REPORT DOCUMENTATION PAGE	Form Approved OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)* 06-01-2006	**2. REPORT TYPE** Final Report	**3. DATES COVERED** *(From – To)* 1 January 2005 - 19-Jun-06

4. TITLE AND SUBTITLE Micro-Plasma Protective Coatings for 2024 and 7085 Aluminium Alloys	**5a. CONTRACT NUMBER** FA8655-03-D-0001, Delivery Order 0019
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S) Professor Vladimir A Nadolinny	**5d. PROJECT NUMBER**
	5d. TASK NUMBER
	5e. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Nikolaev's Institute of Inorganic Chemistry Lavrent'ev Av. Novosibirsk 630090 Russia	**8. PERFORMING ORGANIZATION REPORT NUMBER** N/A
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) EOARD PSC 802 BOX 14 FPO 09499-0014	**10. SPONSOR/MONITOR'S ACRONYM(S)**
	11. SPONSOR/MONITOR'S REPORT NUMBER(S) EOARD Task 04-9008

12. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

This report results from a contract tasking Nikolaev's Institute of Inorganic Chemistry as follows: Two strategies have historically been used to reduce corrosion in AA's: (1) barrier coatings and (2) electrochemically-active corrosion-inhibitors. Barriers are formed from materials impervious to the penetrations or migrations of such corrosion-inducing species as chloride ions, oxygen, water, and/or free electrons. Plasma oxidation would provide an impervious coating on the surface of specific aircraft parts thus enhancing their ability to prevent corrosion from beginning.

15. SUBJECT TERMS

EOARD, Materials, Corrosion

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18, NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON** MATTHEW MORGAN, Lt Col, USAF
a. REPORT UNCLAS	**b. ABSTRACT** UNCLAS	**c. THIS PAGE** UNCLAS	UL	33	**19b. TELEPHONE NUMBER** *(Include area code)* +44 (0)20 7514 4505

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39-18

TECHNICAL REPORT

Title of project: **Micro-Plasma Protective Coatings for 2024 and 7085 Aluminum Alloys**

Project director: Prof. V.A. Nadolinny

CRDF project number: RUE2-1502-NO-04

Reporting period: January – March 2005

Nomeclature page:

MPO process – micro plasma oxidation process.
A – Ampere (current).
AA – aluminum alloy.
MPa – mega Pascale.

Summary:

According plane for first quarter we have developed conditions of MPO process for preparing corrosion protective coatings on the surface of aluminum alloy 2024 –T3.

Introduction:

Military aircraft are largely constructed of special aluminum alloys (AA's) such as AA 2024-T3 and AA 7075-T6. These alloys are composed of aluminum (>90%) with the addition of comparatively insoluble metal components that form secondary precipitate phases (under appropriate heat treatments), with a substantial gain in mechanical strength. The presence of the secondary-phase regions, typically rich in a transition-metal species (*e.g.*, copper in AA 2024-T3), provides an area where corrosion to occur. Exposure to such common environmental conditions as acid rain, saltwater, and thermal cycling dramatically increases the rate of corrosion in these alloy systems. It has been estimated that the U.S. Air Force expends approximately $1 billion per year, or approximately 1% of its budget, on corrosion-related maintenance issues for its fleets of aluminum-skinned aircraft. This problem has become more severe as the fleet ages. Between 1990 and 1997, corrosion costs increased by more than 30% per aircraft per year across the USAF fleets.

In this proposal the method of formation of a protective coating is micro-plasma oxidization. This method allows the formation of a ceramic-like oxide coating using a micro-plasma discharge. Technologically this method is arranged similarly to anodizing in electrolytes solutions, but oxides are formed under the conditions of high velocities of coating material via heating by electric discharges and high cooling velocities (10^6-10^7 degrees/sec), that promote the formation of high temperature oxide. The coating formation in the MPO mode depends on the composition, concentrations and temperature of electrolyte and the current modes of process.

The MPO process is based on electrochemical oxidation of a metal surface in an electrolyte when microplasmic discharges occur. Local temperature in the zone of the plasma channel reaches several thousands of degrees, pressure – tens of MPa. Growth of the oxide coating and formation of its structure occur as a direct result of microplasma discharge. We supposed that MPO coatings produced in such aggressive conditions would begin to take the corrosion protective properties.

The major problem during a first quarter was development of MPO process for preparing coatings of high density, low open porosity and corrosion protective properties on the surface of aluminum alloy 2024 – T3.

Technical description:

To solve this problem we used Russian aluminum alloy D-16 similar in composition to aluminum alloy 2024 – T3 according to international ISO standards. For developing corrosion protective MPO coatings, we have made a series of the cylindrical samples of sizes in diameter 23 mm, in height 6 mm (see Fig.1).

Fig. 1. Samples of aluminum alloy 2024 – T3 prepared for the MPO process.

We have made a hole with a thread in the cylindrical part of each sample to ensure electrical contact with a power supply. The sample fixed to a sample holder was submerged in electrolytic tank. And after turning on power supply MPO process occurs. Technological scheme of MPO process is shown in Fig.2.

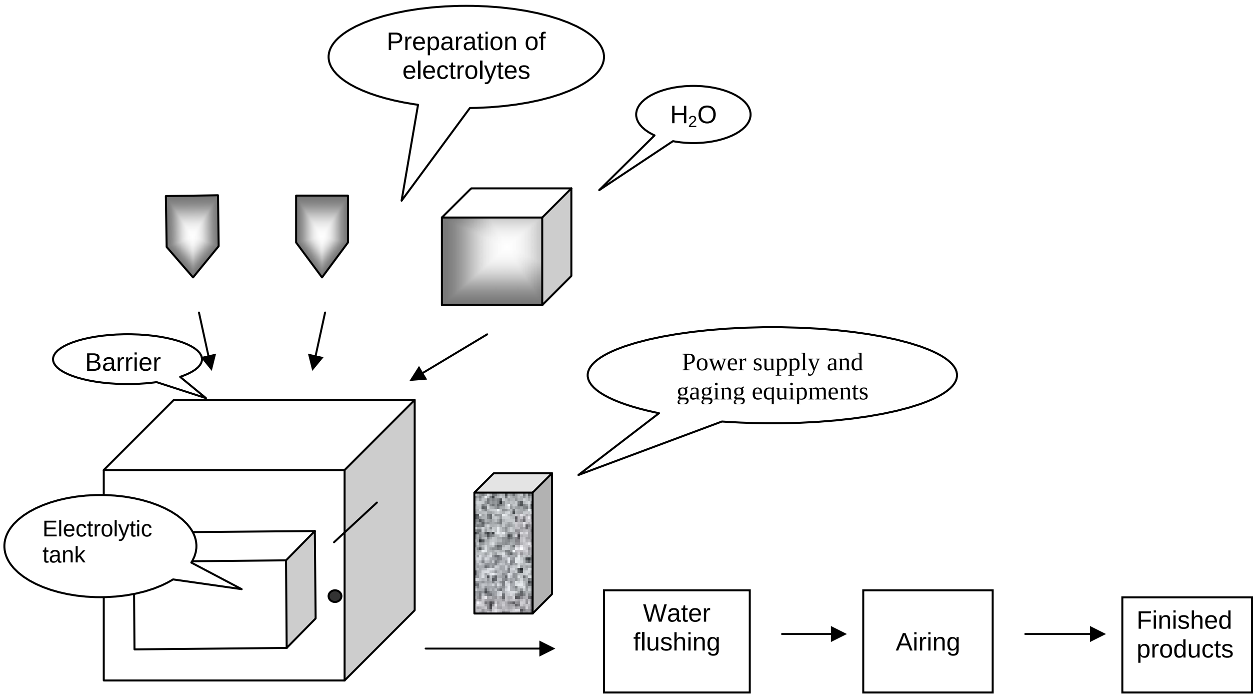


Fig. 2.Technologocal scheme of MPO process.

Needs to remark, that one of many advantages of MPO method lies in the freedom from preliminary treatment of sample surface before MPO procedure.

To form corrosion protective coatings we used electrolytes containing such components: Na_2CO_3, KOH, lemon acid. Concentration of these components was varied from 0.2 to 10 g/liter.

We inspected all regimes of MPO equipment: anodic, anodic-cathodic and anodic-cathodic with cathoding in mode of variable and direct currents. Temperature of electrolyte was varied from 18 to 35 ^oC. We studied influence of current parameters on the properties of MPO coating in the range of 0.01 – 0.1 A/ cm^2. Under these conditions a growth rate of MPO coating was 0.035 – 0.1 micron/min. The optimal current in MPO process was between 0.02 – 0.03 A/cm^2.

A special method was developed to study corrosion protective properties of coatings by estimating gas formation rate when the sample was inserted into aqua solution of HCl acid (12-19%). Views of samples after MPO treatment are shown in Fig. 3.

Fig.3. Views of samples of aluminum alloy 2024 – T3 after MPO processing. Black – in KOH electrolyte, white – in Na_2CO_3 electrolyte.

Results:
The corrosion tests showed the best results with MPO coatings prepared in KOH electrolytes under anodic- cathodic regime with current density of 0.02- 0.03 A/cm^2 and growth rate of 0.07 micron/min.

Future work planned:

Task 2: **Production of corrosion protective coatings of 10, 25, 50, 75 and 150 microns thickness for 2024-T3 aluminum alloys.**

To have an optimum economics and for studying coatings properties the coatings of different thickness (gradation – 10, 25, 50, 75 and 150 microns) will be prepared. 5 samples will be used in each step of this gradation. Total number of T3 samples with coatings will be 25.

Task 3: **The study of coating characteristics for T3 aluminum alloy.**

The coatings prepared will be studied in Novosibirsk. Thickness, microhardness, electro resistance (in air) and RFA are planned to be measured. All these data will be collected in a final report.

Project director, prof.	V.A. Nadolinny
Technologist	I.B. Kireenko

TECHNICAL REPORT №2

Title of project: **Micro-Plasma Protective Coatings for 2024 and 7085 Aluminum Alloys**

Project director: Prof. V.A. Nadolinny

CRDF project number: RUE2-1502-NO-04

Reporting period: April – June 2005

Nomeclature page:

MPO process – micro plasma oxidation process.
AA – aluminum alloy.
ST SEW 1195-78 – Russian standard of Wiccers method.
EPR- electron paramagnetic resonance.
HFS- hyper fine structure.

Summary:

According plane for second quarter of project we have prepared 30 samples of 2024 aluminum alloy, grown on the surface MPO coatings with thickness 10, 25, 50, 75, and 150 μ and have tested mixture, structure and such properties of MPO coatings as: microhardness and voltage of discharge.

Microhardness of micro-plasma coatings on the 2024 aluminum alloy

Measurements microhardness carried out by diamond instruments indentation (Wiccers measurement) ST SEW 1195-78. Before experiment we remove technological layer of MPO coating by corundum up to mirror surface.

Microhardness testing by restored imprint of indentation consists from preparing of imprint on the surface of the coating by diamond tip at 200 gram of weight during 15 seconds. After raising of weight and measuring of imprint a microhardness is calculated by expression:

$$H_V = 0{,}189\ F/d^2$$

where F is weight and d^2 – area of imprint .
Results of these measurements are shown in Table 1 and Fig. 1.

Table 1.

Dependence of microhardness on the thickness of coatings

Thickness of coating, μm	$H_{V\ ev.}$, GPa	Отношение $H_{coat.}/H_{metal}$
0	2,0	1
10	6,2	3,1
25	11,0	5,5
50	17,8	8,9
75	20,6	10,3
150	26,88	13,44

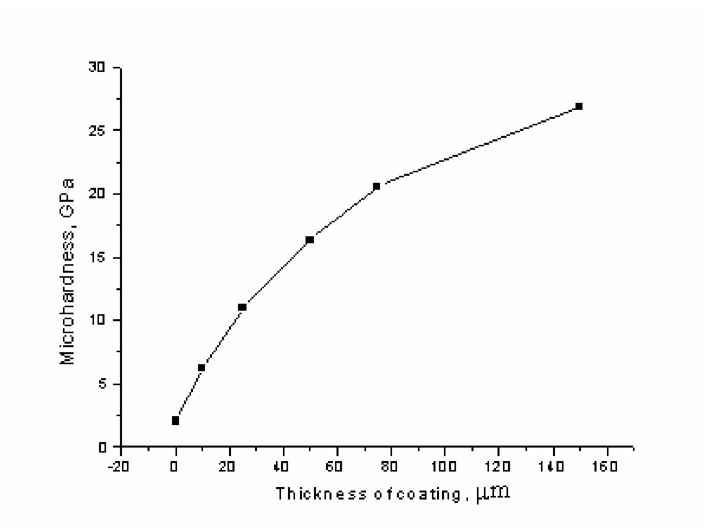


Fig. 1. Dependence of microhardness on the thickness of coatings.

Beginning from 25 microns thickness in the MPO coatings there is appeared hard layer. Later at the increasing of thickness there are increased content of δ and α phases of Al_2O_3. It is the reason of hardness increasing. The coating with thickness 150 microns has microhardness 24.5 – 26.8 GPa. And towards metal microhardness is increased up to 44 GPa.

Tests on the discharge voltage

Discharge voltage on the MPO coating was tested by direct current. Positive contact was connected to surface of coating and negative – to metal of substrate. Each value of discharge voltage in the Fig.2 is average value of ten measurements for the each sample. As it follows from Fig.2 there is linear dependence of discharge voltage on the thickness.

