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Mateusz Jędrusik, Aleksandra Dębowska, Agnieszka Kopia, Paweł Petrzak, Damian Kocłęga, Izabela Kalemba-Rec

Characterization of oxide layers made on aluminum alloy 7075 by different methods

Charakterystyka warstw tlenkowych wytworzonych na stopie aluminium 7075 z zastosowaniem różnych metod

Abstract

Aluminum and aluminum alloys are now being widely used as materials for structural applications due to a number of valuable properties. Improvement in the functional and decorative properties of aluminum can be obtained by forming an oxide layer on its surface. The aim of the present study was to produce and compare the properties of oxide layers on the surface of aluminum alloy 7075 and compare their properties. The methods that were used during the study were as follows: phosphating, micro-arc oxidation, and a chemical method involving the formation of a passive layer. The layers were subjected to corrosion tests. SEM and EDS methods were used for characterization of the received results. Also, some tests on an optical profilometer were done. It was proven that the micro-arc oxidation method allowed us to obtain a layer with the greatest thickness and highest corrosion resistance.

Keywords: oxide layers, aluminum alloy 7075, micro-arc oxidation, phosphate coating, the chemical method

Streszczenie

Glin i jego stopy są obecnie powszechnie wykorzystywanym materiałem do zastosowań konstrukcyjnych ze względu stosunek masy do wytrzymałości. Poprawę własności funkcyjnych i dekoracyjnych aluminium uzyskać można przez wytworzenie warstwy tlenku na jego powierzchni. Celem badań było wytworzenie warstw tlenkowych na podłożu ze stopu aluminium 7075 i porównanie ich właściwości. Zastosowano trzy metody: fosforanowanie, micro-arc oxidation oraz metodę chemiczną polegającą na wytworzeniu warstwy pasywnej. Otrzymane powłoki poddano

Mateusz Jędrusik M.Sc. Eng., Aleksandra Dębowska M.Sc., Agnieszka Kopia D.Sc. Ph.D. Eng., Paweł Petrzak M.Sc. Eng., Damian Kocłęga M.Sc. Eng., Izabela Kalemba-Rec Ph.D. Eng.: AGH University of Science and Technology, Faculty of Metals Engineering and Industrial Computer Science, Krakow, Poland; mj.jedrusik@gmail.com

testom korozyjnym oraz charakteryzowano z zastosowaniem następujących metod: SEM, EDS. Wykonano też badania na profilometrze optycznym. Metoda micro-arc oxidation pozwala na uzyskanie warstwy o największej grubości oraz najlepszej odporności na korozję.

Słowa kluczowe: warstwy tlenkowe, stop aluminium 7075, MAO, fosforanowanie, metoda chemiczna

1. Introduction

Aluminum and its alloys have many very interesting properties that make this material valuable to many different industrial sectors, such as the aerospace, automotive, biomedicine, electronics, energy, textile, shipbuilding, machinery, and chemical industries [1–3].

Advantages of aluminum and aluminum alloys are as follows: low density, ease of modification of strength properties by adding other elements (light alloys), and approximately five-times-greater thermal conductivity than iron alloys. The use of this material will likely continue to grow in the future.

There are still many problems that often occur during aluminum's service life, such as poor wear resistance, corrosion resistance, and a low level of hardness [4]. To overcome these disadvantages, some surface treatments are used to improve the aforementioned properties; e.g., anodic oxidation, rare earth conversion coating, ion implantation, and laser processing [5–9].

Aluminum has a high affinity for oxygen, and a very thin passivation layer of aluminum oxide is produced naturally [10, 11]. This layer ensures resistance to atmospheric corrosion but is insufficient in providing resistance to the influence of alkalis and most oxidizing acids because of its amphoteric character.

One method to improve the surface properties of metals (e.g., corrosion resistance, abrasion resistance, and hardness) is to produce so-called "conversion coatings" [12]. These are oxide layers, chromate, or phosphate. Oxide coatings are usually produced during the electrolysis process called anodizing.

Another method used for the production of oxide layers on the surface of metals (aluminum, titanium, magnesium, etc.) and its alloys is Micro-Arc Oxidation (MAO), also known as Plasma Electrolytic oxidation (PEO) [13, 14]. This method is considered as one of the most promising methods of creating thick oxide coatings by an electrochemical process with plasma discharges and melting–sintering in the adequate electrolytes.

2. Methodology

The chemical composition of the 7075 alloy is presented in Table 1.

Table 1. Chemical composition of aluminum alloy 7075

Element	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Al
Quantity [%] wt	0.4	0.5	1.2–2	0.3	2.1–2.9	0.18–0.28	5.1–6.1	0.2	Bal.

