Corrosion-resistant MAO coatings on aluminum alloys

Pavel Butyagin
MANEL JSC, Tomsk

Introduction.

Aluminum and its alloys are used in many areas of industry. Due to its lightness, sufficient strength, ability to alloy with many other metals and good electrical conductivity, aluminum is used in electrical engineering, as well as structural material in engineering, aircraft and shipbuilding, construction of residential and public buildings, agricultural facilities and other industries.

The protective film formed on the aluminum surface defends the metal from oxidation. But for the long-term operation of products in different climatic conditions, this protection is not enough.

Almost every customer is interested in a coating that has a complex of properties. Corrosion resistance is a property that is found in combination with almost all others - electrical insulation properties, decorative appearance, wear-resistant, optically black.

There are many methods for obtaining protective coatings on aluminum alloys: anodic oxidation, phosphating, chromating, and others.

A promising method of protecting parts from aluminum alloys is microarc oxidation (MAO)

1. Microarc oxidation

MAO is a kind of electrochemical surface treatment, close in mechanism to anodizing. A distinctive feature is the participation in the process of forming a surface micro-discharge coating. The effect of high temperatures in the breakdown zone (~ 2000 ° C) for a short time (the discharge lifetime is hundreds of microseconds) leads to the formation of coatings substantially different in composition and properties from coatings obtained by anodizing. Most MANEL customers use MAO coatings as a replacement for anodized coatings.

2. Comparison of anodizing and MAO MANEL

Production of MAO-coatings by MANEL for seven years, has allowed accumulating a significant technological experience. Table 1 shows the advantages and disadvantages of the two technologies - anodizing and microarc oxidation.

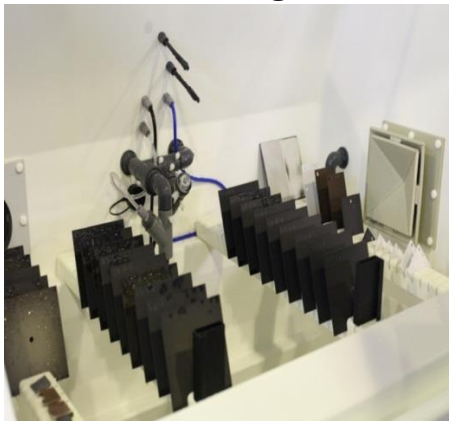
Table 1. Comparison of Anodization and Microarc Oxidation MANEL

characteristics	**Anodization**	**MAO MANEL**
Ecology		
Electrolytes	Highly concentrated solutions of sulfuric acid	Weak alkaline solutions pH = 8-8.6, in composition are close to the detergent powder. There are no heavy metals in the solution, chromium (VI)
Power consumption, kW / m^2	0,17	0,12
Technological operations		
Degreasing	+	+

Washing in warm water	+	+
Etching	+	-
Washing in warm water	+	-
Rinsing in cold water	+	-
Lightening	+	-
Rinsing in cold water	+	-
Coating process	+	+
Rinsing in cold water	two baths	one bath
Sealing	+	+
Total	10	5
Rate of coating formation, μm / min	0,45	1-1,5
Properties of coatings		
Adhesion of polymeric materials GOST 15140 (evaluation by the method of notches), scores	1	1
The thickness of the coating, μm	Up to 60	Up to 150
Microhardness, HV	Up to 500	Up to 2200
Porosity,%	10-26	1-26
Roughness Ra, Rz, μm	Ra 1,2-1,4	0,8-4
	Rz 7-8	5-25;
Temperature resistance, ° C	Up to 100 (GOST 9.303-84)	Up to 300
Thermocyclicity at t = 280 ° C, GOST 9.302-88 cycles	Depends on the coating type	100
Wear resistance according to Taber (10,000 cycles, 40 μm, weight in mg), TWI according to ISO 10074-2010 and ISO 8251-2011	2	7
Coefficient of friction	-	1,1-0,4
Breakdown voltage, V (according to GOST 6433.3-71)	Up to 600	1700
Specific resistance, Ohm · m (according to GOST 6433.3-71)	10^7-10^12 (GOST 9.303-84)	10^9
Degree of blackness (for black coating),%		93,3
Corrosion resistance in neutral salt fog, hours (GOST 9.308-85, method 1)	Up to 480	720÷1000

3. Testing of MAO coatings MANEL for corrosion resistance

All tests of the samples were carried out in a chamber of **salt fog** Ascott CC450**.**



a b

Fig.2

a- Ascott CC450 chamber for corrosion resistance testing, b - sample placement in the chamber

1.1. Tests in accordance with GOST 9.308-85, method 1 (neutral salt fog).

In 2012, the first tests of MAO-coatings MANEL were carried out in the Promethey Research Institute (St. Petersburg) - Coatings MANEL on the EN AW-5251 alloy in accordance with GOST 9.308-85, method 1 (neutral salt fog).

