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Structure, Properties and Element Composition of Alumina Coatings, Obtained by Micro-Arc Oxidation Method

A.D. Pogrebnjak[1,*], O.V. Sobol[2], F.F. Komarov[3], A.Sh. Kaverina[1,†], Yu.N. Tyurin[4], I.V. Yakuschenko[1], A.A. Drozdenko[1], J. Partyka[5]

[1] *Sumy State University, 2, Rymsky Korsakov Str., 40007 Sumy, Ukraine*
[2] *Kharkov Technical University, 21, Frunze Str., 61002 Kharkiv, Ukraine*
[3] *Belarusian State University, 4, Nezavisimosti Ave., 220030 Minsk, Republic of Belarus*
[4] *The E.O. Paton electric welding institute of the NAS of Ukraine, 11, Bozhenko Str., 03680 Kyiv-150, Ukraine*
[5] *Lublin University of Technology, 38A, Nadbystrzyska Str., 20-618 Lublin, Poland*

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Coatings of aluminium oxide Al_2O_3 were obtained by micro-arc oxidation under different conditions of deposition. They were analysed by such methods as: positron annihilation spectroscopy (PAS), Rutherford backscattering (RBS), X-ray diffraction (XRD) and scanning electron microscopy with microanalysis (SEM with EDS). Investigated samples showed good adhesion to the substrate, low concentration of nanopores in the bulk. Content of amorphous phase in the coating was about 20 vol.%, and metastable θ-Al_2O_3 η- Al_2O_3 phases about less than 10 vol.%. It was demonstrated that by varying of parameters of deposition, it is possible to control the physical – mechanical properties of obtained coatings as well as their element composition and surface morphology.

Keywords: micro-arc oxidation, Al_2O_3, crystalline and amorphous phase, the annihilation of positrons

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1. DESCRIPTION OF METHOD OF PREPARING OF COATINGS

Micro-arc oxidation method of depositing coatings features high productivity and cost-effectiveness. Obtained coatings have good physical-mechanical properties, but often contain pores (from 0.5 to 2 vol.%) and uncontrolled impurities from the solution in which the oxidation is carried out. The thickness of obtained oxide coatings depends on the electric field and can be 5 – 1000 μm [1, 2]. The physical basis of the method is described in works [3-6].

Technological parameters of coatings deposition are shown in table 1 below.

Table 1 – Parameters of the aluminium samples exposed to oxidation

Number of samples	**Modes of samples' oxidation with voltage source**							
	300 V		400 V		500 V		400 V	
	el. current, A	time of oxidation, min.	el. current, A	time of oxidation, min.	el. current, A	time of oxidation, min.	el. current, A	time of oxidation, min.
1	2→0	1	1.5→0	30	3→0	1	0.2→0	5
2	2→0	2	2→0	25	1.5→0	1	0	5
3	2→0	5	1.5→0	30	3→1	10	0	3
Number of samples	**The square of the sample in the electrolyte, in mm**		**Thickness of the plate before the oxidation, in mm**		**Thickness of the sample after the oxidation, in mm**			
1	13×15		2.82		2.865			
2	8×15		1.45		1.51			
3	10×15		1.45		1.5			

2. RESULTS AND DISCUSSION

Fig. 1 shows images of surface of obtained coatings (fig. 1, a, c, e) and its cross sections (fig. 1, b, d, f). Images were made using scanning electron microscope, at magnification of 1000 and 500 times. Fig. 2 shows fragments of diffraction patterns obtained from samples with coatings, obtained under different technological parameters of deposition. Curve 1 indicates, that content of Al_2O_3 of crystalline phase with hexagonal lattice (γ-Al_2O_3) nearly 60 vol.%, with rhombohedral lattice (α-Al_2O_3) about 35 vol.%, and with cubic lattice (η-Al_2O_3) less than 3 vol.%. For curve 2 formation of amorphous phase (halo in the range of angles of 20-40 deg.), about 10 vol.% was discovered. Content of Al_2O_3 crystalline phase with hexagonal lattice is about 10 vol.%, with rhombohedral lattice about 60 vol.%, and with cubic lattice – nearly 10 vol.%.