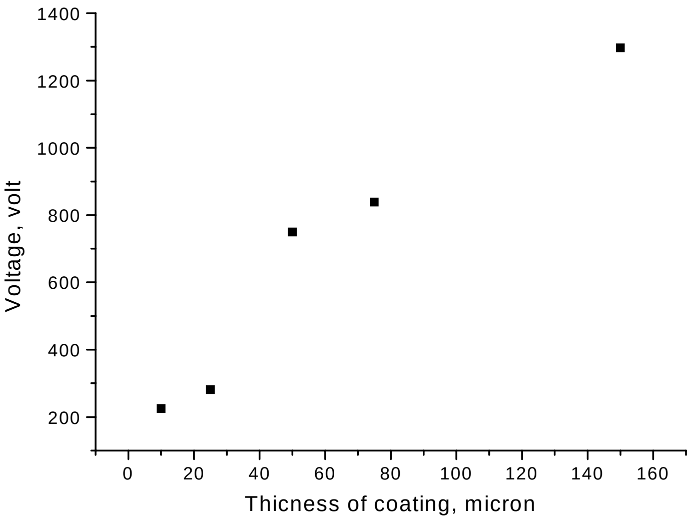


Fig. 2. Dependence of discharge voltage on the thickness of coating.

Influence of microplasma oxidation processes on the oxidation state of transition metals presented in 2024 aluminum alloy.

Microplasma processes, underlying technology of polyfunctional coatings formation, are electrochemical processes and produce an oxidation metal surface in canal of microdischarge.

Coatings containing high temperature phase of aluminum oxide have many interesting applications. Such coatings are grown as from material of detail, so as from aluminum compounds of electrolytes - aluminates. The properties of created coatings depend on variations of anode and cathode components of voltage, value of current, temperature of electrolyte and its content. Created coatings contain two layers – inner layer located close to metal contains high temperature phase of aluminum oxides (α- Al_2O_3), outer layer consists from low temperature phase of aluminum oxides. Namely due to hardness of α- Al_2O_3 crystallites these coatings have high microhardness, high wear resistance, low friction coefficient and so. In this part of report we discuss results obtained by EPR spectroscopy at the study of microplasma coatings grown on aluminum alloy AA 2024 at different regimes and electrolytes. Because aluminum alloy AA-2024 contains cupper (3,8 – 4,9%) and manganese (0,3-0,9%), we hoped to determine peculiarities of these metals incorporation into the structure of different phase of Al_2O_3 at the different stages of their growth.

We have studied microplasma oxidation coatings grown:

1) in electrolyte containing Na_2CO_3 at the anodic process;
2) in electrolyte containing KOH + Na_2SiO_3 at the anodic process;
3) in electrolyte containing KOH + Na_2SiO_3 at the anodic – cathodic process.

In all three groups of samples we studied EPR spectra at the increasing of coating thickness. Usually at the increasing of coating thickness the discharge voltage is increased. Samples for this investigation were plates of aluminum alloys AA-2024 with the size 10 x 5 x 0,5 mm cut from one sample. We studied these samples by Varian EPR spectrometer E-109 in X- band at room temperature. For the calculation of g-values we used etalon of diphenyl – picryl –hydrazyl (DPPH) with g = 2.0036. The thickness of coatings was measured by thickness meter Quanix –1500.

Anodic regime of micro plasma oxidation in electrolyte of aqua solution of Na_2CO_3

On the Figure 3 there are shown EPR spectra of samples with MPO anodic coating in the order of increasing of coating thickness. As it is possible to see from this figure, the content of paramagnetic centers is increased at the increasing of coating thickness. EPR spectrum presents single line with the linewidth 160 Gauss and g-value 2,07. The same spectrum was observed early in bulk sample of γ- Al_2O_3 and was due to cupper ions Cu^{2+} [1]. Existence of this spectrum in these samples is evidence of low temperature phase of aluminum oxide in coatings prepared by this regime. The content of cupper ions is increased droningly to coating thickness. This dependence is shown on the Fig. 4.

The absence of hyperfine structure (HFS) from cupper ions is due to exchange interaction at high concentration of Cu^{2+}.

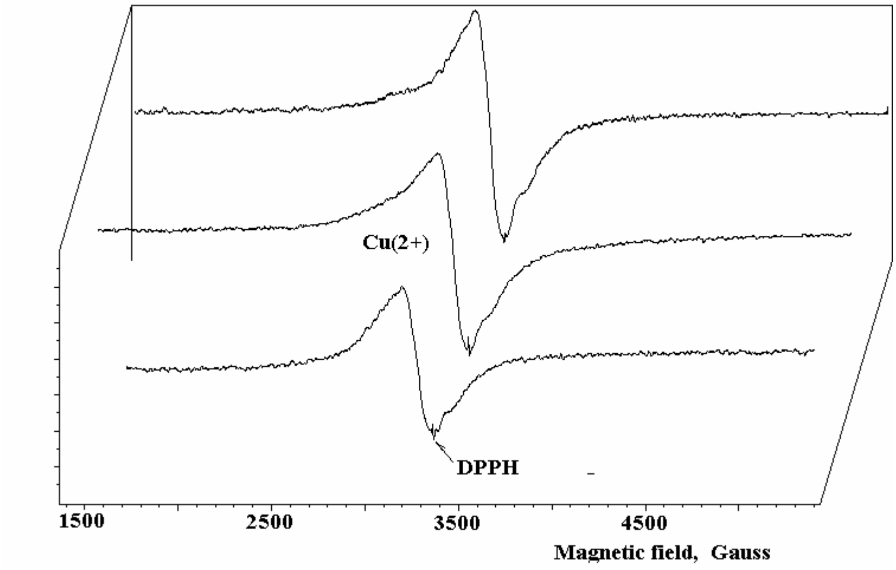


Fig. 3. EPR spectrum of Cu^{2+} and dynamic of its changing on the increasing of MPO coating thickness on the aluminum alloy D-16 prepared in aqua solution of Na_2CO_3.

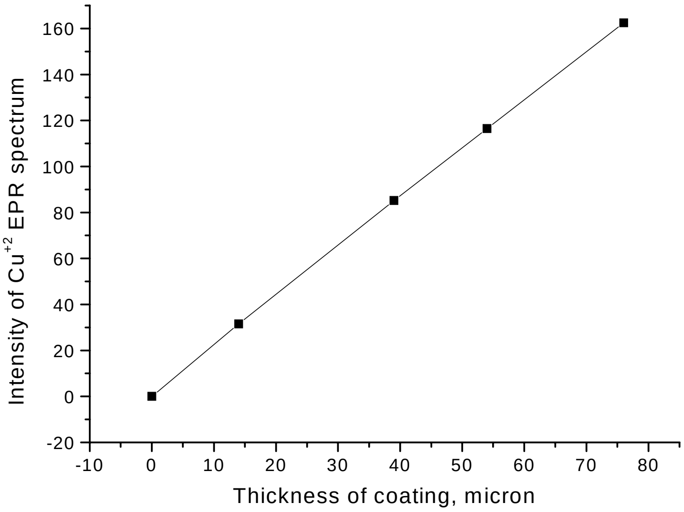


Fig. 4. Dependence of Cu^{2+} content on the increasing of MPO coating thickness prepared by MPO anodic regime in aqua solution of Na_2CO_3.

MPO anodic regime in electrolyte of aqua solution of KOH + Na_2SiO_3.

EPR spectrum of coating prepared by MPO anodic regime in electrolyte of aqua solution of KOH + Na_2SiO_3 is the same as in electrolyte of aqua solution of Na_2CO_3 (Fig.5). The line width of this spectrum is wider, but g-value was the same than for aqua solution of Na_2CO_3. This fact is evidence that in this case we have low temperature phase of aluminum oxide. As in previous case content of cupper ions is increased droningly to thickness of coating (see Fig.6).

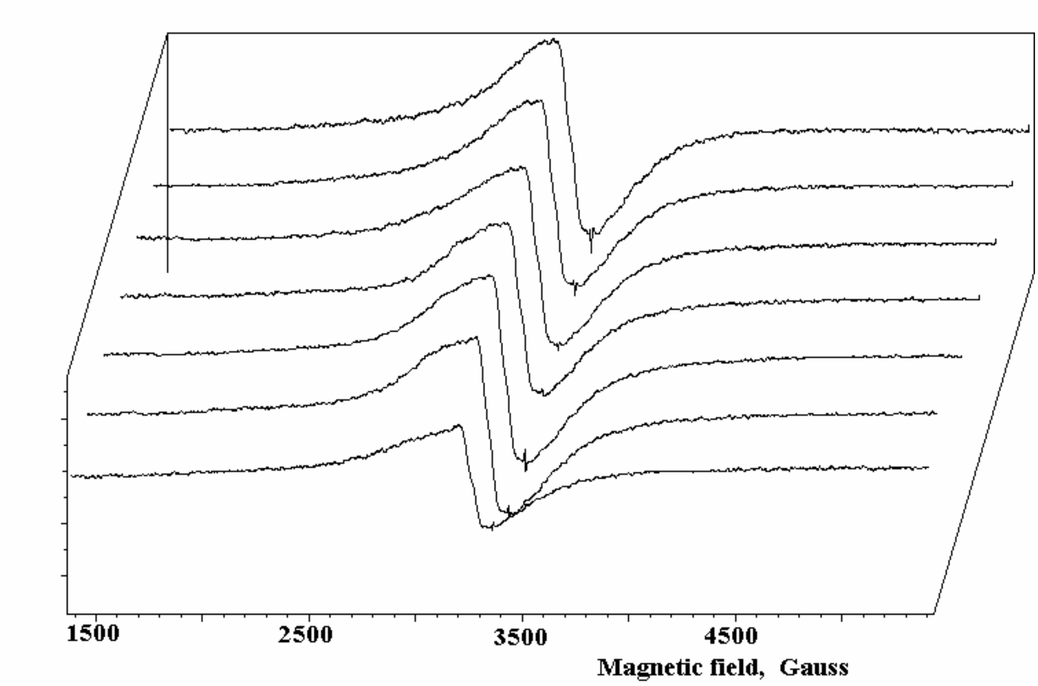


Fig. 5. EPR spectrum of Cu^{2+} and dynamic of its changing on the increasing of MPO coating thickness on the aluminum alloy D-16 prepared by anodic process in aqua solution of KOH + Na_2SiO_3.

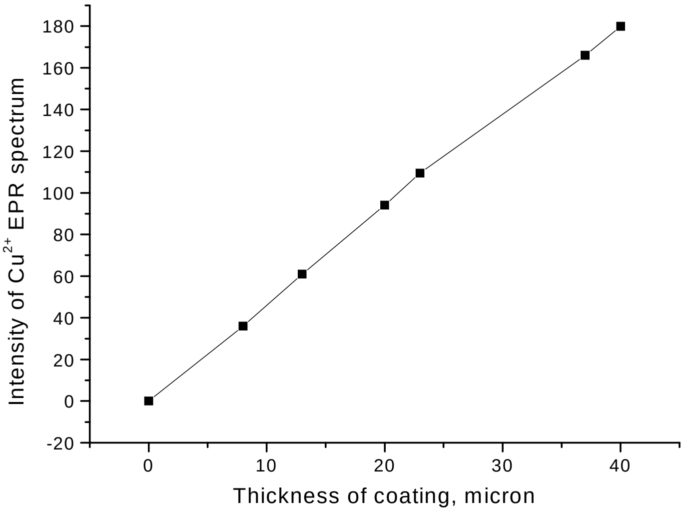


Fig. 6. Dependence of Cu^{2+} content on the increasing of MPO coating thickness prepared by MPO anodic regime in aqua solution of KOH + Na_2SiO_3.

MPO anodic – cathodic regime in aqua solution of KOH + Na_2SiO_3 electrolyte

EPR spectra of MPO coatings obtained by anodic – cathodic regime differ from spectra of MPO coatings prepared by MPO anodic regime. Dynamic of EPR spectra changes depending on thickness of coating is shown on the Fig.7. Line in the low magnetic field with g-value g=4,3 is due to incorporation of iron ions in the structure of Al_2O_3. The same spectrum was observed in bulk samples of α- phase of Al_2O_3 [2]. In the range of g-values close to g=2 there is observed complicated system of lines. Decomposition and simulation of this experimental spectrum show that this complicated system is due to two spectra from cupper ions (Cu^{2+}) and manganese ions (Mn^{2+}). Result of this decomposition was shown on the Fig. 8a-8c.

