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ELECTROPHORETIC DEPOSITION OF Na$_2$O-TiO$_2$-SiO$_2$ COLLOIDAL SYSTEM

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Abstract. The possibility of electrophoretic deposition of colloid solution based on liquid glass have been studied. Parameters of Na$_2$O-TiO$_2$-SiO$_2$ coating applied over nickel surface have been established.

Keywords: electrophoresis, colloid solution, liquid glass, potential, deposition.

1. Introduction

Glass-ceramic and ceramic coatings for anticorrosive protection are of great interest last decade [1, 2]. Sol-gel deposition *via* dipping with following low-temperature formation of homogeneous transparent films is one of the effective methods of coatings applying over metal surface [3-5]. However the thickness of obtained coatings from colloid solutions does not exceed 2 mcm [6]. The application of electrophoretic deposition (EPD) from colloid solutions with similar composition gives the possibility to increase the coatings thickness and regulate their compositions [5]. EPD also gives the possibility to apply coatings over undercoats with complicated form of the surface [4]. Special attention is paid to EPD from the solutions based on colloid SiO$_2$ [6, 7] and SiO$_2$-ZrO$_2$ [4, 5]. The aim of this work is to examine EPD of Na$_2$O-TiO$_2$-SiO$_2$ colloid solution. The mentioned system has been studied with the aim of obtaining glass-ceramic coatings from colloid solutions [8].

2. Experimental

The colloid solution of Na$_2$O-TiO$_2$-SiO$_2$ system was used for EPD. The system was selected using method [8], based on eutectic compositions of Na$_2$O-SiO$_2$ and SiO$_2$-TiO$_2$ systems with minimum melting temperatures. Such composition corresponds to the following composition of dry deposit (mas %): SiO$_2$ – 71.4; Na$_2$O – 24.6 and TiO$_2$ – 4.0. The colloid solution was prepared using previously developed two-staged technology [9]. At the first stage water was added to the tetrabutoxytitanium butanol solution (TBT) under intensive stirring till full TBT hydrolysis. At the second stage the obtained suspension was mixed with liquid glass by Na$_2$O·3SiO$_2$ composition till the homogeneous colloid system was formed. Electrolysis was carried out in three-electrode thermostated glass electrolyzer by volume of 50 cm^3. Films from colloid solution were deposited at anode made of nickel foil which was placed in dielectric film-holder (Fig. 1) with the diameter of working surface of 14 mm. The main and graphite electrodes were vertically installed in electrolyzer at the distance of 10 mm between each other.

IPC-Pro potentiostate was used for characterization of polarization curves and electrolysis. Chloride-silver
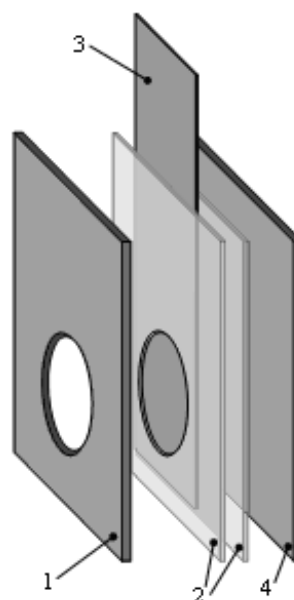

Fig. 1. Scheme of dielectric (ceramic) film-holder: front wall with a hole (1); silicone seal (2); main electrode (3) and backwall (4)

electrode was used as a reference electrode. It was placed into glass vessel with KCl saturated aqueous solution and joined with electrolyzer by means of Luggin-Haber capillary. The characteristics of polarization curves were obtained with scanning speed of 5 mV·s⁻¹. Electrolysis was carried out at 293 K within anode potentials range of 1.0–2.5 V (potentials were adduced relative to standard hydrogen electrode). After EPD samples were removed from the holder and dried at 373 K on the air. Then topography of coating surface was examined using ZEISS EVO 40XVP scanning electron microscope. Chemical composition of the surface was controlled by the analysis of characteristic X-ray spectrum which was recorded using INCA Energy 350 energy-dispersive spectrometer. X-ray radiation excitation was carried out by samples radiation using electron bunch with energy of 15 keV.

3. Results and Discussion

Fig. 2 represents anode polarization curves in colloid solutions of Na_2O-SiO_2 and Na_2O-SiO_2-TiO_2 systems (curves 4 and 5 correspondingly). Three areas of EPD may be noted: I (E_p–1.2 V) and III (>1.4 V) correspond to the increase of anode current with the potential increase, and II (1.2–1.4 V) corresponds to the practical absence of anode current increase (plateau). Such character of the curves may be explained by the following. At EPD process the increase of anode potentials to the values of oxygen active electrowinning (area I) leads to the compacting of film accompanied with the increase of its Ohmic resistance. The absence of anode current growth (area II) together with film growth rate is the consequences of the mentioned fact. At $E > 1.4$ V (area III) the anode current growth is determined by the increase of a part of conjugated anode reaction of oxygen electrowinning as well as of EPD process. Curves of base electrolyte solutions (curves 1-3) when oxygen electrowinning is the main anode process indirectly confirm the stated facts.