The change in the state of the coatings was determined by visual inspection after 24, 72, 120, 240, 480, 720 and 1000 hours of testing. After 1000 hours of testing, corrosion damage was assessed for the percentage of the area affected by corrosion, with respect to the evaluated surface of the part.

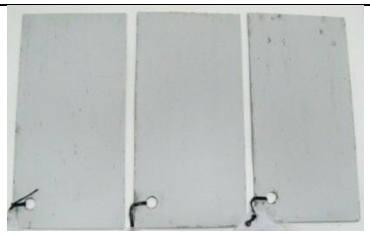
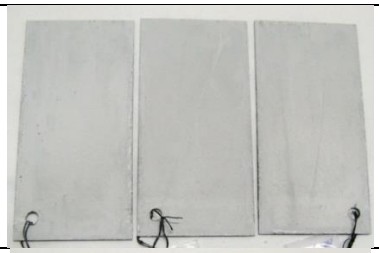
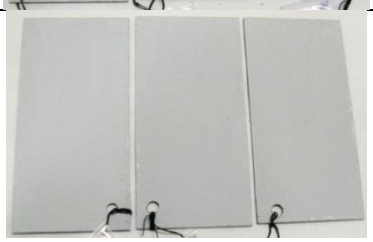
Table 2 shows photographs of the samples before the corrosion resistance tests and after the tests.

Table 2. The MAO coatings on EN AW-5251 alloy before and after corrosion tests

MAO Coatings MANEL	Appearance of samples before testing	Appearance of samples after testing
MANEL - W		
MANEL - B		

Also, the tests were carried out on EN AW-2024, EN AW-7075alloys.

Table 3 Corrosion test results on EN AW-2024, EN AW-7075 alloys

Alloy and coating thickness	Appearance of samples before testing	Appearance of samples after testing	Number of hours
EN AW-7075, 10 µm			480
EN AW-7075, 40 µm			480
EN AW-2024, 10 µm			100
EN AW-2024, 40 µm			1000

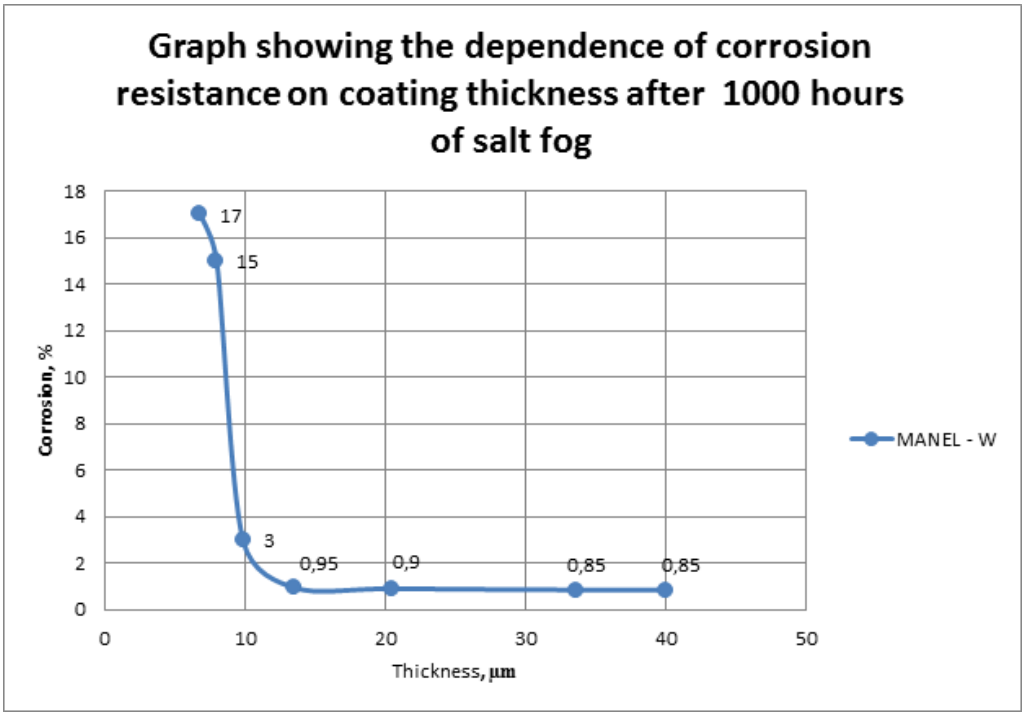


Fig.1 Corrosion resistance of MAO coatings MANEL depending on coating thickness

According to the results of tests of MAO-coating on EN AW-5251, thickness over 30 µm, withstood more than 720 hours of testing.