Before the oxidation process, alloys were ground with SiC paper (gradation 400–800) and then washed in distilled water and ethanol.

The oxide layers on aluminum alloys were produced by three different methods. In the process of MAO, an Na_2SiO_4 and KOH electrolyte solution was used at temperature $t = 22°C$, the voltage was slowly increased from 80 V to 400 V, and the process time was as follows: $t_1 = 3$ min, $t_2 = 5$ min. During the phosphating process, the following reagents were used: 15% vol. HCl (Digestion), 5% vol. $C_2H_2O_4$ (activating bath), and Zn $(H_2PO_4)_2$ (phosphating bath). The process was carried out for 3 and 5 minutes on each sample.

In the chemical methods, the passive layer was produced in two nitric acid (V) concentrations: 1: 1 and 1: 8. Samples were immersed for 24 hours in an acid solution at a temperature of $t = 25°C$.

The layers and alloy 7075 were subjected to a corrosive environment. Alloys were submerged in 5% vol. HCl. The roughness parameters before and after corrosion test were then measured and compared.

For analysis of the structure and chemical composition, the following methods were selected: SEM (FEI Inspect S50), together with an analysis of EDS and optical profiler (WYKO NT930). The symbols used to denote the produced layers are presented in Table 2.

Table 2. Symbols of produced layers

Method		
MAO_t [min]	**Chemical_[concentrations]**	**Phosphating_t [min]**
MAO_3	CH_1:1	PH_3
MAO_5	CH_1:8	PH_5

3. Results and discussion

SEM images of the surfaces of the produced layers on aluminum alloys are presented in Figure 1. The layers produced by different methods have radically different microstructures. The layer formed by the chemical method is porous, as many irregularities (pits and cracks) caused by impacts in the acid are visible (Fig. 1a/b); however, the layers produced by MAO have non-porous microstructures without cracks and pits (Fig. 1c/d). The layer formed by phosphating also has no visible cracks nor pores (Fig. 1e/f).

The cross section of the chemical and MAO layers are presented in Figure 2. The chemical method does not guarantee the production of a tight layer (Fig. 2a). The layers that were prepared at a concentration of 1:8 are thicker and covered more than the layers formed at a concentration of 1:1 acid. The MAO method made it possible to produce layers that covered the entire surface of the alloys (Fig. 2b). The figures confirm earlier findings about the structure of the nonporous layers produced by MAO. During the three minutes of oxidation, the formed layer can be divided into two parts. The first layer closer to the substrate is cracked and is thinner than the second one (which is thicker and free of cracks). When the process lasted five minutes, the layer is thicker, but more cracks are visible in the layer. The layers produced by MAO had two areas (Fig. 2b).

