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CHARACTERISATION OF OXIDE COATINGS PRODUCED ON ALUMINUM ALLOYS BY MAO AND CHEMICAL METHODS

The study compared the properties of oxide coatings formed on aluminium alloys produced by: MAO (micro – arc oxidation), and the chemical method (oxidation in acid). Morphology, microstructure and of the coatings was analysed with a scanning electron microscope SEM. Corrosion resistance were tested in potentiometer – dynamic. The layers produced by MAO significantly improved corrosion resistance. Coatings produced after 3 minutes of oxidation had better corrosion resistance than the coatings after 5 minutes of oxidation. The layers produced by chemical method didn't improve corrosion resistance of aluminium alloy.

Keywords: MAO, chemical method, corrosion resistance, aluminium alloys, Al_2O_3

1. Introduction

Aluminium is widely used due to its low density and low cost compare to. Titanium. Pure aluminium is a soft material of low strength. Aluminium has a high affinity for oxygen therefore encrusts with a passive oxide film. The natural oxide is not effective protection for the material against corrosion, this is due to the small thickness of the low resistance to abrasion and long-time sealing pores that can absorb water from the air and accelerate the corrosion process. Therefore, the construction materials of aluminium alloys are covered by artificially produced oxide layer that provides protection against corrosion and improves abrasion resistance. Oxide layers also have a decorative character.

Layer on the aluminium material can be prepared by various technologies, the most commonly used are:

- Mechanical and thermo-mechanical (application layer roller, plating by rolling, plating, galvanizing, plating, plasma spraying and detonation)
- Chemical (nitriding, phosphate coating, chrome plating, oxidation, deposition of the metal layers, eg. Ni, Cu, Cr, Fe, etc.)
- Electrochemical
- Physical-chemical deposition PVD (physical vapour deposition, CVD (chemical vapour deposition) [1].

By applying these technologies is increased corrosion resistance, abrasion resistance and improved adhesion properties.

The properties of the surface layers of aluminium alloy can be varied by changing the chemical composition of the alloys and their heat treatment [1].

The main task of the layers produced by chemical methods is corrosion protection. The thickness of layers produced by this method is greater than that produced naturally. Nitriding, chromium and phosphate coating are methods with dry contact, whereas the oxidation and deposition of the metal layers may occur due to chemical reactions and electrochemical phenomena [1]. To produce layers by chemical method no complicated aperture or highly specialized staff is required and process temperature is low.

Method MAO (*Micro-Arc Oxidation*) is an electrochemical method with high performance and significantly improves the corrosion resistance of the material [2-4]. Micro discharge formed at the surface of the material have a strong relationship with the properties of the resulting layer, the phenomena occurring during the process have been described by R.O. Hussein'a [5]. Studies have shown that the frequency of the discharge is dependent on the electrolyte used [6-9]. Layer in the plasma oxidation process is formed in a two-stages, which was observed by X.H. Liu [10]. No porosity, no need for additional treatment and no toxic electrolyte make the MAO method superior to conventional anode oxidation. Aim of the paper was comparing layers formed by MAO and chemical method. Many industries like aerospace, marine, automotive are interested Al_2O_3 layers on light materials due to their high hardness excellent wear and corrosion resistance also high thermal and chemical resistance.

2. Methodology

Oxide layers were produced on aluminium alloy by using the chemical and MAO method. Surface of specimen was polished down to an average roughness of 0,5 μm using SiC abrasive paper. Cleaned in acetone charged ultrasonic cleaner

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and rinsing in deionized water, dried in air. Prepared specimens were then directly transferred to the layers bath.

In the process of the MAO was used Na2SiO4 + KOH solution, electrolyte temperature of $T = 22°C$, the voltage was slowly increased from 80 V to 400 V. Process time $t_1 = 3$ $t_2 =$ min and 5 min.

The chemical method uses two nitric acid concentrations of 1:1 and 1:8. Samples were immersed for 24 hours in an acid solution at a temperature of $T = 25°C$. Sample without layer and alloys with layer were subjected to the corrosive environment. For the analysis of the structure, chemical composition and phase, the following test methods: SEM (FEI Inspect S50) together with an analysis, optical profiler (WYKO NT930).

TABLE 1

Naming of produced coatings

Method	MAO_t[min]	Chemical [concentration]
Alloy 2017	MAO_2017_3	x
Alloy 2017	MAO_2017_5	x
Alloy 5083	x	CH_5083_1:1
Alloy 5083	x	CH_5083_1:1

3. Results and discussion

The surfaces of the samples are shown in Fig. 1. Samples CH_5083_1:1 and CH_5083_1:8 were immersed in nitric acid for 24 hours at two concentrations 1-1 and 1-8.