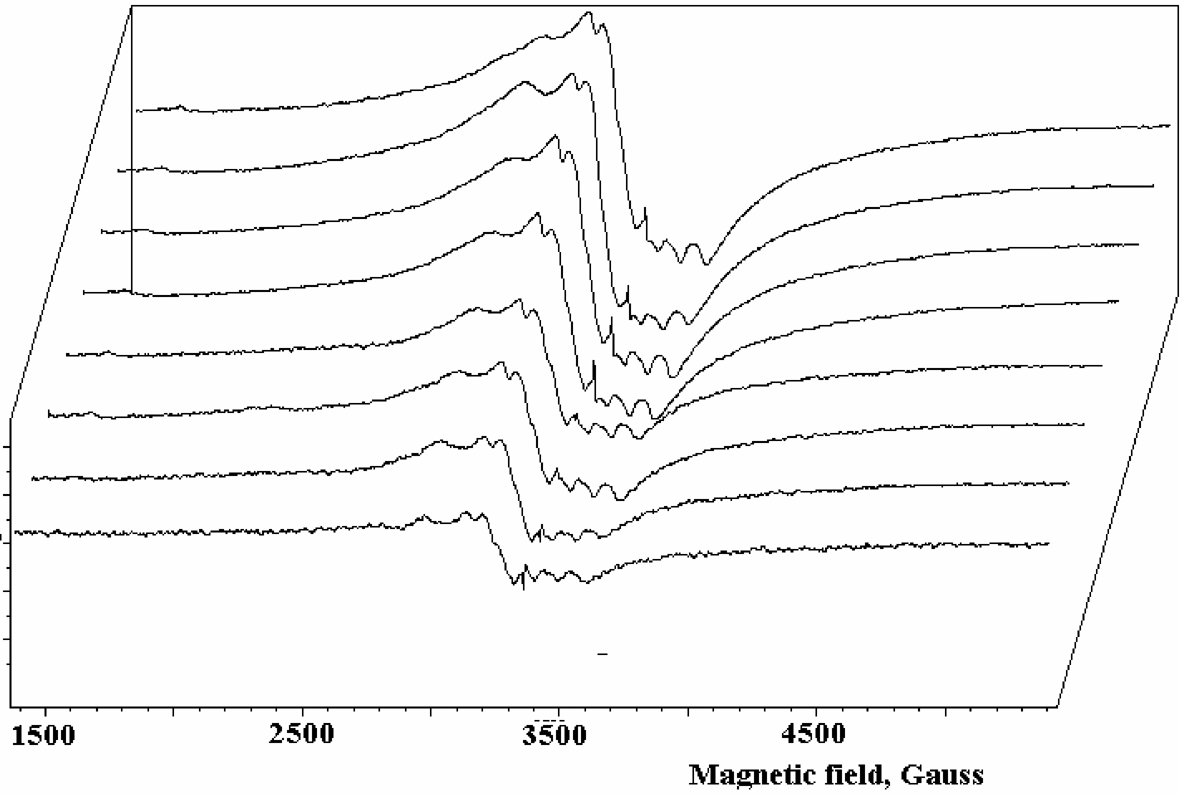
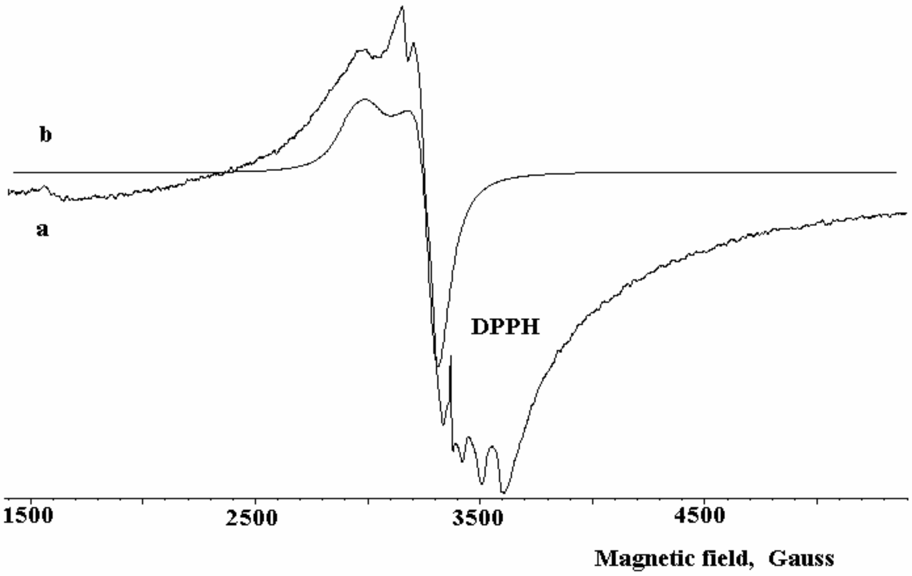


Fig. 7. Dynamic of EPR spectra changes at the increasing of MPO coatings thickness obtained at the anodic – cathodic process in aqua solution of KOH + Na_2SiO_3 electrolyte.



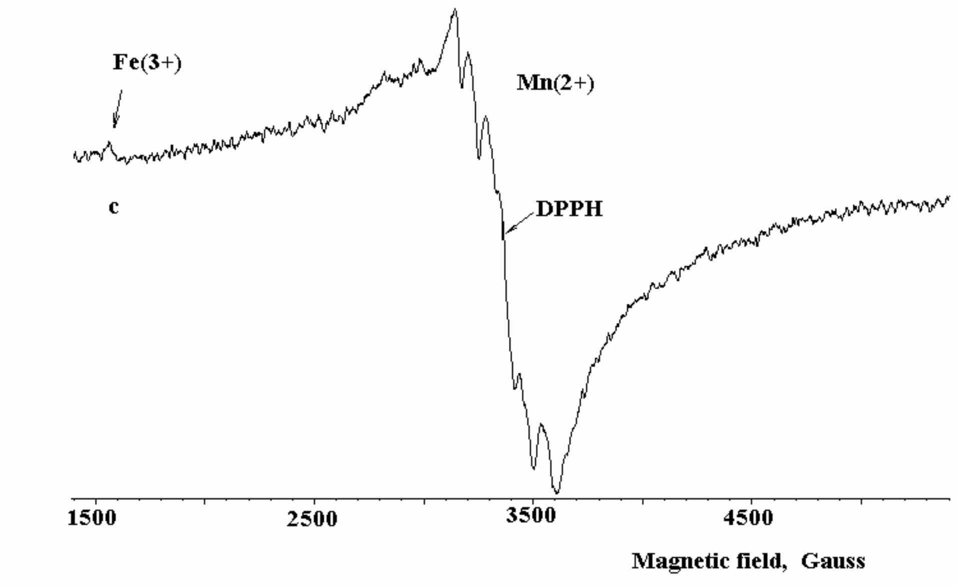


Fig. 8. EPR spectra of transition metal ions incorporated in MPO coatings, prepared by anodic – cathodic regime in aqua solution of KOH + Na_2SiO_3.

a – experimental spectrum,

b – simulated EPR spectrum of cupper ions Cu^{2+},

c – substrated EPR spectrum of manganese ions Mn^{2+}.

Simulation of EPR spectrum of cupper ions let us calculate g-values $g_{\|} = 2.2876$, $g_{\perp}= 2.050$ and linewidth $\Delta H_{1/2}= 90$ Gauss. The center with the same parameters of spin- gamiltonian is observed in bulk sample of high temperature phase of Al_2O_3 [3].

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Subtraction of cupper ions spectrum from experimental gives typical spectrum of manganese ions (Mn^{2+}) with g- value g=2.00 and parameter HFS A=83.7 Gauss (Fig.8c). Such spectrum was observed in the bulk crystal of α- phase of Al_2O_3 [4].

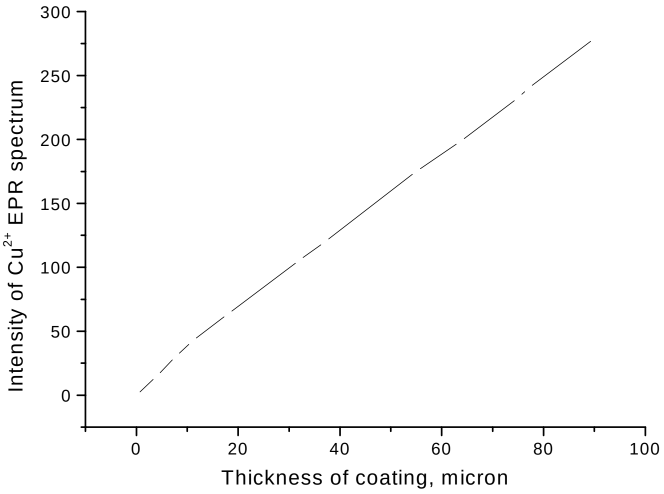

Fig. 9. Dependence of paramagnetic centers on the increasing of MPO coating prepared by MPO process in anodic – cathodic regime in aqua solution of KOH + Na_2SiO_3 electrolyte.

As it should be from Fig. 7 and 9 the content of paramagnetic centers grows droningly with increasing of coating thickness.

Discussion of obtained results

Early published data [5] show that the MPO coatings contain different ratio of low and high temperature phase of Al_2O_3. Because the structure of these phases of Al_2O_3 has different symmetry, impurity ions incorporating into the structure of Al_2O_3 are paramagnetic probes for the diagnostic of Al_2O_3 phases and peculiarities of their distribution in the MPO coatings.

Our studies show that micro plasma oxidation in anodic regime produces low temperature phases of Al_2O_3, which have not high micro hardness. In both electrolytes grown coatings have typical EPR spectrum of cupper ions with $g = 2,07$. Follow to note, that the content of cupper ions depends on thickness of coatings droningly. In the coating grown by MPO anodic – cathodic process due to presence of α- phase of Al_2O_3 EPR spectroscopy fixes typical electronic states of transition metal ions (Cu, Mn, Fe) in this phase of Al_2O_3. Very nice resolved HFS from manganese means that these ions place in more perfect lattice and don't interact with cupper ions. Such perfect lattice in the coatings occurs in grains of α- phase of Al_2O_3.

Mixture and structure of MPO coatings

We studied mixture and structure of MPO coatings by differential temperature analysis (DTA), infrared spectroscopy (IR), X-ray diffraction, X-ray phase analysis (XRPA) and X-ray electron spectroscopy (XRES) methods. Content of impurities (Mg, Cu), which are present at the MPO coatings, is equal or lower than at the AA 2024 alloy.

Table 2.

Chemical mixture of alloying elements in AA 2024, %

Mg	Mn	Cu	Si	Zn	Fe	Ti
1,2-1,8	0,3-0,9	3,8-4,9	0,5	0,3	0,5	0,1

Changes of concentrations of alloying elements occur on the boundary of coating – aluminum alloy. It is very interesting that there is zone in the coating on the distance 30-50 μ from the metal where concentration of alloying elements is lower on 3-4 times than on the boundary coating – metal (see Table 3). Increasing of voltage at the end of MPO process produces increasing of diffusion and concentration of alloying elements in the coatings.

Distribution of Cu and Mg in aluminum alloy is nonhomogeneous, there are places with concentration of Cu up to 20% and Mg up to 6% due to intermetallides.

When we use electrolyte contained KOH, analysis shows presence of K in the coatings and concentration of K on the boundary coating – metal is higher in 1,5-3 times than in bulk of coatings. This element may diffuse only in catodic part of MPO process. It means that mass transfer of cations occur from electrolyte into coating and concentration of these cations are increased at the increasing of voltage (see Table 3).

Phase analysis of coatings on the boundary coating – metal shows that cupper on the surface of metal has charge state Cu^{1+}, but in the coating cupper has charge state Cu^{2+}. These data support by EPR spectroscopy. During micro plasma oxidation process there is occurred changing of temperature condition. In thin coating melted material in channel of discharge has more low temperature and is cooled fast. It is the reason that thin coatings contain only low temperature phase of Al_2O_3. In thick coating material in discharge channel has more high temperature and is cooled slowly. At the anodic – catodic regime temperature of coating is more higher then at the anodic because in last case there is absent catodic component, which produces additional heating.

Table 3.

Chemical mixture of anodic – catodic coatings prepared in KOH solution on the 2024 aluminum alloy

$C_{KOH.}$, g/l	$Q\cdot10^3$. Coul.	Element, weight %											
		Cu				Mg				K			
		metal	boundary	coating	surface	metal	boundary	coating	surface	metal	boundary	coating	surface
2	10,5	3,80	2,30	2,60	1,40	2,24	1,60	1,60	1,10	Level of background (L/bg)			
	15,8	4,40	5,50	2,20	2,50	2,50	1,90	1,10	1,60	Level of background			
	19,6	4,80	19,0	4,40	3,10	2,30	5,80	2,40	0,94	L/bg	0,20	0,17	-
4	3,6	4,20	5,70	2,70	1,10	2,50	3,90	2,50	2,00	L/bg			
	20,2	4,60	9,70	3,30	1,40	1,92	2,70	1,40	0,80	L/bg	0,35	0,20	0,03
6	2,1	3,50	12,1	6,60	3,30	2,40	4,50	0,90	1,90	-	0,80	0,20	0,20
	3,6	6,60	2,60	6,00	1,60	2,80	4,20	1,80	0,70	L/bg	0,25	0,45	0,10
	5,5	6,90	4,20	1,60	3,60	1,70	1,40	0,60	1,20	L/bg	0,30	0,15	0,25
	6,2	7,50	4,50	2,40	3,10	1,60	1,80	0,50	0,90	L/bg	0,26	0,12	0,40

Data for the metals concern to the 100 μ depth and data for the coating – to 30-50 μ from the boundary metal-coating

What is the reason of such inhomogeneous of impurities distribution in the coatings? If we will return to the structure of coatings, we will be reminding that the MPO coatings consist from two layers – functional layer, which contains mainly α – phase of Al_2O_3, and technological layer, main part of which is low temperature phases of Al_2O_3. Presence oxides of manganese, cupper and iron in Al_2O_3 mean their solid solution in Al_2O_3. At the high temperature (after discharge) oxides of manganese, cupper and iron have homogeneous distribution in the channel. But at the cooling of coatings solubility of these oxides in low and high temperature phases of Al_2O_3 are different and are decreased. And at the cooling of coating oxides of manganese, cupper and iron diffuse from the grains of α-Al_2O_3 and from volumes of η, δ phases of Al_2O_3 to the boundaries between them. The same process occurs between metal and coating. Surplus of manganese, cupper and iron oxides accumulates in these boundaries and fixes by chemical analysis. Observed situation with impurities distribution reflects organization of boundary between metal and coating and high and low temperature phases of Al_2O_3. In last case it means boundary between functional and technological layers.

Table 4.

