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Plasma Coatings on Aluminium-Silicon Alloy Surfaces

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Abstract

Plasma oxidation, similarly to anodic oxidation (anodizing), are classified as electrochemical surface treatment of metals such as Al, Mg, Ti and their alloys. This type of treatment is used to make surface of castings, plastically processed products, shaped with incremental methods to suitable for certain requirements. The most important role of the micro plasma coating is to protect the metal surface against corrosion. It is well known that coating of aluminium alloys containing silicon using anodic oxidation causes significant difficulties. They are linked to the eutectic nature of this alloy and result in a lack of coverage in silicon-related areas. The coating structure in these areas is discontinuous. In order to eliminate this phenomenon, it is required to apply oxidation coatings using the PEO (Plasma Electrolytic Oxidation) method. It allows a consistent, crystalline coating to be formed. This study presents the mechanical properties of the coatings applied to Al-Si alloy using the PEO method. As part of the testing, the coating thickness, microhardness and scratch resistance were determined. On the basis of the results obtained, it was concluded that the thickness of the coatings complies with the requirements of conventional anodizing. Additionally, microhardness values exceeded the results obtained with standard methods.

Keywords: Plasma electrolytic oxidation, Al-Si alloy, Anodizing

1. Introduction

The exceptional popularity of aluminum alloys in aerospace and automotive sectors is primarily due to the high strength-to-weight ratio, easy workability, and low cost. Despite the ability to passivate (to create a natural protective layers in the form of oxides), aluminum alloys are susceptible to various types of local corrosion, such as stress corrosion cracking, pitting corrosion, intergranular corrosion and exfoliating corrosion, that appears especially under extreme conditions [1]. Problem concern both alloys for plastic processing, casting alloys [2, 3], aluminum alloys based composites [4-6], as well as aluminum and its alloys used for additive shaping (3D printing) [7].

One of the most popular methods of their protection consists in the application of protective coatings. In most cases, aluminium alloys covered with a conversion coating – the coating requiring electrolyte – very often in the form of concentrated acid [1]. When an electric current flows through the electrolyte, the top alloy layers oxidise and form a protective coating. Such coatings are tight since the volume of metal oxide is greater than the volume of the oxide itself. For aluminium and silicon alloys, the coating application becomes difficult as the silicon content increases. It occurs due to the lack of reaction of sulphuric acid with eutectic silicon present in the alloy. Thus, the surface being covered includes void areas extending as the silicon content in the alloy increases. The discontinuities reduce both physical and anti-corrosive resistance of the coating.

One of the methods permitting the application of coatings on aluminium alloys irrespective of the silicon content is the Plasma Electrolytic Oxidation (PEO) method [8-13]. Plasma electrolytic oxidation (PEO) occurs as micro-arc oxidation (MAO) [14], spark anodization [15] or anodic spark deposition (ASD) [16]. Some authors call it the electrochemical microplasma process [17-18], and in many cases also microplasma oxidation (MPO) or micro-arc oxidation (MADO) [1]. Due to the application of both process voltage with values up to 1000V and alkaline electrolytes, this method enables to oxidise simultaneously surfaces of alfa-Al and eutectic Si. The utilisation of high voltage enables a thicker coating to be produced than in standard anodizing process. As a result, a ceramic coating is formed. The advantages of such oxide layer are strong adhesion to the surface, good wear and corrosion resistance [19-22]. Moreover, this protective coating is distinguished by integrity and tightness [23-24]. The coatings produced using the PEO method, similar to the coatings produced under standard anodizing method, are porous, which allows them to be covered with an additional dye.

The subject of the testing carried out as part of this study are coatings produced on aluminium alloy AlSi9Cu3(Fe) using the Plasma Electrolytic Oxidation (PEO) method. Their aim was to verify mechanical properties (thickness, microhardness and scratch resistance) of the coatings, so that the material with a properly applied coating performed its function under specified operating conditions. A schematic diagram of film electrodeposition is shown in Figure 1.