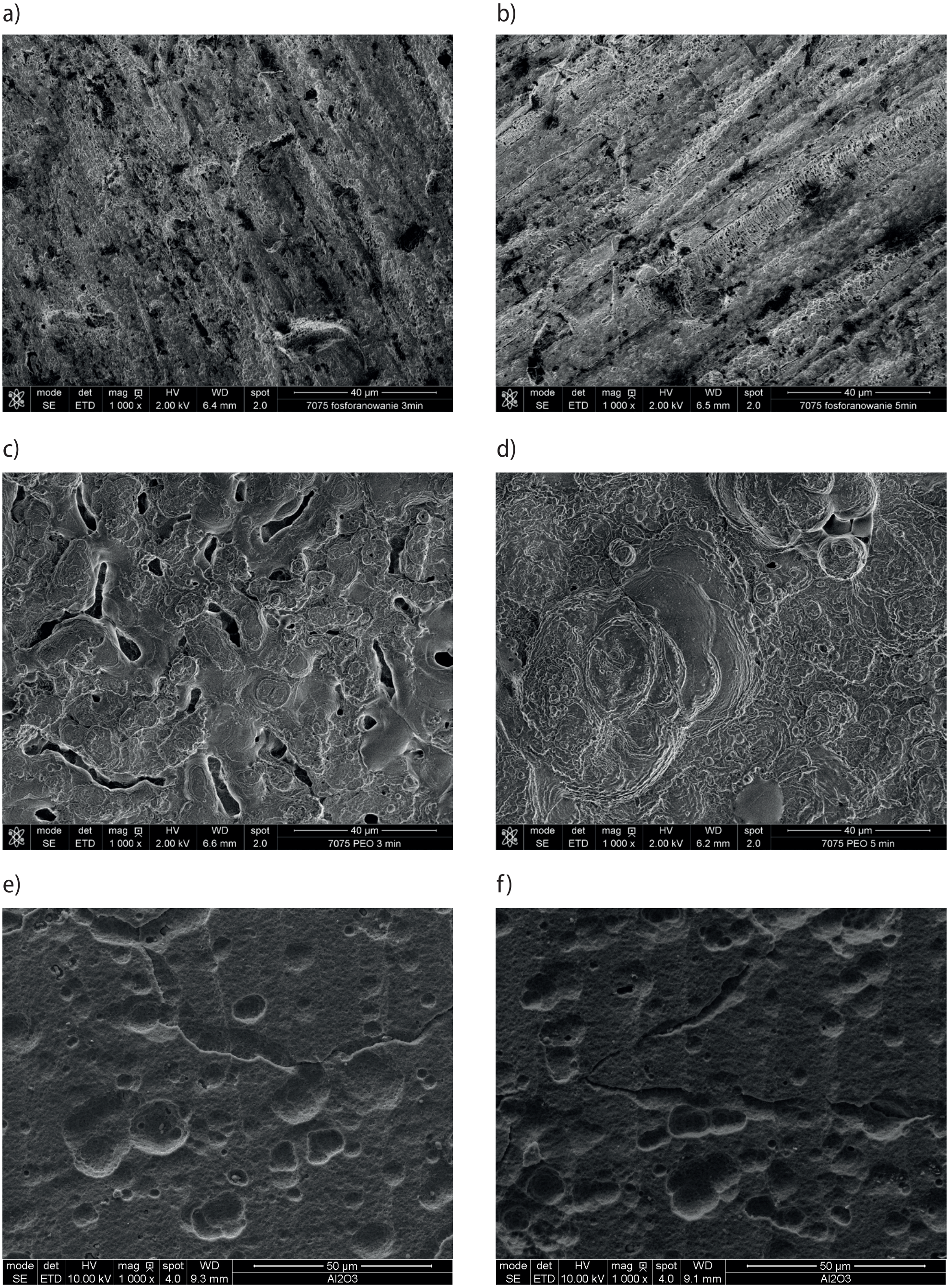

Fig. 1. SEM micrograph of the surface of: a) CH_1:1; b) CH_1:8; c) MAO_3; d) MAO_5; e) PH_3; f) PH_5