Judging by the curve 3 (halo is at angels of 20-40 deg.), the coating has great concentration (about 20

* alexp@i.ua
† mixifox@mail.ru

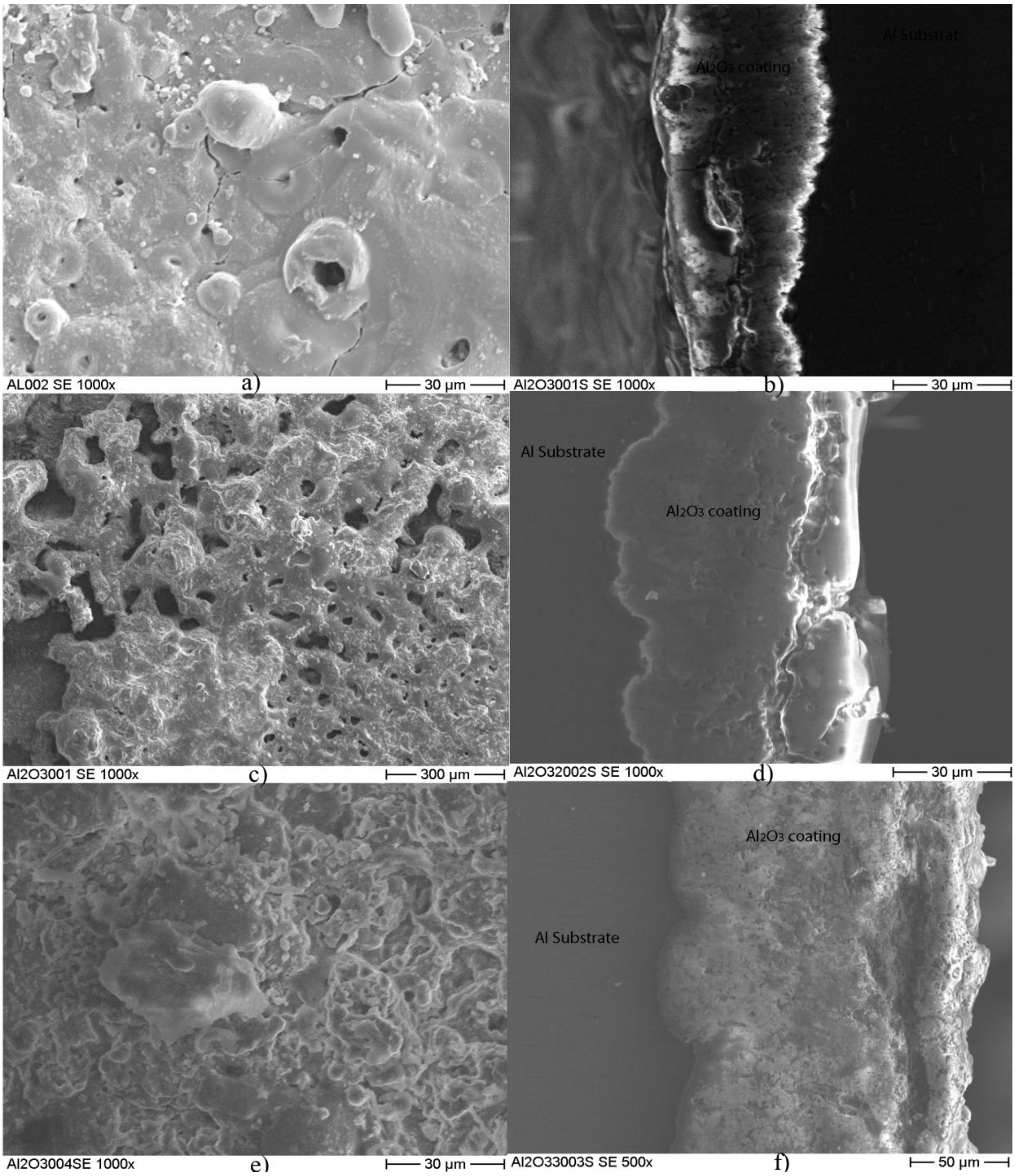

Fig. 1 – SEM images of the surface (a), (c), (e) and cross section (b), (d), (f)

vol.%) of amorphous phase, content of Al_2O_3 crystalline phase with hexagonal lattice is nearly 24 vol.%, and with rhombohedral lattice about 70 vol.%, and with cubic lattice – almost 6 vol.%. All results are shown in table 2, from which follows, than oxygen concentration is about 60 at.%, but concentration of Al, depending of deposition mode is significantly different – for the third mode it is nearly 20.5 at.%, for the first and the second mode these values are close to 25.5 at.% and 26 at.%. at.%.