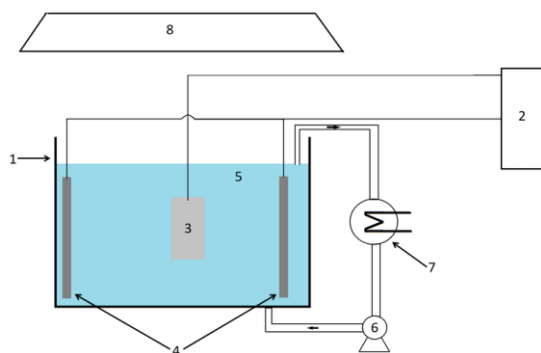


Fig. 1. A schematic diagram of film electrodeposition: 1) Electrolytic tank, 2) High voltage AC power source, 3) sample (anode), 4) cathode, 5) electrolyte, 6) electrolyte pump (stirring system), 7) heat exchanger, 8) vapors extraction hood

2. Materials and Methods

Mechanical properties of the oxidized surface were tested on the commercial AlSi9Cu3(Fe) alloy, cast into a permanent mold – die. Two types of specimens were made: specimen 1 with plasma oxidation coating and specimen 2 of black plasma dyed oxidation.

The oxidation coating was produced using the Plasma Electrolytic Oxidation (PEO) method. Surface of the substrate was not preliminary degreased for keeping the surface of the specimens in as-cast condition. The coating was applied in an electrolyser in which electrolyte in the form of a solution containing sodium

hydroxide (2 g/L NaOH) and sodium silicate (10 g/L Na₂SiO₃) was used. During the PEO process, the samples and the wall of the stainless steel container were used as the anode and the cathode, respectively. The electrolyte temperature was maintained below 20°C using a cooling system. During the tests, constant current density at the level of 5 A/dm² and voltage between the electrodes amounting to ~ 420 V were maintained.

The thickness of the oxidation coatings produced on the sample surfaces was measured using Nikon Eclipse LV150 optical microscope by determining the coating width in several randomly selected locations.

The morphology and topography of the coating surfaces produced using the PEO method were analysed on Dual Beam FEI Scios scanning electron microscope.

Substrate adhesion tests were executed and other mechanical damage were determined during the scratch test using a Rockwell penetrator. This test was carried out on a multi-purpose measuring station provided with an Anton Paar scratch test head according to PN-EN 2536:1997. The scratch was 5 mm long. The tests were carried out using a Rockwell C diamond indenter with a fillet radius of 100 µm under linear increase of normal force applied to the penetrator in the range of 1–20 N. The indenter travel velocity was 5 mm/min. During this test, indenter penetration depth Pd, post-scratch depth Rd, force applied to the indenter FN and acoustic emission signal Ae were measured. Hardness of the coatings was determined using the following Equation 1 [25]:

$$HS_p = \frac{8P}{\pi W^2} \quad (1)$$

where:

P – force [N]

W – indentation width [m].

3. Results and Discussion

The results of coating thickness testing carried out in randomly selected sample locations are presented in Table 1. It was observed that depending on measuring point the thickness of the coating was in the range between 7 and 16 µm.

Table 1.

Average coating thickness on the basis of measuring samples

Sample No 1		Sample No 2	
first measurement	second measurement	first measurement	second measurement
Coating thickness [µm]			
8.42	4.73	13.40	15.25
4.81	9.99	16.46	7.40
7.21	6.31	16.98	17.20
8.77	6.16	14.03	17.75
-	6.49	14.24	6.86
-	-	-	15.76
Average thickness [µm]			
7.30	6.74	15.02	13.37

Microstructure analysis performed using the scanning electron microscope was accompanied by the measurement of coating thickness. Representative results are provided in Figures 2 and 3.

SEM analysis confirmed adequate adhesion of the coatings to the aluminium alloy. Moreover, areas with discontinuities and porosities can be seen on the coating's cross-section. Despite the fact that the coating thickness complies with the range specified in PN-EN 2536:1997, it varies depending on the location of measuring point. This issue arises from the selection of process current parameters [26].

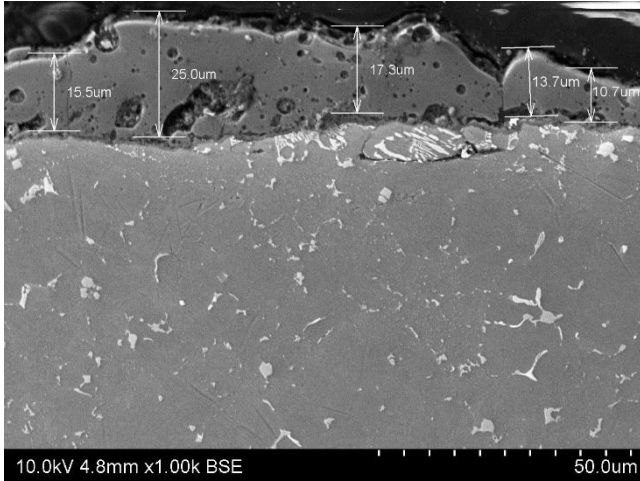


Fig. 2. SEM Micrograph of the coating and its thickness measurement carried out for sample No 1

