Journal of Achievements in Materials and Manufacturing Engineering
International Scientific Journal published monthly by the World Academy of Materials and Manufacturing Engineering

Study of the oxide layers on metals by local electrochemical analysis

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Received 10.04.2014; published in revised form 01.06.2014

ABSTRACT

Purpose: In this given work we consider a method CVA that at on one polarization curve allows us to trace the process of formation of the oxide film on the metal surface (anodic part of the curve), while the cathodic part of the curve to estimate the phase composition and its resistivity.

Design/methodology/approach: Anodic polarization of metal surfaces in alkaline solutions used for obtaining oxide nanolayers with certain functional properties. To control the process of obtaining nanofilms apply a variety of physical, physicochemical and electrochemical methods.

Findings: Theoretical analytical expressions describing the kinetics of growth of the oxide layers are supported by experimental studies of anodic polarization of Pb in alkaline solution.

Research limitations/implications: A special place among those methods takes Local Electrochemical Analysis (LEA), allowing localizing electrochemical process at any given point on the surface.

Originality/value: Originality of this work is study of the oxide layers on metals by local electrochemical analysis.

Keywords: Local electrochemical analysis; Oxide layers; Resistivity

Reference to this paper should be given in the following way:

Y. Rublinetskaya, V. Slepushkin, A. Gukin, E. Ilinykh, B. Stifatov, Study of the oxide layers on metals by local electrochemical analysis, Journal of Achievements in Materials and Manufacturing Engineering 64/2 (2014) 90-92.

ANALYSIS AND MODELLING

1. Introduction

An important characteristic of the oxide nanofilms is their resistivity, which determines many of the electrical properties of such coatings [1]. The problem is the control of this parameter in the technological process. The resistivity of nanofilms obtained on the metal surface by electrochemical method, is possible to control by the potentiometric method [2]. In the given work we consider a method CVA that at on one polarization curve allows to trace the process of formation of the oxide film on the metal surface (anodic part of the curve), while the cathodic part of the curve to estimate the phase composition and its resistivity.

2. Experimental

Cyclic voltammetric curves were obtained in the solution of 0.1 M NaOH, in the pressed-on cell of special design [3], on polarographic analyzer RA-2 (Czech Republic). Used potentiodynamic polarization mode ($E = E_{initial} + vt$) at a scan rate of 20 mV/s, starting at $E_{initial}$ = -1.5 V for both the cathodic as well as the anodic sides.

3. Results and discussion

Fig. 1 shows the polarization curve of Pb in 0.1 M NaOH. In the anodic side of the voltage-current curve appear two peak anode current, the first of which corresponds to the formation of oxide PbO on the electrode surface, and the second peak corresponds to the transformation of PbO in PbO_2 [3]. In the cathodic side of the polarization curve marked by a maximum of cathodic current corresponding to the recovery process PbO_2 to metal [3].

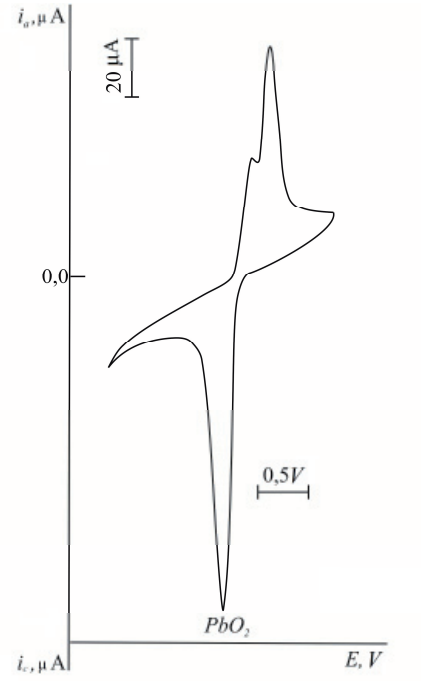

Fig. 1. Electrochemical recovery process parameters PbO_2 in 0.1 M NaOH

Expressions for the cathode current oxide dissolution can be represented by the following equation [4]:

$$i = i_o \, exp\left\{\frac{\alpha nF}{RT}\left(vt - iR_o - iR_{ox}\right)\right\} \quad (1)$$

where α is a transfer coefficient of the cathodic process. The total resistance of the circuit $R_{total} = R_o + R_{ox}$ calculated by the equation (1) varies with the voltage sweep (vt) on the complex dependence which character is defined by dissolution of the oxide from the surface of the anodic side in a cyclic voltage curve. As the cathodic process of the total resistance decreases and approaches R_o the ohmic resistance of the electrolyte solution in the pressed-on cell – Table 1.