Phase mixture of anodic-catodic coating prepared in KOH solution on the 2024 aluminum alloy

$C_{\text{кон.}}$, g/l	$Q \cdot 10^3$. Coul.	η— : δ— : $\alpha - Al_2O_3$
2	3,3	13,0 : 2,2 : 1,0
	3,7	11,0 : 2,0 : 1,0
	10,5	6,2 : 1,3 : 1,0
	15,8	5,6 : 1,3 : 1,0
4	5,0	15,2 : 1,5 : 1,0
	9,7	7,6 : 1,0 : 1,5
	13,8	5,8 : 1,1 : 1,0
	16,7	4,6 : 1,4 : 1,0
6	2,9	16,2 : 2,5 : 1,0
	3,6	15,3 : 2,4 : 1,0
	5,6	7,9 : 1,5 : 1,0
	6,6	6,2 : 1,0 : 1,3

At the increasing of Q (Coulomb) – quantity of passed charge, volume ratio η:δ:α Al_2O_3 is stabilized and is equal 6:1:1. Content of α - Al_2O_3 on the metal-coating boundary is increased and on the boundary coating-electrolyte is close in volume of coating (see Table 4 and 5).

Table 5.

Phase mixture of coating on the boundary of coating-electrolyte and coating-metal

$C_{\text{кон.}}$, g/l	$Q \cdot 10^3$. Coul.	η— : α—Al_2O_3	
		boundary	
		Coating-metal	Coating-electrolyte
2	10,5	1 : 1	4,8 : 1
	26,0	1 : 1,7	6,9 : 1
	46,9	1 : 3,4	6,4 : 1
	232,2	1 : 6,3	8,2 : 1

Evidences of more strong heating of anodic-catodic coatings and metal close to boundary in comparison to anodic coatings are:

- increasing of (310) and (202) reflexes intensities of Al_2Cu phase in metal (close to boundary of metal-coating) in comparison to metal in bulk;
- appearance of new reflex with $d_\alpha = 1.78$ from substrate;

Thus, anodic-catodic coatings on the metal-coating boundary have more smooth conditions of hardening. High value of microhardness are due to presence of α—Al_2O_3 in the bulk of coatings. Data of phase analysis shows that anodic-catodic coatings are dispersing strengthered composite materials, where η—Al_2O_3 is base and δ, α - Al_2O_3 are inclusions.

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Results:

We have prepared 30 samples of 2024 AA with MPO coatings by anodic-cathodic regime. Gradation of coating thickness was 10, 25, 50, 75 and 150 microns and for the each thickness there were prepared 6 samples. The investigation of the structure shown that α- phase of Al_2O_3 appears beginning from 25 micron thickness of coating and the ratio high and low temperature phases of Al_2O_3 changes from 1:1 up to 6.1:1 on the boundary metal-coating for the 150 micron thickness of coating. Chemical analysis of coatings shown non homogeneous distribution of alloying elements in the coatings. Observed two anomalies on the boundaries of metal-coating and functional – technological layers are due to peculiarities of solubility of alloying elements in different phases of Al_2O_3. EPR data reflect peculiarities of incorporation of alloying elements (Cu, Mn, Fe) into different phases of Al_2O_3 and support conclusions obtained by X-ray phase analysis about existence high and low temperature phases of Al_2O_3 in anodic-cathodic coatings and about absence of high temperature phase of Al_2O_3 in anodic coatings. Investigation of hardness shows that observed dependence of it on the coating thickness is due to increasing of α-Al_2O_3 content at the increase of coating thickness. As microhardness discharge voltage is increased at the increase of coating thickness.

Future work planned:

Task 4: **Development and optimization of MPO process parameters for the preparing of corrosion protective coatings for 7075-T6 aluminum alloys.**

Two coupons of T6 aluminum alloy will be used for selection of parameters of MPO process

There will be selected types of chemical compounds and they definite concentrations for electrolyte,

There will be developed and optimized current, voltage and alternation of anode and cathode processes.

At the solution of this task we must take into account all steps pointed to Task 1.

Project director, prof. V.A. Nadolinny
Technologist I.B. Kireenko

TECHNICAL REPORT №3

Title of project: **Micro-Plasma Protective Coatings for 2024 and 7085 Aluminum Alloys**

Project director: Prof. V.A. Nadolinny

CRDF project number: RUE2-1502-NO-04

Reporting period: July – September, 2005

Nomeclature page:

MPO process – micro plasma oxidation process.
AA – aluminum alloy.
EPR- electron paramagnetic resonance.
HFS- hyper fine structure.

Summary:

Two coupons of T6 aluminum alloy were used for selection of parameters of MPO process.

There were selected types of chemical compounds and they definite concentrations for electrolyte.

There were developed and optimized current, voltage of anode - cathode processes .

According plane for third quarter of project we have prepared series of 7075 aluminum alloy samples , grown on the surface MPO coatings with thickness 10, 25, 50, 75, and 150 μ .

Main energies of this project stage were aimed at the solution of Task 4.

Task 4: **Development and optimization of MPO process parameters for the preparing of corrosion protective coatings for 7075-T6 aluminum alloys.**

For the solution of Task 4 we have found Russian analogue of 7075 – T6 aluminum alloy. It is aluminum alloy V-95. In the Table 1 there is shown composition of V-95 and 7075- T6 aluminum alloys.

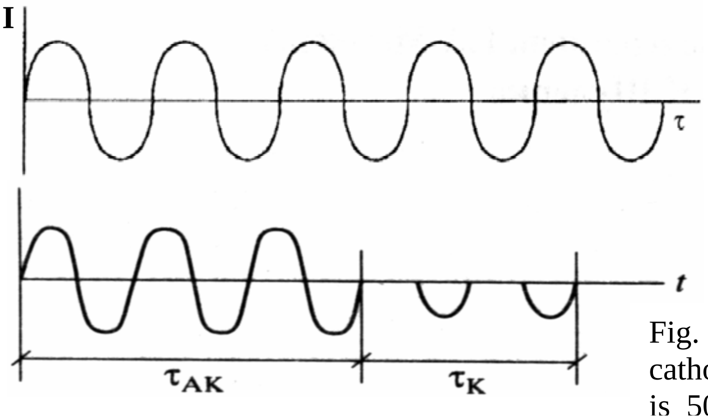
Table 1.

Aluminum alloy	Mg, %	Mn, %	Cu, %	Si, %	Zn, %	Fe, %	Ti, %	Cr, %	Ni, %
V-95 (7075-T6)	1.8-2.8	0.2-0.6	1.4-2.0	0.5	5.0-7.0	0.5	0.5	0.1-0.25	0.1

Development of microplasma oxidation process for the 7075-T6 aluminum alloy

As we have shown earlier anodic-cathodic process is more universal for the creation of micro plasma oxidation coatings with different properties. Existence of two discharge types (anodic and cathodic) lets organize complicate electrochemical processes.

Anodic-cathodic modes



Anodic – cathodic mode

Fig. 1. A shape of current pulses at anodic-cathodic and cathodic MPO processes. Frequency is 50 Hz.

At the increasing of current density thickness of MPO coating is increased mainly due to technological layer. It is not good because technological layer consists from low temperature Al_2O_3, has friable structure and not good mechanical properties. The main aim of this project is development of MPO process for the creation of corrosion protective coating for the aviation, where corrosion is accompanied an erosion of details from aluminum alloys. It means that protective MPO coatings must be not only corrosion protective, but have wire resistance properties. Our studies shown, that these properties are created at low growth rate and low density of current, lower that 0.1 A /cm^2. By this way it is possible to prepare coatings with low porosity.

Selection of electrolyte composition for the formation of corrosion protective coatings on the surface of aluminum alloy 7075

There are four types of electrolytes, which are used in microplasma oxidation processes:

1. Electrolytes, in which MPO coatings are created at the oxidation of metals.
2. Electrolytes, in which MPO coatings are created due to anions of electrolytes.
3. Electrolytes, in which both processes take place.
4. And solutions, in which MPO coatings are created due to electrophoresis.

Our studies shown that MPO coatings containing α- phase of Al_2O_3 and mix of α Al_2O_3 and SiO_2 have corrosion protective properties in acid and alkali. For preparing of these properties of MPO coatings it needs to use electrolytes of first and thirds types. For the 7075 aluminum alloy we have studied MPO process and created coatings in electrolytes containing KOH in concentration range 0,1 – 4,0 g/liter. In range of KOH concentration 0,1-1,5 g/l created MPO coatings have small thickness, enough density and low hardness. At the KOH concentration higher 2 g/l MPO process forms two layers coatings (functional and technological) on the surface of aluminum alloy. At further increasing of KOH concentration process of dissolution of metal dominates under process of MPO coating creation.

On the Fig. 2 there is shown dynamic of discharge voltage changing in time scale.

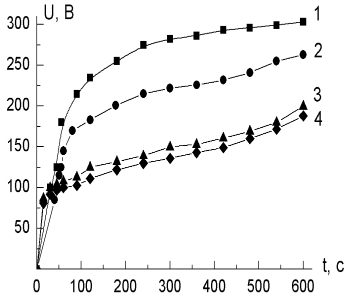


Fig.1. Behaviour of discharge voltage in the anodic- cathodic MPO process on the 7075 aluminum alloy. Current *I* = 0.0718 A/ cm^2. Electrolytes : 1 – KOH + Na_2 SiO_3, 2 – KOH 1g/l, KOH 2 g/l, 3 – KOH 2 g/l, 4 – KOH 4g/l.

As it is possible to notice from Fig.1, increasing of electrolyte concentration decreases discharge voltage and electrical power of MPO process is decreased also. Our study shows that MPO coatings of definite thickness grows twice longer in electrolytes of first type than in electrolytes of third type. That is due to oxidation process of metal in first case, but in second case growth of MPO coating there is presented oxidation of metal plus participation in this process metal oxides from electrolyte.

For the formation of MPO coatings on the start of electrochemical process needs organize critical thickness of oxide layer at the creation of which there is beginning formation of functional layer from α- phase of Al_2O_3. In the case of silicate – alkali electrolytes this thickness is equal to 30 μ, in the case of alkali electrolyte – 50 μ.

Analyses of obtained results lets us determine next electrolyte for the formation of corrosion protective MPO coating: KOH – 5g/liter + Na_2SiO_3 – 8g/liter. Using of this electrolyte lets us decrease time to the step of microplasma oxidation process and decrease time for growth of definite thickness of MPO coating.

Using this electrolyte we have prepared MPO coatings on the 7075 aluminum alloy with thickness 10; 25; 50; 75 and 150 μ. For the each thickness of MPO coatings there were prepared 8 samples. These results were shown in the Table 2 and Fig. 3.

Table 2.

Oxidation time	Sample № 1	Sample № 2	Sample № 3	Sample № 4	Sample № 5	Sample № 6	Sample № 7	Sample № 8
37 min	10,75	11,23	11,80	11,67	11,31	11,36	11,23	11,41
92 min	25,61	25,78	25,71	25,51	25,83	25,30	25,50	25,30
183 min	51,03	52,02	52,01	52,07	52,03	51,05	50,05	51,08
275,4 min	74,48	75,06	76,81	76,01	78,73	75,84	76,02	75,64
550,5 min	150,18	151,06	157,60	160,20	149,40	153,85	154,62	150,65

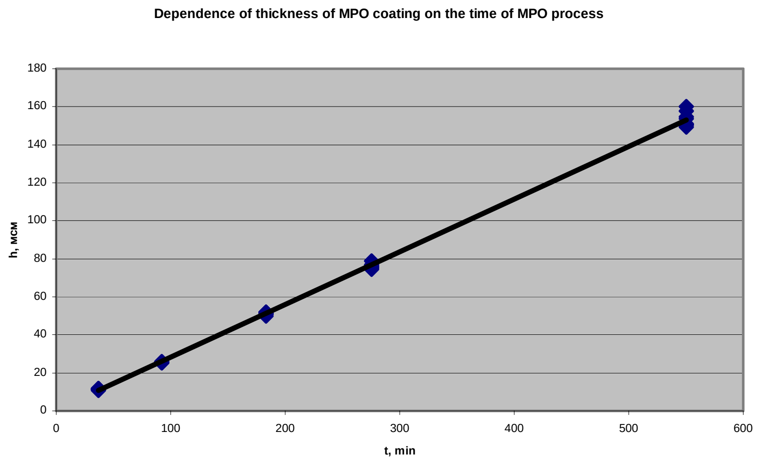


Fig. 3. Dependence of MPO coating thickness during oxidation process.

Influence of electrolyte temperature on the properties of MPO coatings.

Temperature of electrolyte influents on growth rate of MPO coatings and they properties. We have studied temperature interval between 20 and 60 ^{o}C. At the increasing of temperature the growth rate of MPO coatings is increased (see Fig.4). But at the increasing of electrolyte temperature the coating porosity is increased and micro hardness is decreased. Besides that, electrolyte temperature influents on the ratio of high and low temperature oxides of aluminum, which influents on the properties of coatings.