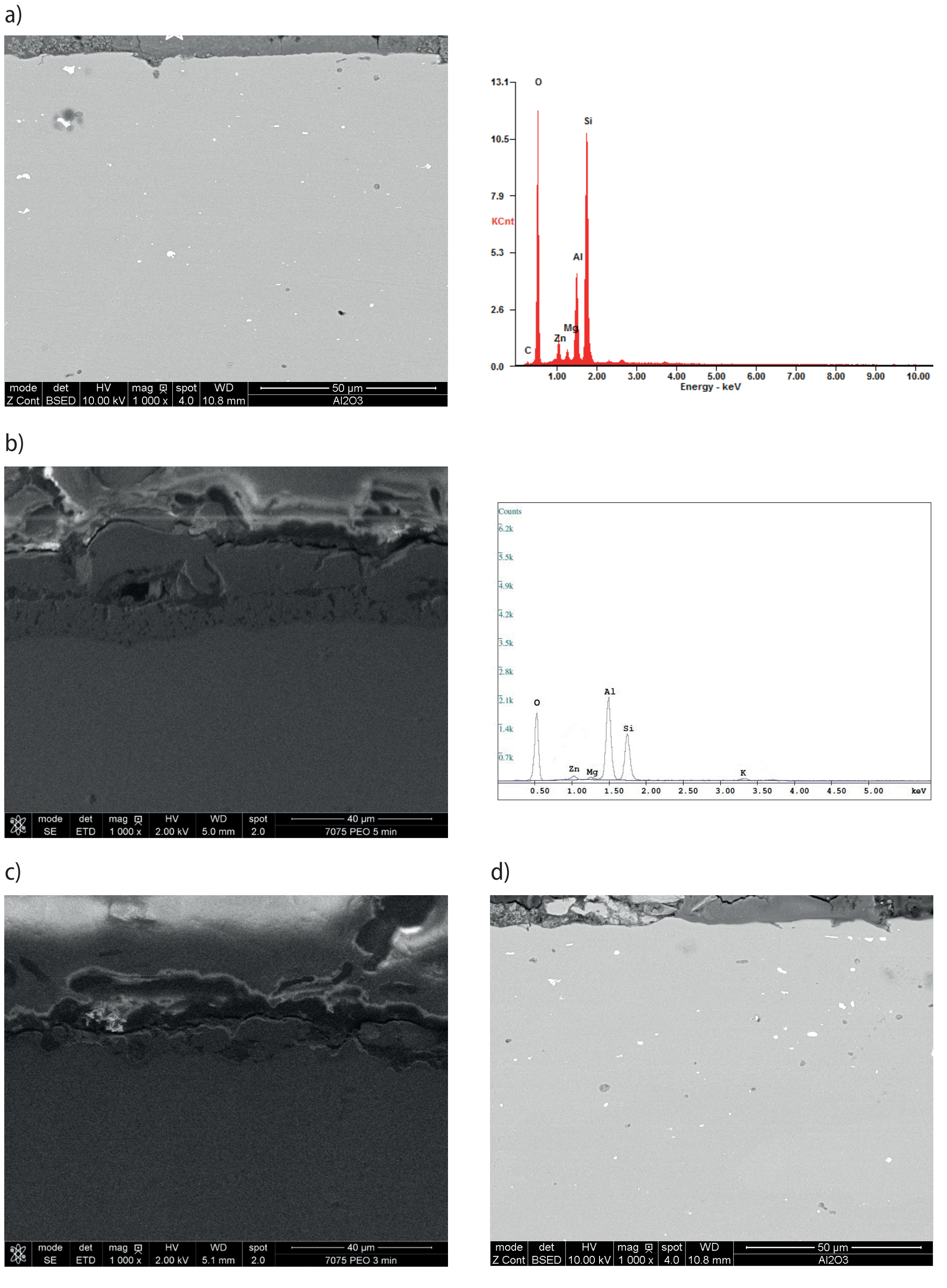

Fig. 2. SEM structure of layer cross section a) CH_1:8; b) MAO_5; c) MAO_3; d) CH_1:1

The EDS method helped us to determine the chemical composition of the produced layers. The layers formed by the chemical method formed a layer contains Si, Al, and O instead of the expected Al and O. Such a high content of Si can be the result of the sample preparation process.

The average roughness parameters *Ra* of the sample that were determined by an optical profilometer before and after the corrosion test are presented in Table 3. The roughness *Ra* was analyzed on untreated alloy 7075 samples as well as after formation of the layers. Then, all samples were subjected to corrosion. After the corrosion process, all samples were examined by the profilometer again, and the *Ra* parameters were compared to determine the corrosion resistance of the samples.

Table 3. Average roughness parameter Ra calculated before and after corrosion test

Parameter	**Original alloy 7075**	**Method**			
		MAO		**Phosphating**	
Time [min]	0	3	5	3	5
Roughness *Ra* before corrosion [μm]	0.62	3.61	5.07	0.94	0.83
Roughness *Ra* after corrosion [μm]	38	4.22	5.1	19.08	26.69
Roughness increase [%]	6129	117	101	2030	3216

The sample of 7075 alloy without any layer had the largest increase in roughness (6129%), and the second largest increase (3216%) was recorded for the sample after five minutes of phosphatizing. The sample after three minutes of phosphating had the smallest increase in roughness (2030%). The measurements results above indicate that alloy 7075 was the least resistant to corrosion as evidenced by the biggest change in the *Ra* parameter. The sample with the MAO layer had the smallest change of parameter *Ra* corresponding to samples after three- and five-minute oxidation are 117% and 101%, respectively. The difference in the roughness change for the sample after three and five minutes of oxidation may be due to the different thicknesses of the layers. The layer formed by oxidation for five minutes by MAO is significantly thicker than the layers produced by the process lasting three minutes. Cracks found in the first two layers from the method of MAO did not have an adverse effect on corrosion resistance. Changes at levels of 17% and 1% in the roughness lead to the conclusion that the corrosion resistance of alloy 7075 is improved significantly by the presence of an MAO layer. These results confirm the poor corrosion resistance of alloy 7075 as a result of the addition of copper. The phosphating method improves corrosion resistance, but only to a small extent; also, the *Ra* parameter was increased significantly after the corrosion test, so this method is not an effective one to protect the 7075 alloy against corrosion. The layers produced by MAO have very high corrosion resistance.

4. Conclusion

Three different methods of producing an oxide layer on the 7075 aluminum alloy were used and compared: the chemical method, phosphating, and MAO. The microstructures of the layers produced by these methods are radically different. The chemical method was not effective in producing a good-quality passive layer that provides protection against a corrosive environment. On the contrary, the other methods achieved the expected results. The oxide layers obtained by MAO have greater thickness and better corrosion resistance than the layers prepared by phosphating.

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