The increase of anode potential value increases film deposition rate. The growth of EPD products mass on the main electrodes indicates this fact (Fig. 3). It should be noted that at $E > 2$ V the film growth rate practically achieves its maximum.

The mass of silicate film for every value of potential achieves maximum in time (Fig. 4). It should be noted
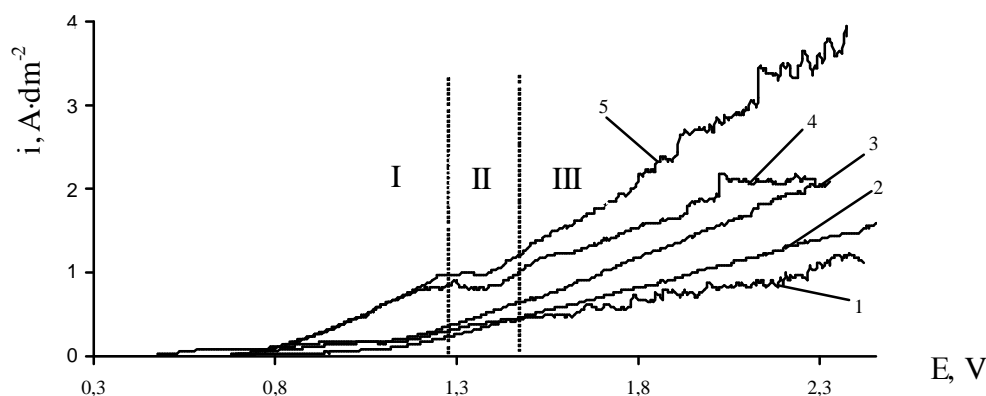

Fig. 2. Voltammetric curves of solutions on nickel electrode: 0.023 M butanol in 0.05 M Na_2CO_3 (1); 0.11 M TBT in 0.05 M Na_2CO_3 (2); 0.05 M–Na_2CO_3 (3); 0.3 M–working solution (4) and 0.3 M–$Na_2O·3SiO_2$ (5)
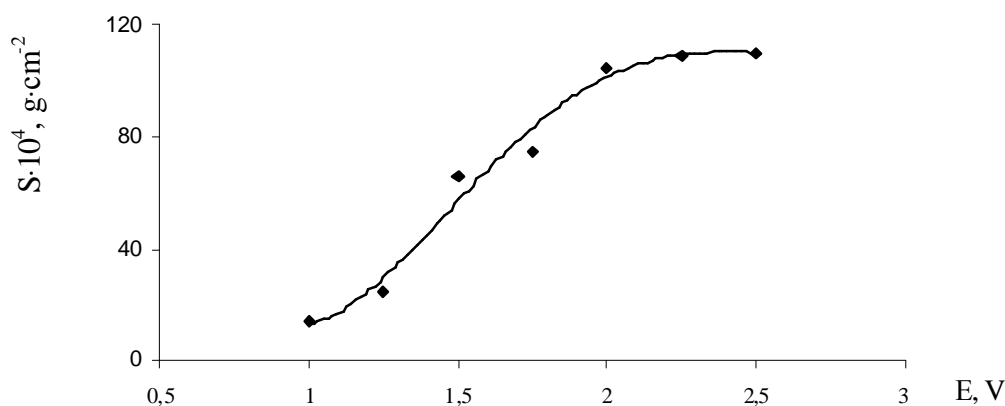

Fig. 3. Dependence of deposited products mass at EPD upon anode potential during 15 minutes of electrolysis
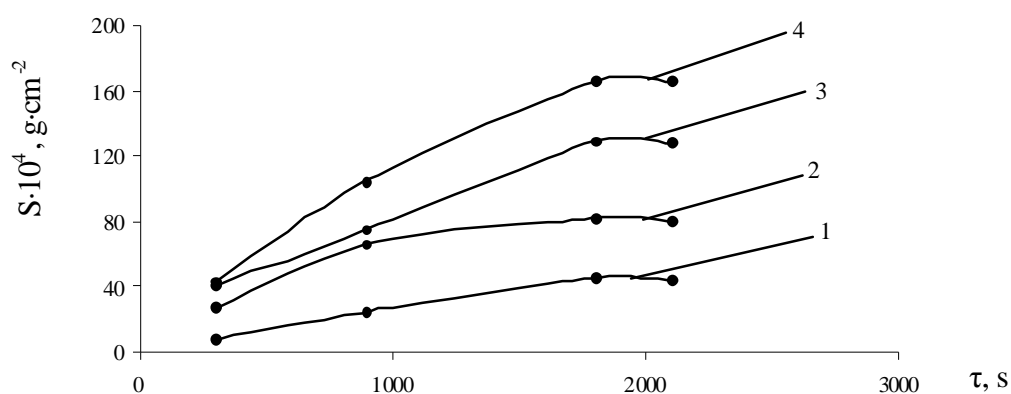
Fig. 4. Dependence of deposited products mass upon time at potentials (V): 1.25 (1); 1.5 (2); 1.75 (3) and 2.00 (4)