MAO coatings at a thickness of 40 µm withstood 1000 hours of tests in salt fog

4. Study of the resistance of coating samples to the effect of mold mushrooms according to GOST 9.048-89

The research was carried out at the Institute of Ecology and Evolution, A.N. Severtsova.

4.1. Method of testing

Conducting material research on the resistance to mold fungi, especially the new coatings developed, is an important part of increasing their resistance to bio deterioration. Bio-damage is implied when living organisms, by their vital activity, cause changes (disturbances) in the structural and functional characteristics of objects and materials.

Mushroom resistance of coating samples under laboratory conditions was evaluated in accordance with GOST 9.048-89 and GOST 9.050-75.

For the tests, a spore suspension of test cultures of fungi with a concentration of 1-2 million / ml was prepared**:***Aspergillus niger* van Tieghem, *Aspergillus terreus* Thom, *Aspergillus oryzae* (Ahlburg) Cohn, *Chaetomium globosum* Kunze, *Paecilomyces varioti* Bainier, *Penicillium funiculosum* Thom, *Penicillium chrysogenum* Thom, *Penicillium cyclopium* Westling, *Trichoderma viride* Pers. ex Fr. In addition, the test culture of fungi recommended by GOST 9.050-75 was introduced into the suspension, *Alternaria alternata* (Fr.) Keissler and *Fusarium moniliforme* Sheldon.

Spraying of spore mold spores was carried out in a box using a spray gun, making sure that the droplets of the suspension did not merge. The suspension was sprayed onto both sides of the samples. After applying the suspension, the samples were kept in the box until the droplets dried (not more than 60 minutes). Infected samples were placed in open Petri dishes in a desiccator, the bottom of which was filled with water, and the desiccator, closed with a lid, was placed in a thermostat. At that, the incubation regimes optimal for growth of fungi were maintained: temperature (29 ± 1) ° C and relative humidity not more than 90% for 28 days. Interim inspections of the samples (visually and with microscopy) were performed after 14 days. The results of the

evaluation of the resistance to mold mushrooms exposure of coating samples after 28 days of testing are shown in Table 4.

Table 4. Results of MAO-coatings MANEL tests on mushroom resistance

№	Type of MAO-coating MANEL	Sample material, aluminum alloy	Appearance of coatings after testing	Score in accordance with GOST 9.048-89
1	Black	EN AW-2024	Under a microscope: spores of spores and conidia are not found	0
2	White	EN AW-2024	Under the microscope: spores of spores and conidia are not found, on the surface are traces of the suspension	0
3	White	EN AW-5251	Under a microscope: sprouted spores and slightly developed mycelium	1
4	White	EN AW-2024, impregnation by PTFE	Under a microscope: spores of spores and conidia are not found	0
5	White	EN AW-2024 impregnation by Cramolin Urethane	Under the microscope: sprouted spores of mushrooms	1

For 28 days on coatings Nos. 1, 2, 4 visually and under the microscope sprouting spores of fungi and development of the mycelium was not observed, their mushroom resistance was rated 0.
On coatings Nos. 3 and 5, after 28 days of testing, sprouted spores of fungi were detected under one microscope on one of the three samples, their mushroom resistance was estimated by a score of 1. The normalized value of the degree of biological fouling of coatings is no more than 2 points. According to the normative documents, these coating samples also have been tested for mushroom resistance, but do not possess fungicidal properties (ie biocidal action against mold fungi).
Thus, all investigated coatings of the "Manel" type tested for mushroom resistance in accordance with GOST 9.048-89 passed the test.

5. Application of MAO-coatings MANEL for protection against corrosion

5.1. Sublayer for subsequent polymer staining:
The coating thickness is 5-15 μm.
Provides adhesion of polymeric materials
in accordance with GOST 15140-78
Corrosion resistance in salt fog 720 hours

5.2. Black coating:
• Coating thickness 40 μm
• Degree of blackness - 0.94
• Corrosion resistance in salt fog 1000 hours
For optical instruments



5.3. For Instrumentation industry
Protective-decorative coatings
• Coating thickness 20 - 70 μm
• Corrosion resistance in salt fog 1000 hours
• Coating on alloys: EN AW-2024, EN AW-5251, EN AW-5356, EN AW-3003, EN AW-6063, EN AW-7075 and cast alloys 355.0, 357.0, A13600, A14130