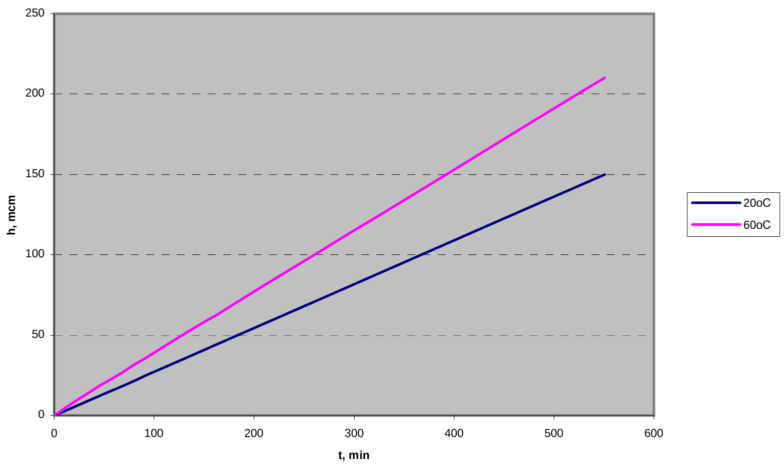
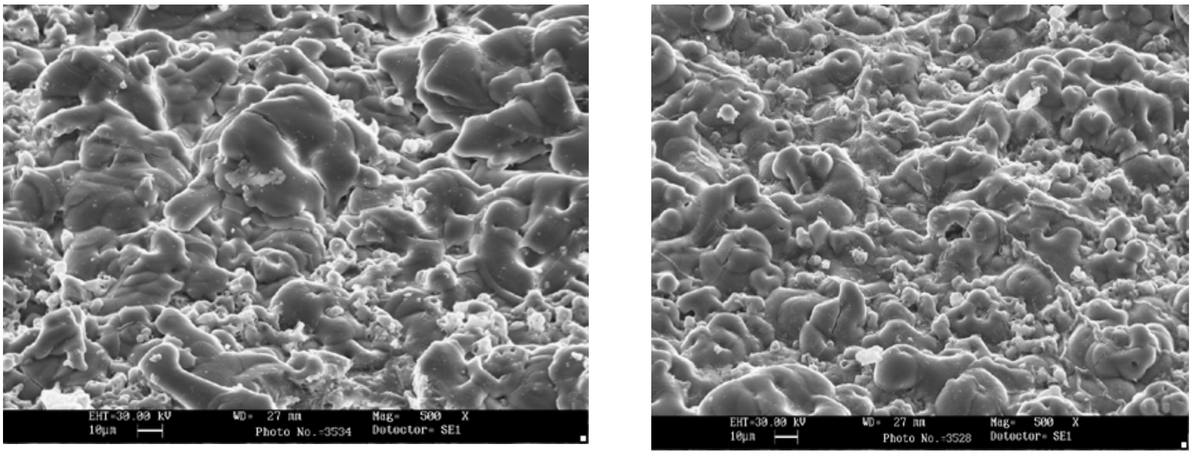


Fig. 4. Growth rate of MPO coatings at 20^{0}C and 60^{0}C.



a) b)

Fig. 5. Surface of MPO coatings (technological layer) grown in anodic- cathodic regime at the temperature 20°C (a) and 60°C (b).

Table 3. Influence of electrolyte temperature on the properties of MPO coating of 7075 aluminum alloy. Frequency – 50 Hz, I = 0,0718 A/cm^2, time – 183 minutes.

№	Temperature, °C	Thickness, μ	Crystalline phase, relative intensity of peaks
1.	20	50	γ : η- Al_2O_3. 13,0; 9,2.
2.	60	78	γ : η- Al_2O_3. 10,2; 6,1.

Obtained results lets us to make conclusion, that preferred electrolyte temperature for the preparing of corrosion protective MPO coatings is 20°C.

Figure 6 shows forming curve of voltage growth during oxidation process.

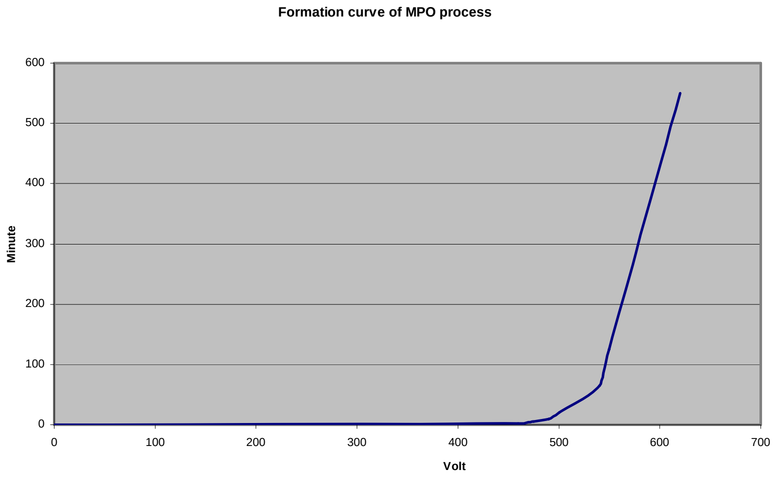


Fig.6. Forming curve of voltage during MPO process.

EPR study of MPO coatings on the 7075-T6 aluminum alloy

For the EPR study there were prepared MPO coatings on 5 samples of 7075 aluminum alloy at the same parameters of MPO process as it was shown in the Table 2. The sizes of these samples were 1 x 5 x 10 mm. Thickness of MPO coating of these samples measured by Quonix were 10, 25, 50, 75 and 150 μ. EPR spectra were recorded using EPR spectrometer E-109 Varian. Samples with thickness of MPO coating 10 and 25 μ have in EPR wide line with g-value 2,07 (the same as we observed for the 2024 aluminum alloy). Beginning from thickness of MPO coating 25 μ in EPR spectra there is appeared spectrum of Mn^{2+}. Intensity of this spectrum increases at the increasing of thickness of MPO coating (see Fig. 7). According results obtained early hard functional layer is appeared in these coatings beginning from the thickness 30 μ. It means that resolved EPR spectrum of Mn^{2+} is due to incorporation of manganese ion into high temperature aluminum oxides. By another words, EPR spectrum of manganese ions is indicator of appearance of functional layer. For the testing of this assumption we removed technological layer. After this treatment in EPR spectra we see little decreasing of wide line and without changing Mn^{2+} spectrum. It is additional evidence that manganese spectrum is due to incorporation of manganese ions into high temperature phase of aluminum oxides. Wide line with g-value 2,07, which is appeared beginning from the start of MPO process, is due to exchange interaction between different paramagnetic ions – Cu^{2+} and may be a characteristic of barrier and technological layers. We don't exclude that different electro conductivity of MPO coatings in opposite directions is also due to mixture of oxides of paramagnetic ions.

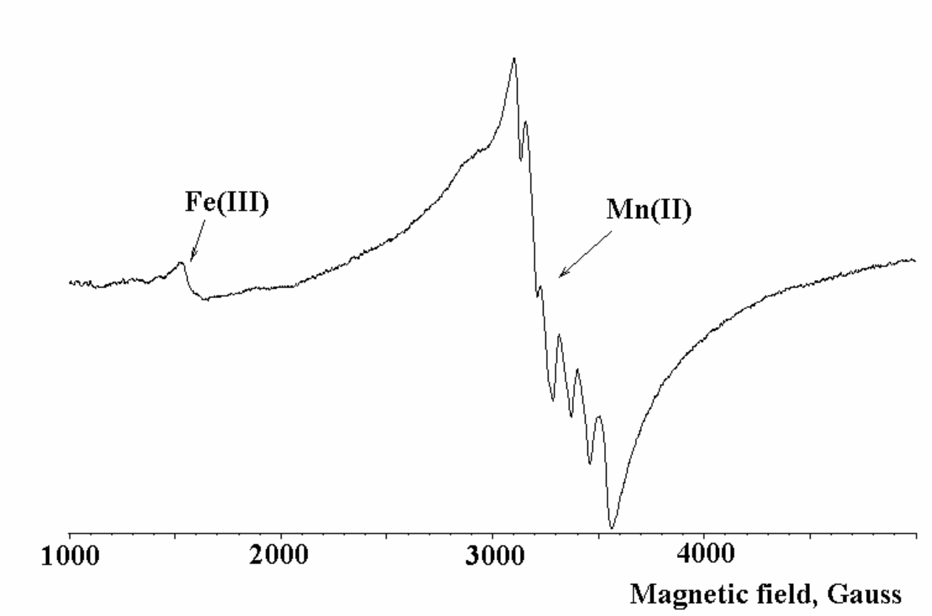


Fig. 7. EPR spectrum of MPO coating on the surface of 7075 aluminum alloy.
Thickness of coating is 150 μ.

In the next period of our project we will solve Task 5 and Task 6.

Task 5: Production of corrosion protective coatings for 7075-T6 aluminum alloys.
Task 6: The study of coating characteristic for T6 aluminum alloy.

TECHNICAL REPORT №4

Title of project: **Micro-Plasma Protective Coatings for 2024 and 7085 Aluminum Alloys**

Project director: Prof. V.A. Nadolinny

CRDF project number: RUE2-1502-NO-04

Reporting period: October - December, 2005

Nomeclature page:
MPO process – micro plasma oxidation process.
AA – aluminum alloy.
EPR- electron paramagnetic resonance.
HFS- hyper fine structure.

In this period of our project we solved Task 5 and Task 6.

Task 5: Production of corrosion protective coatings for 7075-T6 aluminum alloys.
Task 6: The study of coating characteristic for T6 aluminum alloy.

Summary:

According of Task 5 and 6 of this project there were prepared MPO coatings on the surface of 7075 aluminum alloy with thickness from 10 to 150 μ and have studied corrosion protective properties, microhardness, concentration of different elements in alloy and coatings, charge state of transition metal ions in coatings and dependence of discharge voltage on thickness of MPO coatings. There was shown that increasing of MPO coatings thickness up to 64 μ produce increasing corrosion protective properties in 250 times in comparison with aluminum alloy.
For the testing in USA (in research laboratory of AFOSR/NL) there were prepared two series of aluminum alloy samples (2024 and 7075 AA) covered by corrosion protective MPO coatings with thickness 10, 25, 50, 75 and 150 μ.

Task 5: Production of corrosion protective coatings for 7075-T6 aluminum alloys

Analyses of early obtained results lets us determine next electrolyte for the formation of corrosion protective MPO coating: KOH – 5g/liter + Na_2SiO_3 – 8g/liter. Using this electrolyte we have prepared MPO coatings on the 7075 aluminum alloy with thickness 10; 25; 50; 75 and 150 μ for the study of corrosion protective properties. For the testing of MPO coatings we have developed special equipment. A sample with determined surface is placed in closed volume with 15% solution of HCl. Evolved hydrogen is passed in volume with current conducted solution and displaces this solution. Created drops fall and lock sensor contact of electrical scheme. For the count of drops we have developed special soft and after calculation of drop volume we may estimate a volume of evolved hydrogen. A volume of evolved hydrogen is connected with quantity of aluminum taking part in reaction with HCl. Experimentally there was estimated that one milliliter of evolved hydrogen is equivalent to $8 \cdot 10^{-4}$gramm of aluminum of studied samples.

The rate of metal corrosion is described by equation: $V = \frac{1}{S}\frac{dm}{dt}$, (1)

where *dm* is decreasing of metal mass during *dt* time; S is square of sample surface.

On the Fig. 1-5 there are shown experimental dependences of hydrogen quantity per square of sample during experiment time. Approximation of these dependences shows that evolved hydrogen quality described by next equation:

$$\frac{\Omega}{S} = A \cdot t + Be^{at} - C ,$$

(2)

where Ω/S is hydrogen quantity per square of sample.

Parameters A, B, C and a depend on conditions of MPO process – mixture of alloy, electrolyte, temperature and so.

Because corrosion rate of sample throw MPO coating is negligible quantity (it means that a is small) it is possible take Taylor. In this approximation a- value means corrosion rate and depends on porosity *(c)* and thickness of coating *(h)* as $a = D / h^2 c$, where D has sense of diffusion coefficient. We have estimated that value *D/c* is equal $3.5 \cdot 10^{-9}$cm^2/cek.