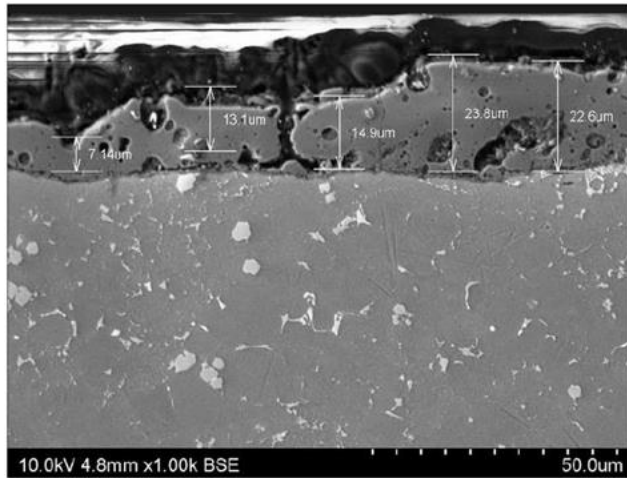


Fig. 3. SEM Micrograph of the coating and its thickness measurement carried out for sample No 2

Hanemann's microhardness test results are given in Table 2. What is more, hardness testing were based on the scratch test. Stylus trace [27] was used to determine the force required to

remove some part of the coating material. The pressure-to-hardness HSp ratio of the tested material amounted to, respectively: for sample No 1 – 12440 [MPa], for sample No 2 – 115620 [MPa]. These values are considerably higher than the maximum hardness expressed in megapascals, for which 2055 [MPa] corresponds to 591 HV. The scratch test results are graphically presented in Figures 4 – 7.

Table 2.

Microhardness sample test results

Sample No 1	Sample No 2
<i>Microhardness [HV]</i>	
270	1030
370	735
513	1013
<i>Average [HV]</i>	
384	926

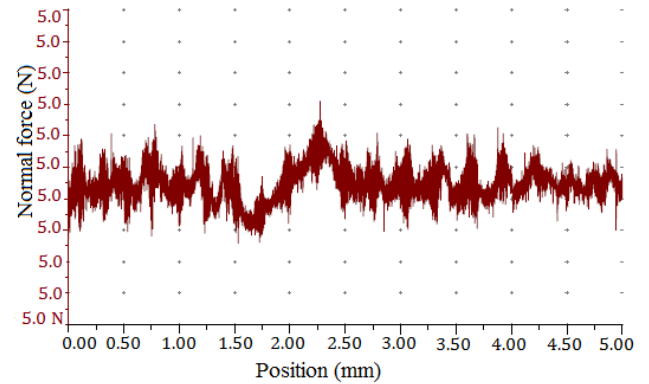


Fig. 4. Scratch test results for sample No 1. Force applied to the indenter F_N ,