Table 1

Results of matrix and EPD dried products chemical analysis

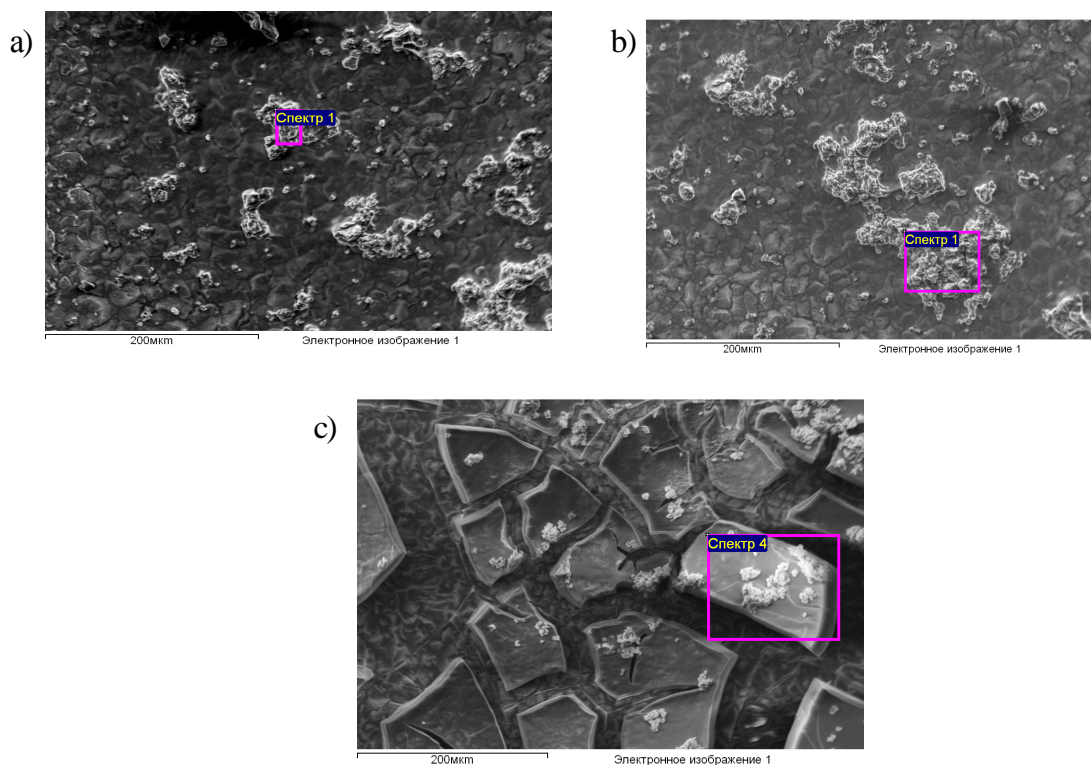| Element	Matrix	mas %			Matrix	atom %		
		Dipping	EPD products			Dipping	EPD products	
			1.25 V	1.50 V			1.25 V	1.50 V
O	55.17	59.15	57.26	59.27	67.57	71.69	70.26	71.61
Na	17.39	11.09	8.18	6.09	14.82	9.35	6.99	5.12
Si	22.12	24.19	29.73	32.66	15.43	16.70	20.78	22.47
Ti	5.32	5.57	4.83	1.98	2.18	2.25	1.98	0.80

Fig. 5. Deposited products obtained as a result of: dipping (a); EPD at E = 1.25 V (b) and EPD at E = 1.50 V (c)

that within a wide range of anode potentials maximum width of the film is observed at deposition for 30 min.

The composition of deposited products also depends upon anode potential. The following regularities are observed: (i) silicium content in EPD films is higher than that in the matrix; (ii) the increase of E value increases silicium content, whereas titanium and sodium content decreases it (see Table 1). This circumstance indicates that in anode layer and on anode surface particles agglomeration is accompanied with polymerization of silicate ions and intensity of this process depends upon anode potential value.

In accordance with the experimental results sodium and silicium are uniformly distributed in dried sample after EPD, whereas titanium is impregnated on the surface in a random way (Fig. 5). Obviously it is determined by the fact that titanium colloid particles insufficiently coagulate during EPD. Mainly they are engaged into deposit as a result of adsorption on the surface of electrodeposited colloid particles of Na_2O-SiO_2 system.

4. Conclusions

1. The possibility of glass-ceramic coatings on nickel anode as a result of electrophoretic deposition has been established. It has been shown that potential growth till E = 2 V increases EPD products mass. The dependence of deposited products mass upon time has an extreme character.

2. Silicium content in EPD films is higher than that in the matrix and increases with the growth of E value.

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ЕЛЕКТРОФОРЕТИЧНЕ ОСАДЖЕННЯ КОЛОЇДНОГО РОЗЧИНУ СИСТЕМИ Na₂O-TiO₂-SiO₂

Анотація. *Вивчено можливість електрофоретичного осадження колоїдного розчину на основі рідкого скла та встановлені параметри нанесення покриття Na₂O-TiO₂-SiO₂ на нікелеву поверхню.*

Ключові слова: *електрофорез, колоїдний розчин, рідке скло, потенціал, осадження.*