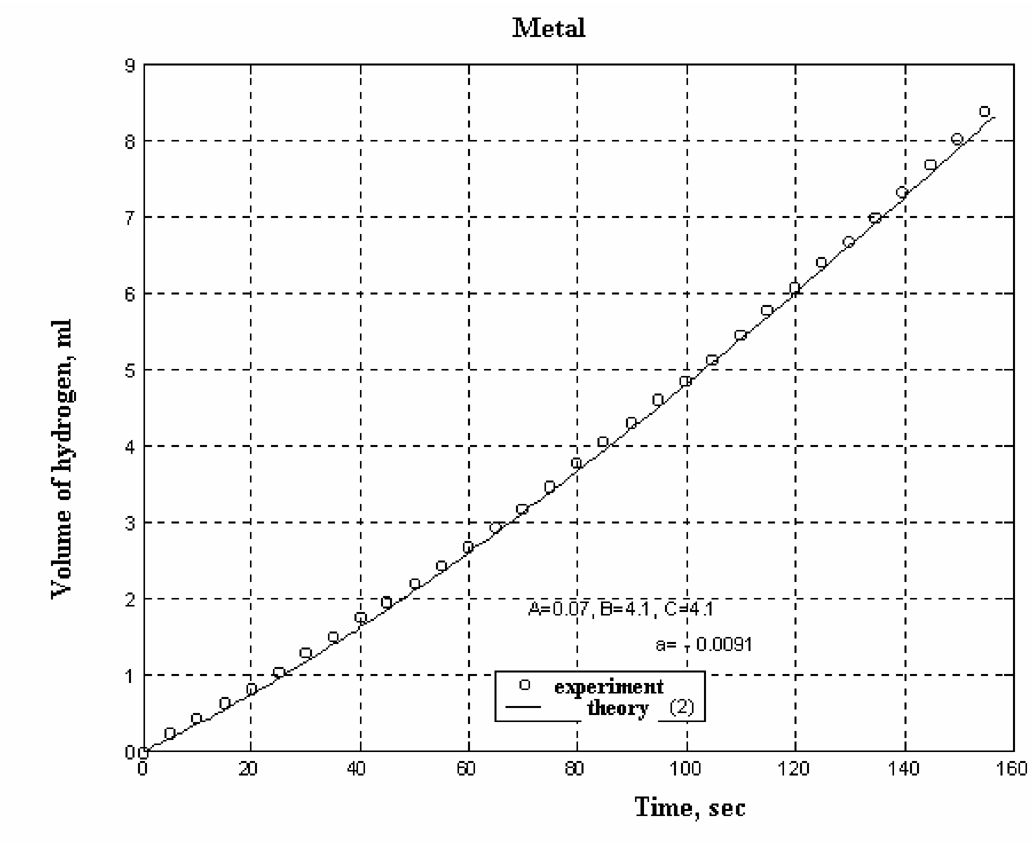


Fig.1. Results of corrosion testing aluminum alloy 7075

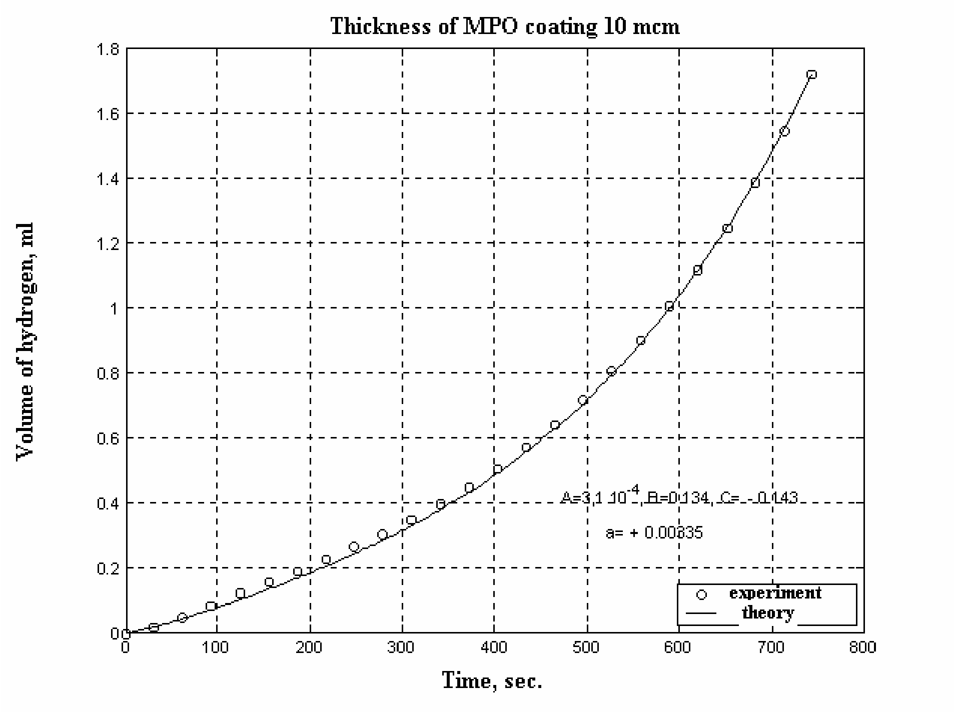


Fig.2. Results of corrosion testing MPO coating with thickness 10 μ (aluminum alloy 7075)

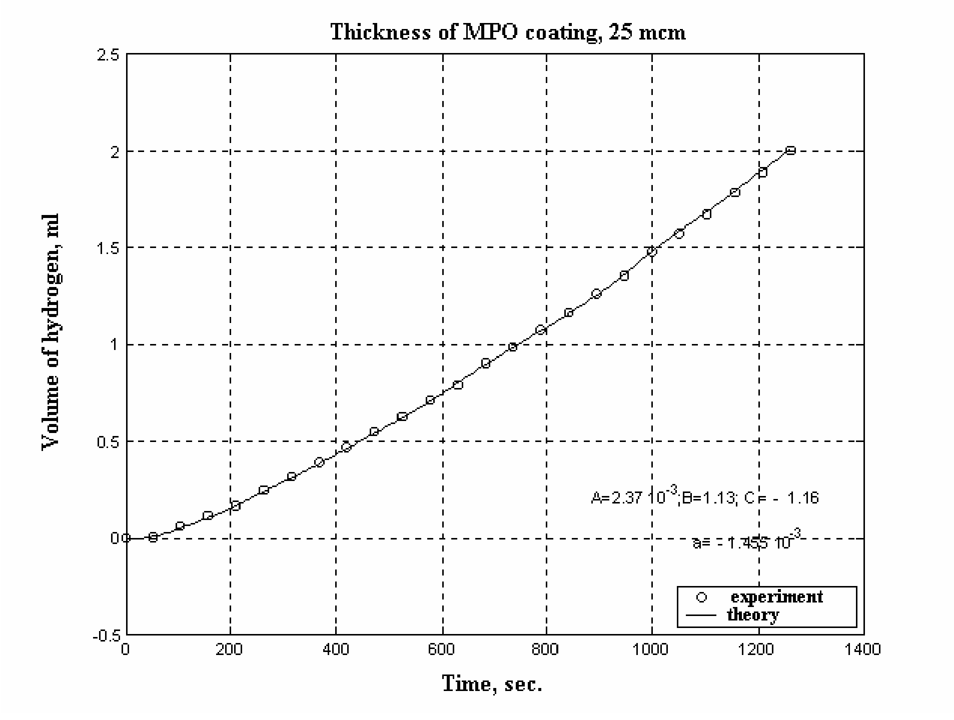


Fig.3. Results of corrosion testing MPO coating with thickness 25 μ (aluminum alloy 7075)

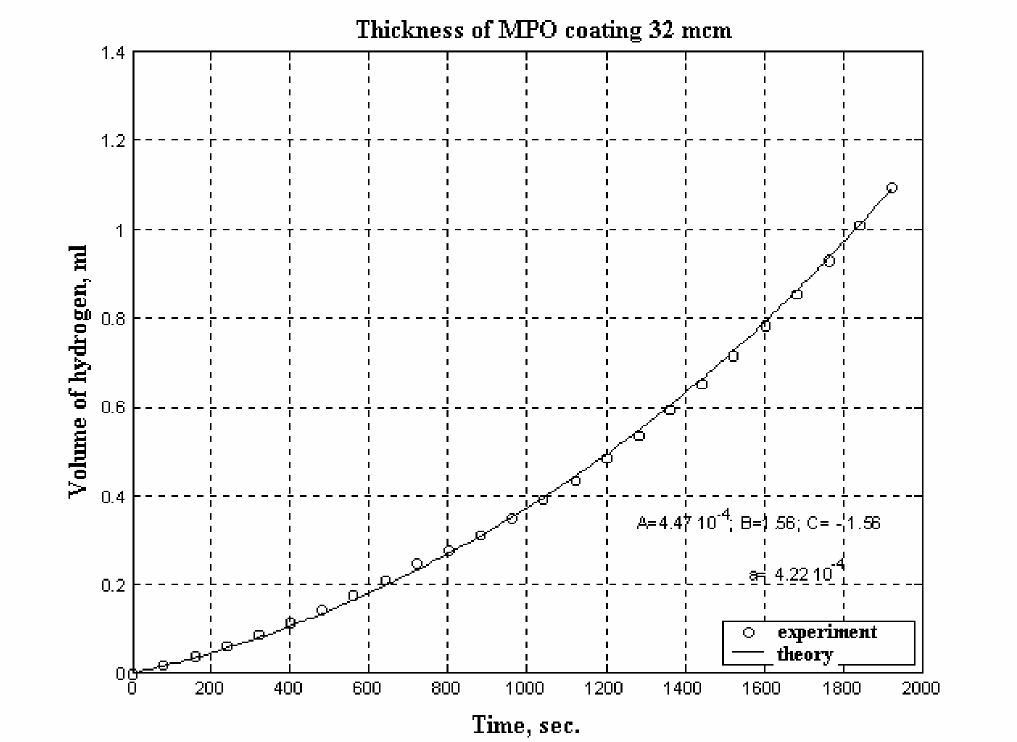


Fig.4. Results of corrosion testing MPO coating with thickness 32 μ (aluminum alloy 7075)

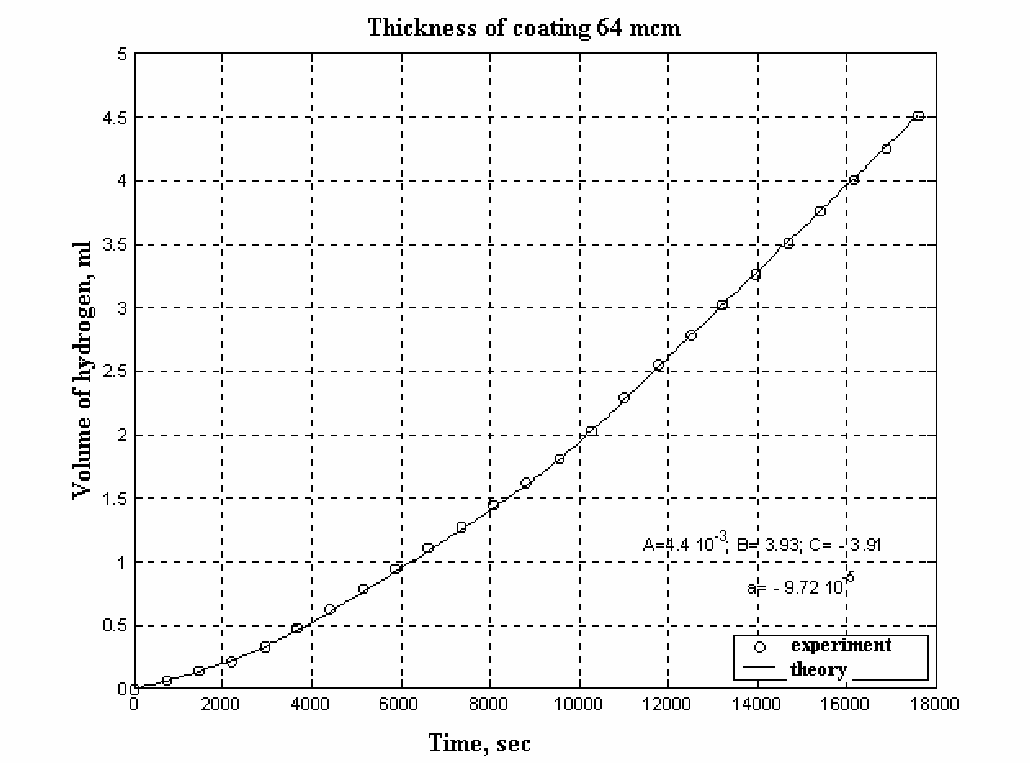


Fig.5. Results of corrosion testing MPO coating with thickness 64 μ (aluminum alloy 7075)

Presented results on the Figures 1-5 show that MPO coatings with thickness 10 μ increases anticorrosion properties of aluminum alloy in 20 times, and with thickness 64 μ these properties are increased in 250 times in comparison of aluminum alloy without MPO coatings.

Extrapolation of corrosion rate to 150 μ MPO coating thickness gives increasing corrosion protective parameter up to 1400 times.
MPO coatings of both aluminum alloys have similar corrosion protective properties.

Task 6: The study of coating characteristic for T6 aluminum alloy.

As we have shown early, microplasma oxidation coatings consist from two layers – technological and hard functional layers. At the anodic – cathodic regime there is critical thickness of coating, when there is beginning formation of hard layer from high temperature aluminum oxides phases. For the alkaline electrolytes this thickness value is 40 – 45 μ. But EPR data show that in some samples hard layer is appeared at the thickness 25 μ.

Microhardness of MPO coatings on the surface of 7075 and 2024 aluminum alloys

The measuring of microhardness was realized on the hardnessmeter by diamond instruments indentation (Wiccers method). Before micro hardness testing the surface of samples was polished by the corundum ring up to mirror. Wiccers method consists from organization of print on the surface of sample by diamond tip at the press of static load 100 gram. After removing of load and measurement of trace parameters, microhardness was calculated by equation:

$$H_v = 0{,}189\frac{F}{d^2}$$

We tested each sample in many places of sample surface. In the Table 1 there are shown experimental data of micro hardness for the 2024 and 7075 aluminum alloys.

Table 1. Microhardness of MPO coatings with different thickness.