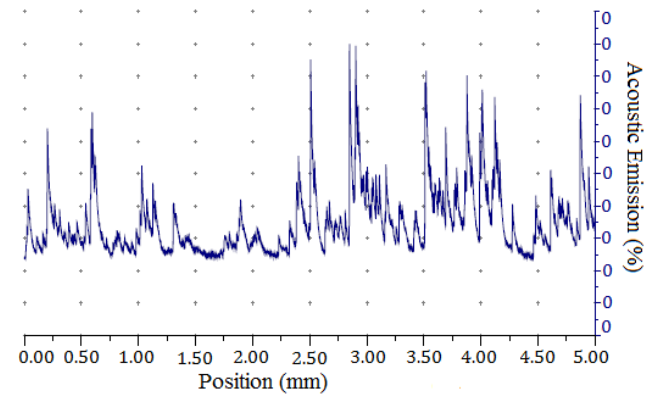


Fig. 5. Scratch test results for sample No 1. Acoustic emission signal A_e

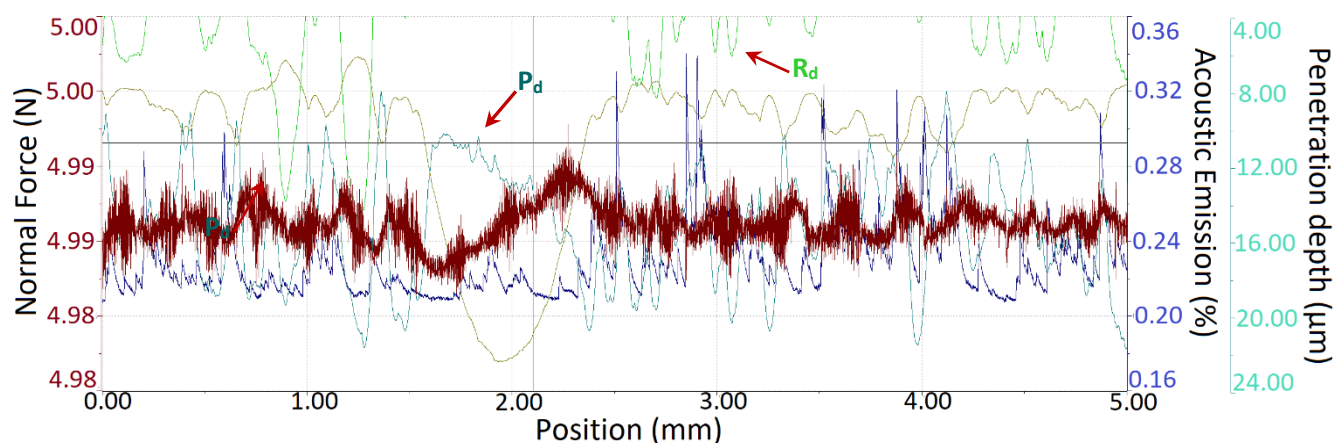


Fig. 6. Scratch test results for sample No 1. Indenter penetration depth P_d and post-scratch depth R_d

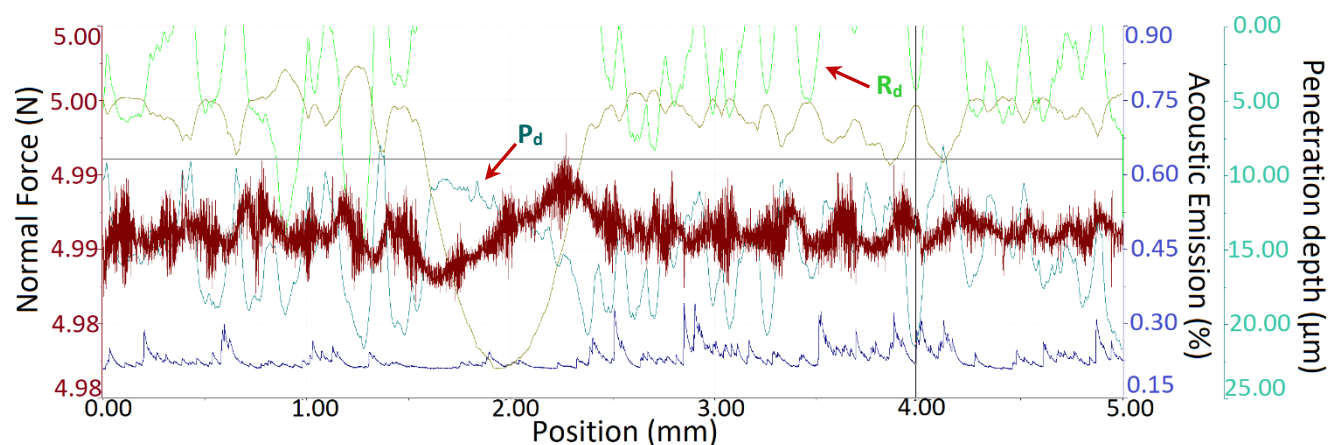


Fig. 7. Cumulative scratch test results for sample No 2: force applied to the indenter FN, acoustic emission signal Ae, indenter penetration depth P_d and post-scratch depth R_d

Analysis of the test results showed that the highest hardness (~ 1030 HV = reached sample No. 2. While sample No. 1 reached the maximum hardness of 513 HV. The obtained results confirm that coating with the PEO coating increases the hardness of the tested elements. Al alloys hardness. -Si is at the level of 80 HV. This is consistent with the results obtained by other authors who noted an increase in hardness from 600 to 1890 HV [4]. In some cases [1] it was possible to achieve a hardness of 2000 HV. According to these authors [1-2, 22, 28-30] such high hardness depends largely on the structure, phase composition, electrolyte temperature, oxidation time and electrolytic parameters.