According to Faraday's law, the resistance of the oxide film R_{ox} can be calculated by the following equation:

$$R_{ox} = \rho_{ox} \cdot \frac{h}{S} = \rho_{ox} \frac{A \cdot Q_i}{nF\gamma S^2} \quad (2)$$

where :

ρ_{ox} – the resistivity of the oxide layer, Ω · cm;
h – the thickness of the oxide layer in cm;
S – area of the contact hole in the pressed-on cells cm^2;
A – molecular mass of oxide g/mol;
n – the number of electrons transferred in the cathodic process;
F – Faraday constant;
γ – oxide density, g/cm^3;
Q_i – the amount of electricity that went to the dissolution of the oxide layer, C.

Then the reduction of the resistance of the oxide layer during dissolution can be represented by the following expression:

$$R_{ox} = \frac{A \cdot \rho_{ox}}{nF\gamma S^2}\left(Q_m - Q_i\right) \quad (3)$$

where Q_m – the quantity of charge, gone for dissolving all the oxide layer formed on the surface of the anode electrode portion of the cyclic voltammograms (corresponds to a maximum at the cathode voltage curve portion – Table 1).

Table 1.
Electrochemical recovery process parameters PbO_2 in 0.1 M NaOH (S = 0.00385 cm^2; n = 4; α = 0.32; i_0 = 2.0 10^{-6} A; R_0 = 600 Ω; γ_{PbO_2} = 9.38 g/cm^3; A = 239.2 g/mol; Q_m = 625 10^{-6} C)

vt, V	0.025	0.050	0.075	0.100	0.125	0.150
$I \cdot 10^6$, A	5.3	12.7	25.0	45.0	70.0	100.0
R_{total}, Ω	1042	1027	980	839	770	718
R_{ox}, Ω	442	427	380	239	170	118
$Q_i \cdot 10^6$, Кл	3.125	18.750	56.250	112.500	203.125	337.500
$\rho_{ox} \cdot 10^{-5}$, Ω · cm	1.61	1.60	1.52	1.06	0.92	0.93

Given by (1) for the cathode current:

$$i = i_o \exp\frac{\alpha n F}{RT}\left[vt - i\left\{R_o + \frac{A \cdot \rho_{ox}}{nF\gamma S^2}\left(Q_m - Q_i\right)\right\}\right] \tag{4}$$

The correctness of the proposed equation is confirmed by calculation of the resistivity of the oxide PbO_2 layer on the converted relatively ρ_{ox} equation (5) – Table 1.

$$\rho_{ox} = \frac{vt - iR_o - \dfrac{RT}{\alpha n F}\ln\dfrac{i}{i_o}}{\dfrac{i \cdot A}{nF\gamma S^2}\left(Q_m - Q_i\right)} \tag{5}$$

4. Conclusions

1) A new method of calculating the resistivity of the oxide film on the metal, by appropriate processing of the cathode metal recovery curve in a local electrochemical analysis is offered.
2) The method was tested on the example of lead oxide films (PbO_2), obtained on the metal surface during its anodic polarization in 0.1 M NaOH.

Acknowledgements

This work was financially supported by the state task in the field of scientific activity in terms of scientific research (basic research, applied research and experimental development) for the project "Investigation of physical and chemical properties of a surface of nano-and supramolecular systems."

Work carried out on the equipment CKP "Research of physico-chemical properties of substances and materials" Samara State Technical University with the financial support of the Ministry of education and science of Russia.

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