Thickness of coating, μ	Type of aluminum alloy							
	2024				7075			
	Arbitrary unite	H_v, kg/mm^2	H_v, GPa	Ratio $H_{coat.}/H_{metal}$	Arbitrary unite	H_v, kg/mm^2	H_v, GPa	ratio $H_{coat.}/H_{metal}$
0	92	291,76	2,86	1,0	84	349,985	3,43	1,0
10	79	395,69	3,88	1,36	71	489,88	4,80	1,40
	80	385,86	3,78	1,32	75	439,02	4,30	1,25
	83	358,47	3,51	1,23	76	427,54	4,19	1,22
	88	318,89	3,12	1,09	82	367,27	3,60	1,05
	90	304,88	2,99	1,04	86	333,90	3,27	0,95
	92	291,76	2,86	1,00	86	333,90	3,27	0,95
	96	267,96	2,63	0,92	95	273,63	2,68	0,78
	100	246,95	2,42	0,85	95	273,63	2,68	0,78
	109	207,85	2,04	0,71	97	262,46	2,57	0,75
	74	450,97	4,42	1,54	50	987,80	9,68	2,82
	75	439,02	4,30	1,50	60	685,97	6,72	1,96
	78	405,90	3,98	1,39	63	622,20	6,10	1,78
	82	367,27	3,60	1,26	70	503,98	4,94	1,44

25	85	341,80	3,35	1,17	76	427,54	4,19	1,22
	94	279,48	2,74	0,96	85	341,80	3,35	0,98
	98	257,13	2,52	0,88	85	341,80	3,35	0,98
	100	246,95	2,42	0,85	86	333,90	3,27	0,95
	114	190,02	1,86	0,65	115	186,73	1,83	0,53
	115	186,73	1,83	0,64	123	163,23	1,60	0,47
50	34	2136,24	20,94	7,32	34	2136,24	20,94	6,10
	35	2015,92	19,76	6,91	35	2015,92	19,76	5,76
	35	2015,92	19,76	6,91	35	2015,92	19,76	5,76
	36	1905,48	18,67	6,53	35	2015,92	19,76	5,76
	36	1905,48	18,67	6,53	38	1710,18	16,76	4,89
	37	1803,87	17,68	6,18	38	1710,18	16,76	4,89
	39	1623,60	15,91	5,56	38	1710,18	16,76	4,89
	39	1623,60	15,91	5,56	39	1623,60	15,91	4,64
	40	1543,44	15,13	5,29	39	1623,60	15,91	4,64
	41	1469,06	14,40	5,03	41	1469,06	14,40	4,20
75	33	2267,67	22,22	7,77	32	2411,62	23,63	6,89
	33	2267,67	22,22	7,77	32	2411,62	23,63	6,89
	34	2136,24	20,94	7,32	34	2136,24	20,94	6,10
	35	2015,92	19,76	6,91	34	2136,24	20,94	6,10
	35	2015,92	19,76	6,91	34	2136,24	20,94	6,10
	35	2015,92	19,76	6,91	35	2015,92	19,76	5,76
	36	1905,48	18,67	6,53	37	1803,87	17,68	5,15
	38	1710,18	16,76	5,86	37	1803,87	17,68	5,15
	38	1710,18	16,76	5,86	37	1803,87	17,68	5,15
	40	1543,44	15,13	5,29	39	1623,60	15,91	4,64
150	28	3149,87	30,87	10,79	22	5102,27	50,00	14,58
	28	3149,87	30,87	10,79	22	5102,27	50,00	14,58
	28	3149,87	30,87	10,79	22	5102,27	50,00	14,58
	29	2936,38	28,78	10,06	24	4287,32	42,02	12,25
	30	2743,89	26,89	9,40	24	4287,32	42,02	12,25
	30	2743,89	26,89	9,40	26	3653,10	35,80	10,44
	30	2743,89	26,89	9,40	26	3653,10	35,80	10,44
	31	2569,72	25,18	8,80	26	3653,10	35,80	10,44
	31	2569,72	25,18	8,80	28	3149,87	30,87	9,00
	34	2136,24	20,94	7,32	29	2936,38	28,78	8,39

Analysis of obtained results lets us to make the next conclusions:

1. Coatings with thickness 10 μ и 25 μ have not high temperatures phases of aluminum oxides with high hardness. Coatings with these thickness are nonhomogeneous and in some points MPO coatings have more low hardness than aluminum alloy. That it is possible to see (see Table 1)for the coatings thickness 25 μ, where diamond indenter sink in loose aluminum oxides.

2. Coatings with thickness 50 μ are polished up to mirror and hardness tests show that in the coating on the surface of 2024 and 7075 aluminum alloys there are created hard layer.

3. At the thickness higher 50 μ there is observed increasing of microhardness. Behaviour of hardness is the same for the both aluminum alloys.

4. MPO coating on the aluminum alloy 7075 with thickness 150 μ has higher hardness than coating on the aluminum alloy 2024 with the same thickness.

Scanning microscopy of surface of MPO coatings

Obtained MPO coatings with thickness 10 and 75 μ were studied by scanning microscope JEOL ISM-6700 F . For the comparison we show on the figures 3-6 surface view of the MPO coatings for 2024 and 7075 aluminum alloys. Conditions of MPO processes were similar for the both alloys: electrolyte – 4 g/liter *KOH* , anodic – cathodic regime, current density 7 A/dm^2, temperature of electrolyte – 20 ^{o}C.

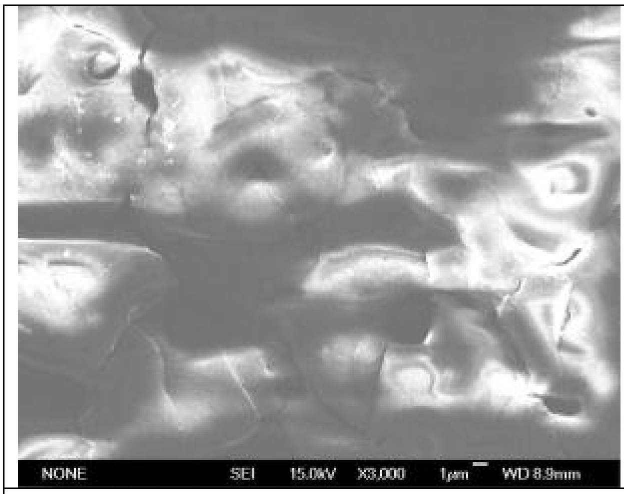
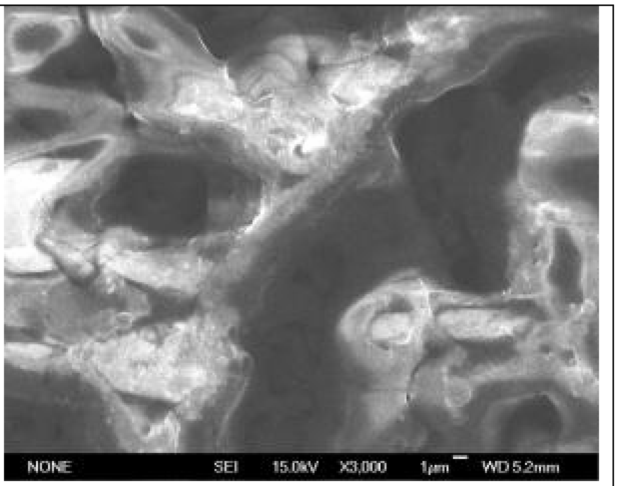
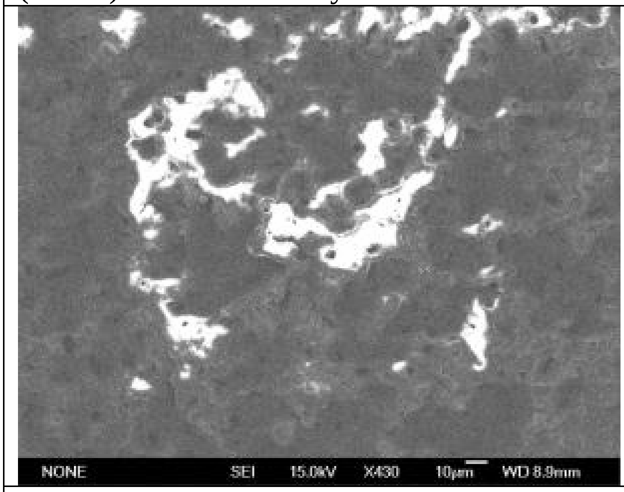
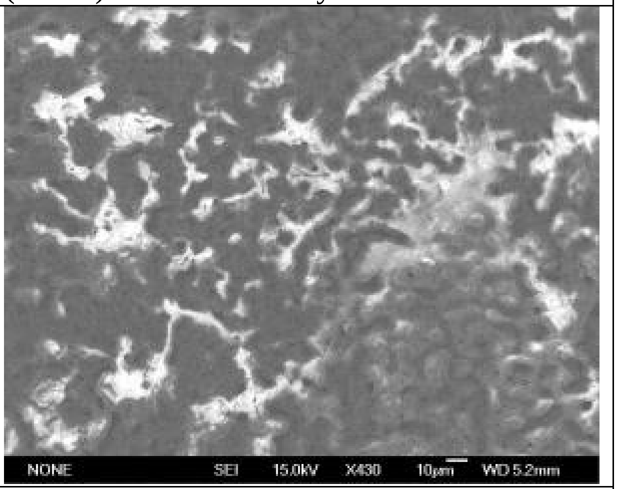
		
SIMS imaging of coating surface at h=10μ (x3000). Aluminum alloy 2024		SIMS imaging of coating surface at h=10μ (x3000). Aluminum alloy 7075.
		
SIMS imaging of coating surface at h=10μ (x430). Aluminum alloy 2024		SIMS imaging of coating surface at h=10μ (x430). Aluminum alloy 7075

Fig. 6. SIMS imaging of MPO coating surface at the thickness of coating 10μ.

At thickness 10 μ MPO coatings on the 7075 aluminum alloy are more porous than on the 2024 alloy. But MPO coatings on the 2024 alloy have a lot micro cracks. Existence of great number of such defects on the surface describes multitude of microhardness parameters.

Growth and formation of MPO coatings are due to oxidation processes on the surface of metal at the discharges and also are due to melting and cooling of coatings volume. At the increasing of magnification of scanning microscopy imaging a surface of coatings looks like as glassy mass. Observed interstices are frozen discharge channels. They may be transparent and closed and increase in the coating volume. At the increasing of coating thickness the number of interstices decreases smoothly (thickness 75 μ). On the place of discharges there were created flashes. Obtained results show that thin coatings contain only low temperature phase $\eta - Al_2O_3$. At the increasing of thickness there is appeared high temperature phase $\alpha - Al_2O_3$.

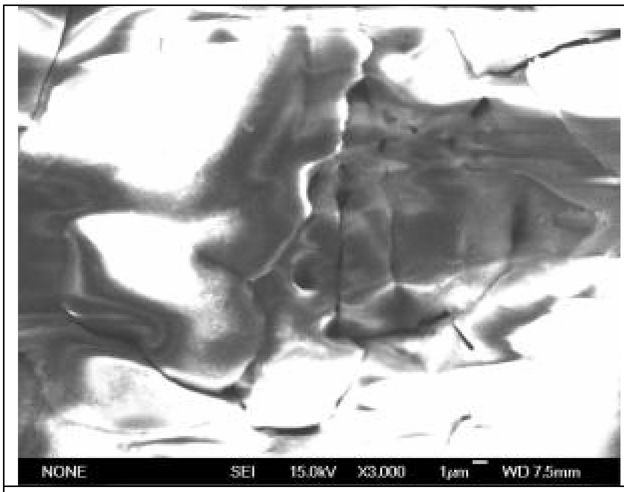
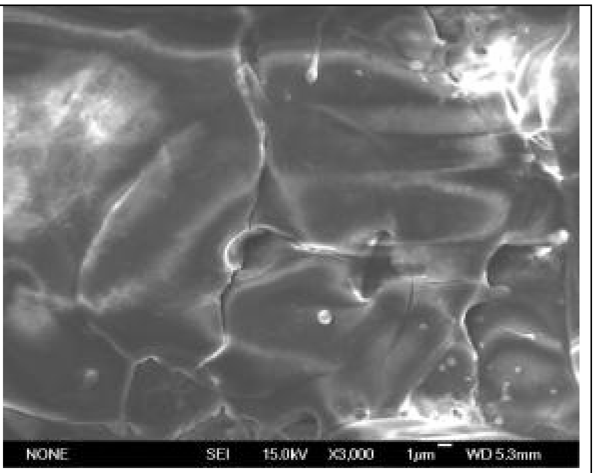
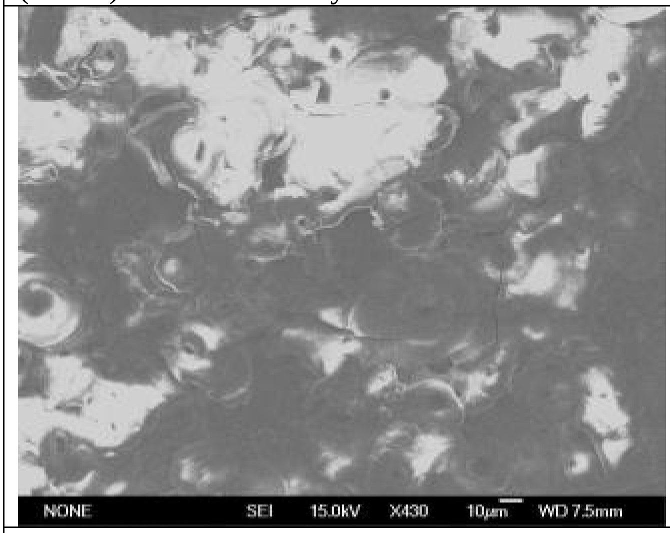
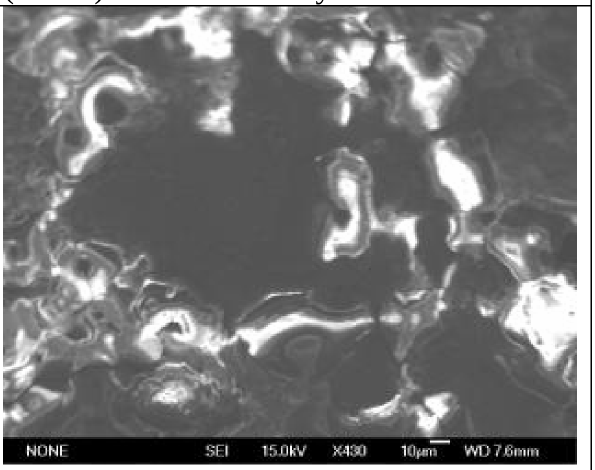
		
SIMS imaging of coating surface at h=75μ (x3000). Aluminum alloy 2024		SIMS imaging of coating surface at h=75μ (x3000). Aluminum alloy 7075.
		
SIMS imaging of coating surface at h=75μ (x430). Aluminum alloy 2024		SIMS imaging of coating surface at h=75μ (x430). Aluminum alloy 7075

Fig. 7. SIMS imaging of MPO coating surface at the thickness of coating 75μ.

Microprobe analyses of MPO coatings (h=75 μ)

It is very interesting to compare chemical compositions of both aluminum alloys (2024 and 7075) and created coatings.

Table 2. Chemical compositions of 2024 and 7075 aluminum alloys.