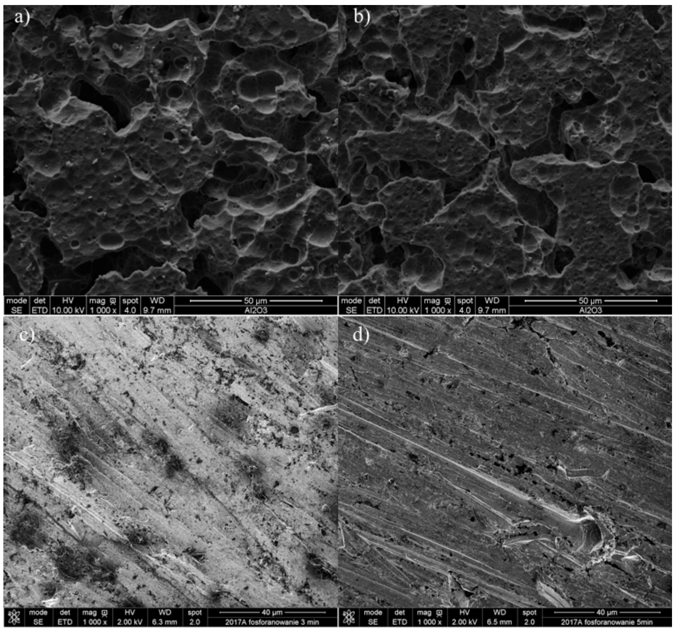

Fig. 1. a) CH_5083_1:1 b) CH_5083_1:8 c) MAO_2017_3 d) MAO_2017 _5

Surface of the samples differ from each other significantly, the layer produced in the chemical method is porous, showing many irregularities and pits caused by impacts in acid material (Fig. 1a,b) while the layer formed from by MAO does not have pits and pores (Fig. 1c,d).

The cross section of the layers is shown in Fig. 2. The layer is cracked and did not cover the entire sample Fig. 2a,b in Fig. 2c,d can be seen, that the layer covered the entire surfaces of the alloy. Photos confirm earlier research about the structure of the layers produced by MAO. During the oxidation of the samples MAO_2017_3 continuous compact layer is formed over the entire length of the sample. When the process lasting five minutes layer is thicker but there is more visible cracks and two section are present in the layer. The layers produced by MAO produced in two stages as seen in cross-section layers of Fig. 2d.

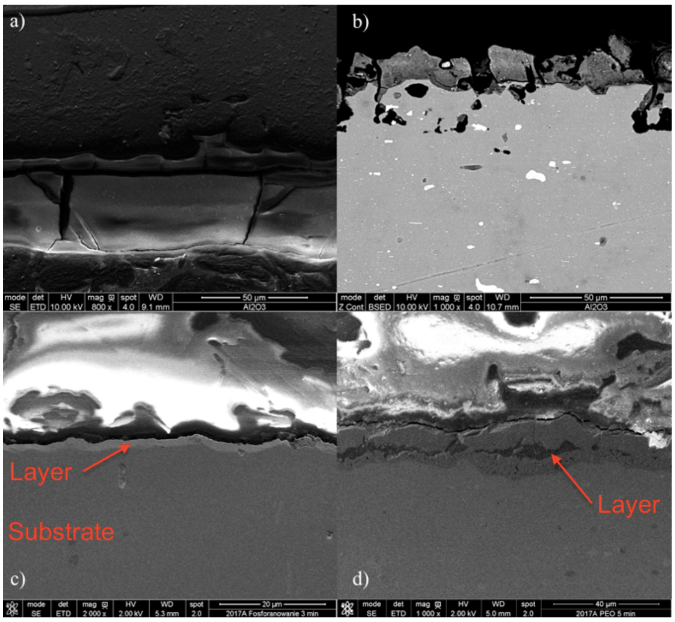

Fig. 2. a) CH_5083_1:1 b) CH_5083_1:8 c) MAO_2017_3 d) MAO_2017 _5

Optical profilometer results are shown in Table 2. The tests were carried out on sample without layer and samples after the formation of the layers and then all samples were subjected to corrosion. After the corrosion process, all samples were examined on the profilometer again in order to compare changes in parameter *Ra*, which made it possible to determine the corrosion resistance.

TABLE 2

Ra parameter before and after corrosion test

After corrosion, average *Ra* (μm)		
Clean	3 min	5 min
0,967	3,82	4,62
After corrosion test, average *Ra* (μm)		
5,05	9,57	14,1
Percentage increase		
522%	251%	305%

The pure sample had the largest increase in roughness (522%), the second largest increase (305%) recorded sample after the oxidation of 5 minutes. Sample 3 minutes after oxidation had the smallest increase in roughness (251%). The sample without the layer was not protected against corrosion, and this is the reason of such a big change of Ra parameter. The difference in the change in roughness of the samples after 3 and 5 minutes of oxidation may have result in different layer structure. The sample after 5 minutes of oxidation has cracks and is divided into two clearly separated layers, which may reduce the corrosion resistance. Layer formed after 3 minutes of oxidation has a uniform construction tightly covers the entire sample and has no cracks, so is the best to protect the material from corrosion of all samples.

