Academy of Science, ISBN 5-7692-0780-9, Novosibirsk (in Russian)

Mamaev A.I., Mamaeva V.A., Borikov V.N, Dorofeeva T.I.,. Butyagin P.I. (2006). Method of definition of electric parameters of high pulse current processes in solutions and computer measurement system. Russia Patent 2284517

Suminov I.A., Apelfeld A.V., Lyudin V.B., Krit B.L., Borisov A.M. (2005). Microarc Oxidation: Theory, Technology, Equipment, Ekonom, ISBN 5-89594-110-9, Moskow (in Russian)