Type of alloy	Chemical composition, %										
	Mg	Mn	Cu	Si	Zn	Fe	Ti	Cr	Cd	Ni	Other elements
2024	1,2-1,8	0,3-0,9	3,8-4,9	0,5	0,3	0,5	0,1	-	-	0,1	-
7075	1,8-2,8	0,2-0,6	1,4-2,0	0,5	5,0-7,0	0,5	0,05	0,1-0,25	-	0,1	-

Table 3. Microprobe data of 2024 aluminum alloy

Element		(keV)	mass%	Error%	At%	Compound	mass%	Cation	K
C	*	0.277	4.20	0.27	6.64			0.6885	
O	*	0.525	54.84	0.18	65.05			67.1524	
Na		1.041	0.21	0.17	0.17			0.1540	
Mg	*	1.253	0.24	0.12	0.19			0.1677	
Al	*	1.486	39.09	0.11	27.49			30.6574	
Si	*								
K		3.312	0.15	0.20	0.07			0.1471	
Ti	*	4.508	0.04	0.30	0.01			0.0319	
Cu	*	8.040	1.23	1.51	0.37			1.0011	
Total			100.00		100.00				

Table 4. Microprobe data of 7075 aluminum alloy

Element		(keV)	mass%	Error%	At%	Compound	mass%	Cation	K
C		0.277	6.02	0.21	9.24			1.0662	
O		0.525	56.89	0.15	65.61			70.0062	
Na		1.041	0.28	0.17	0.22			0.2013	
Mg		1.253	0.64	0.10	0.49			0.4428	
Al		1.486	35.32	0.10	24.15			27.5841	
Si		1.739	0.06	0.14	0.04			0.0389	
K		3.312	0.04	0.17	0.02			0.0412	
Ti		4.508	0.05	0.25	0.02			0.0400	
Cu		8.040	0.24	1.29	0.07			0.1976	
Zn	*	8.630	0.47	1.89	0.13			0.3817	
Total			100.00		100.00				

As it is possible to see from Tables 2-4 main part of chemical elements in alloys are present at the surface of coatings. Potassium ions in the coatings are due to *KOH* in electrolyte. Existence of carbon in the structure of coatings it is possible to explain by presence of CO_2 in the air at using last in interfusion of electrolyte.

Testing of discharge voltage

Discharge voltage on the MPO coating was tested by direct current in the air. Positive contact was connected to metal and negative – to surface of coating. Each value of discharge voltage in the Fig. 8, 9 is average value of ten measurements for the each sample. As it follows from Fig. 8,9 discharge voltage depends on the thickness as equation : $U = Ah^{1/2} + B$.
Discharge voltage has similar behaviour for coatings of both (2024 and 7075) aluminum alloys.

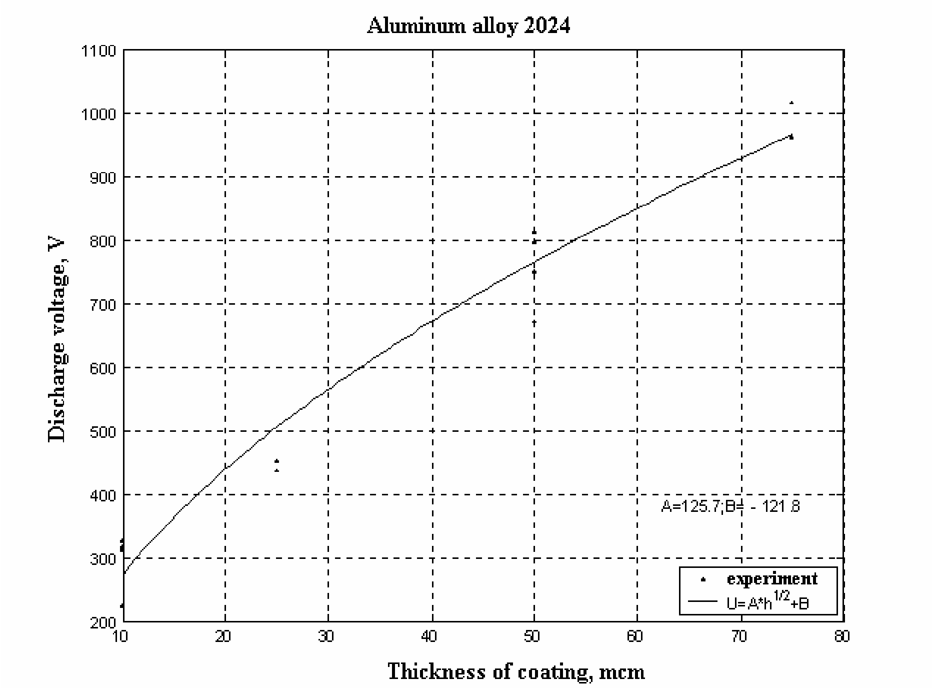


Fig. 8. Dependence of discharge voltage on the thickness of MPO coating. Aluminum alloy 2024.

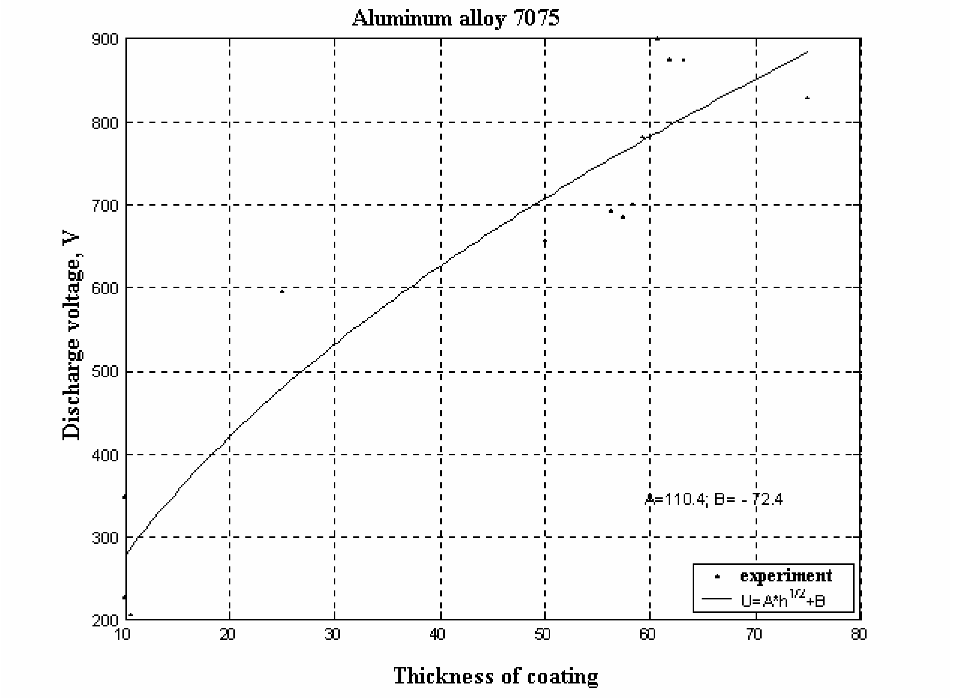


Fig. 9. Dependence of discharge voltage on the thickness of MPO coating. Aluminum alloy 7075.

EPR study of MPO coatings

In this part of our research we tried estimate changing of paramagnetic state concentration of transition metal ions in the structure of MPO coatings depending on thickness of MPO coating.

The main impurity in 2024 and 7075 aluminum alloys is copper. From the data of Table 2 it is possible to see that content of Cu in 2024 aluminum alloy is higher in two times than in 7075 alloy at the same content of manganese. EPR data of MPO coatings with thickness between 9 and 13 microns (see Fig 10, 11) show decreasing of copper ion concentration for the both aluminum alloys at the increasing of coatings. The ratio of copper ion concentration in 2024 and 7075 correspond to ration of copper concentration in aluminum alloys. Beginning from 25 microns of MPO coating thickness and higher concentration of copper ions in the coatings is constant. Little different picture we see for the MPO coating of 7075 aluminum alloy (see Fig.10, 11). At the increasing of coating thickness close to 10 microns we see also decreasing concentration of paramagnetic copper ions. Than, beginning 25 microns we see increasing concentration of paramagnetic centers. But beginning 25 microns in EPR spectra there is appeared spectrum of Mn^{2+} and this increasing of paramagnetic states is due to EPR spectrum of Mn^{2+}. Subsequent increasing of coating thickness shows constant concentration of total copper + manganese ions. Observed peculiarity in behaviour of concentration of copper paramagnetic state is explained by absence of paramagnetic properties of copper oxide (CuO). On the first step MPO process main part of copper ions have in coordination OH groups and have paramagnetic properties. At the increasing of coating thickness oxidation process proceeds at more hard conditions and all hydroxyl groups around copper ions are transformed and create copper oxides.

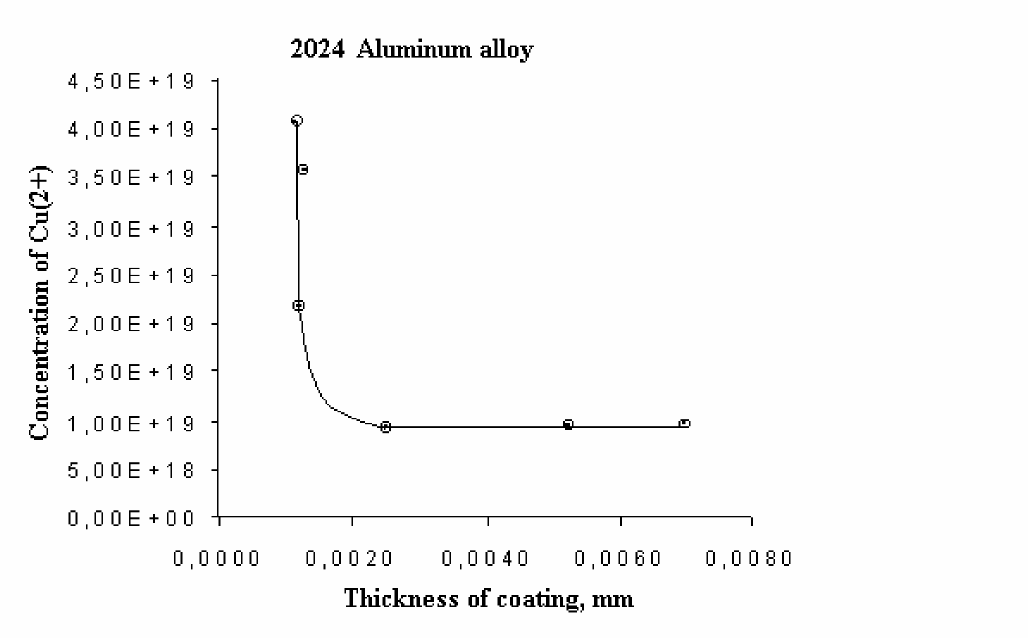


Fig. 10. Dependence of paramagnetic state of cupper ions on the thickness of MPO coating.

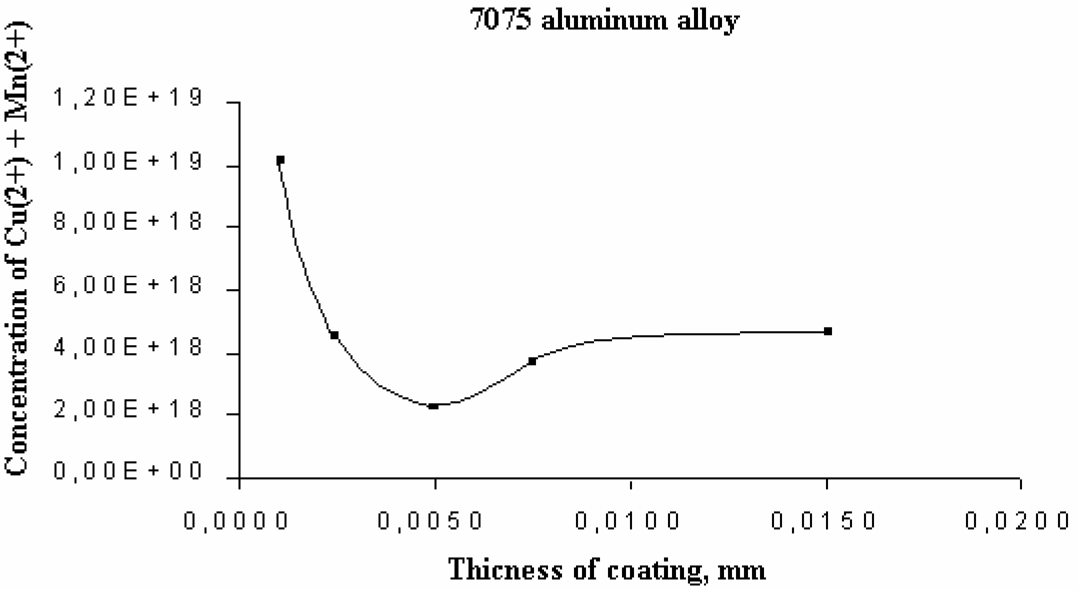


Fig. 11. Dependence of paramagnetic state of cupper and manganese ions on the thickness of MPO coating.

Production of samples for the testing in research laboratory of AFOSR/NL (USA)

According requirement of project we have prepared 25 samples of 2024 aluminum alloy with MPO coatings having next gradation of thickness: 5 samples with coating thickness 10 μ, 5 samples with coating thickness 25 μ, 5 samples with coating thickness 50 μ, 5 samples with coating thickness 75 μ, 5 samples with coating thickness 150 μ.

For the 7075 aluminum alloy there were prepared 25 samples with the same gradation and the same quantity. These samples will be sent in first days of January (after New Year celebration).