Polarized corrosion test are shown on the Fig. 3,4.

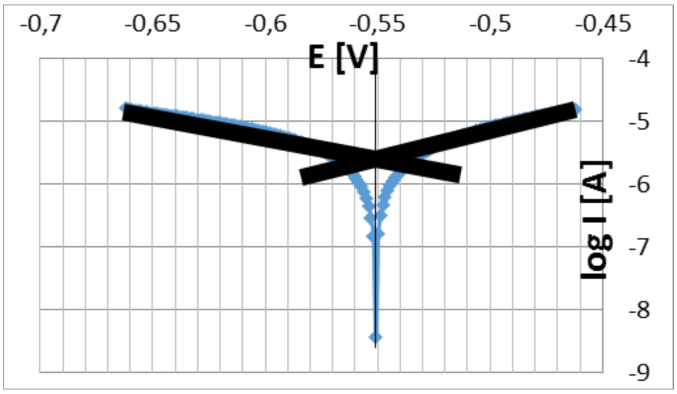

Fig. 3. Potentiodynamic research of MAO_2017_3

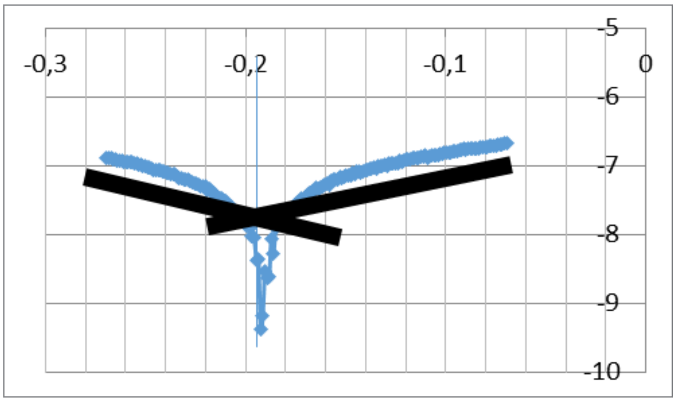

Fig. 4. Potentiodynamic research of MAO_2017_5

MAO_2017_3 sample has corrosion potential shifted to more negative values with respect to the sample MAO_2017_5. MAO_2017_5 exhibits better corrosion resistance than the MAO_2017_3. This is due to the higher thickness, the absence of cracks and lower number of pores in the layer of oxidation after 5 minutes.

Time of process had an impact on the change in the chemical composition produced layers, the sample MAO_2017_5 has peak of Si that has entered in to the layer from preparation process (Fig. 5b). In the layer after 3 minutes Si does not appear (Fig. 5a). Chemical composition are proved by means of EDS. All layers contain Al and Oxygen, Cu and Mg peaks comes from substrate (Fig. 5).

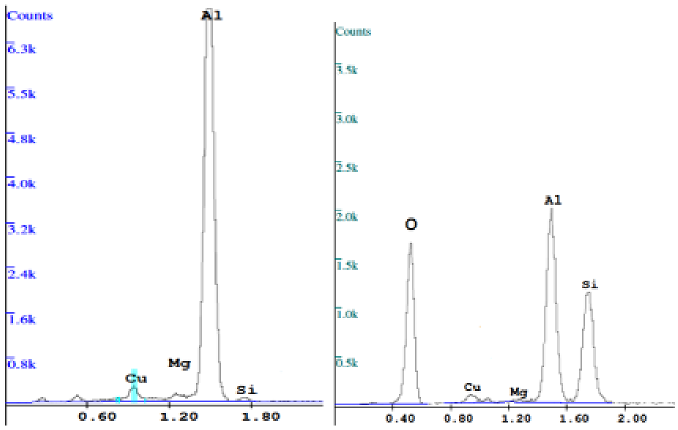

Fig. 5. EDS of a) MAO_2017_3 b) MAO_2017_5

4. Conclusion

MAO method improves the corrosion resistance of aluminium alloys, Time 3 and 5 minutes is sufficient to cover entire surface of the material. Sample with highest corrosion due to polarized corrosion test was MAO_2017_5. Research on profilometer indicated higher corrosion resistance of sample MAO_2017_3 but difference in Ra parameter fit in measurements error. That's why results from polarized corrosion test is more reliable. The layers produced by chemical method is not applicable technology. The sample was not completely covered with a layer, layers has a lot of cracked and pours and does not offer any protection against corrosion. MAO method is a promising alternative to conventional electrochemical methods because of the non-porous layer structure, high corrosion resistance, good adhesion to the substrate. In the plasma oxidation method electrolyte is friendly to the environment which is a further advantage of this method.

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