In addition, Mg is present in the coating (about 11%), Ca (2÷3)%, P (0.5÷3) at.%, and the rest is related elements: Cu from 0.15 to 0.3 % and W 0.01 at.%. If we go back to results for phase content (fig. 2), it is possible to conclude, that such elements as P and Ca in coating are being part of amorphous phase, from which it is difficult to distinguish the contribution of the elements in oxide form. At the same time, the concentration of Mg is similar for all three modes of deposition.

Table 2 – Appointment of special paragraph styles

Sample N°/ Element	O	Mg	Al	S(P)	Ca	Cu	W
3	62	11	20,5	3	3	0.3	0.01
2	60	11	25,5	0.5	3	0.15	0.01
1	60	11	26	0.5	2	0.25	0.01

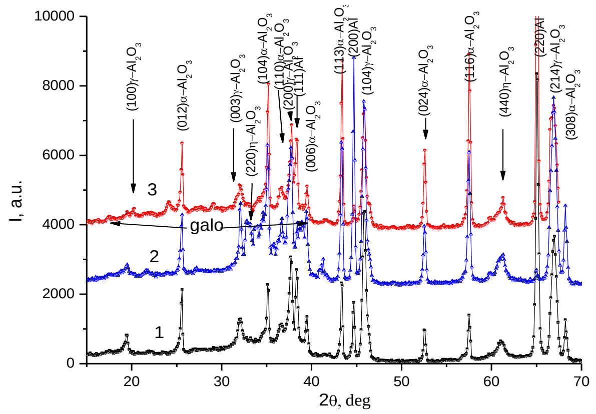

Fig. 2 – Fragments of diffraction patterns of samples

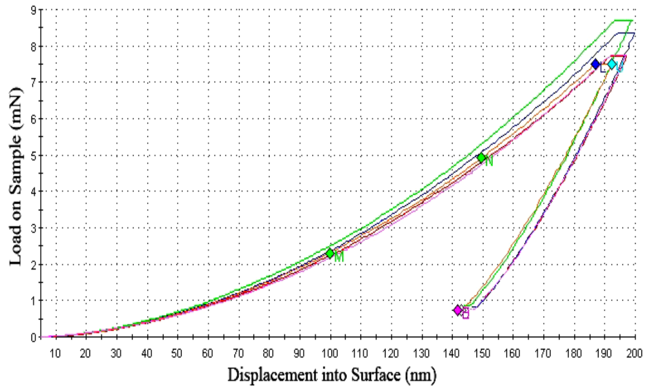

Fig. 3 – The dependence curves indentation depth vs. load on sample

Results of research of mechanical properties of obtained coatings showed the increase of hardness and elastic modulus. Fig. 3 shows the dependence curve of indentation depth on the load for different regimes of deposition. Letters M, N, L, U, E indicate the points, where the load was applied.

It was decided to use method of positrons' annihilation to determine the size of nanopores. It is known, that in ceramic coatings Al_2O_3, which have ion bonds, formation of Ps (atom of positronium) is possible [5]. This atom can be localized in nanovoids. Moreover, using the data obtained by this method, we can estimate the size of pores. For this purpose we used the set up for measuring lifetime of positrons (Na^{22} (β, γ)) at University of Halle, with a time resolution of 180 – 280 ps. Measurements were carried out under room temperature in air.

We investigated three series of samples. By calculating obtained positron lifetime spectras we got the bulk positron lifetimes less then 200 ps. According to experimental works [6-8] it means that there is no formation of Ps atom (which lifetime is much longer, about 400 ps and more). Results of these studies showed, that our coatings have small amount of nanopores and the size of nanopores varies in range from 100 nm to 10μm.

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