Extremely irregular force curve presented in Figure 3a indicates the coating's heterogeneity along the measurement section. Such a condition questions the applicability of the adopted adhesion test method. This characteristic may be caused by moving the stylus across a eutectic-rich area or an interface area. Larger scattering of scratch test results is represented in a cumulative diagram on Figure 4. Changes in current parameters may have an effect on the coating homogenizing process and, thus, influence the curves (namely: force applied to the indenter FN, acoustic emission signal Ae, indenter penetration depth P_d and post-scratch depth R_d). Normal force FN was constant parameter during the test.

The coating is clearly heterogeneous in its thickness and has numerous pores. This can be explained by the course of the process and the parameters used. The applied voltage causes the beginning of the Al_2O_3 layer growth. Aluminum oxide formed on the surface is an insulator, so it is necessary to constantly increase the voltage of the process to maintain the set current intensity. After reaching the critical voltage of 120-350V, the field strength is so high that the film loses its stability. Small sparks begin to be visible on the entire volume of the material, these are electric breakdowns caused by collision or tunnel ionization. The discharge temperature at its very center can be 3500-16000K, under these conditions Al_2O_3 starts to melt and is ejected outside the layer. The temperature difference causes Al_2O_3 to immediately solidify at the outlet of the channel. They form micro craters around the discharge site. The barrier layer begins to homogenize. This is due to the high temperature inside the layer and, at the same time, the low conductivity of Al_2O_3 . Under such conditions, the hitherto amorphous aluminum oxide is transformed into crystalline alpha or beta. The discharge time, which takes place over the entire surface, is in the range of 10-1000 μs , however, inadequate process control may cause too much discharge and, consequently, a local structure defect. The authors did not analyze the layer between the coating

and the substrate - especially at high magnification, because the purpose of the publication was to examine the mechanical properties of the coating and, as the research shows, this heterogeneity affects the course of the graphs shown in Figs 4 and 6. But more detailed metallographic tests will be carried out soon. The phenomenon of porosity may, on the one hand, be disadvantageous because it initiates local cracks, and on the other hand, it constitutes an adhesive substrate for all paints and varnishes. According to the authors, the problem of heterogeneity also results from the chemical heterogeneity of the casting made of the tested alloy. Each phase present in the structure has a different electrical conductivity and reactivity, so the resulting coating may have a completely different thickness. Al-Si alloys up to a silicon content of about 3% are easy to anodize. The increase in the silicon content begins to make it difficult to cover with the oxide layer. The silicon contained in the alloy is in eutectic form, which results in the formation of an aluminum-silicon system, where aluminum is oxidized, while silicon, which does not react with sulfuric acid, may remain unoxidized. This increases the discontinuity of the oxide film on the surface of the alloy. The same may be the case with microplasma oxidation. Interestingly, the coating has a more homogeneous character when the PEO process is applied to products deformed from aluminum alloys for plastic treatment.

4. Conclusions

The increasing requirements as to the quality of the casting surface result directly from the market needs. Increasingly, along with the design of the casting technology, it is necessary to prepare the technology of surface protection of casting. The expected coatings should provide increased corrosion resistance, resistance to abrasion, scratches and impacts, while maintaining the aesthetics and decorativeness. These coatings, having an impact on the thermal and electrical conductivity of alloys, can significantly affect the parameters of castings used in electrical engineering, in the lighting industry.

The aim of the tests was to determine the effectiveness of the formation of coatings on aluminium alloys containing silicon using the Plasma Electrolytic Oxidation (PEO) method. Analysis of microstructure confirmed the existence of a substrate-bonded, heterogeneous oxidation coating with thickness corresponding to the thickness of standard anodized coatings. Microhardness measurements showed that the PEO coatings are characterized by considerably higher hardness than anodized coatings. Values higher than 1000 HV may signify the crystalline nature of the coatings. When they are formed, aluminium oxide may be produced in the form of corundum. In view of further testing, optimization of current and voltage parameters of the PEO method seems to be the best solution to obtain homogenous coatings on Al-Si alloys in terms of thickness and strength.

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