

THE COMPARISON OF POSSIBILITIES AT USING OF DIFFERENT ELECTROLYTES IN THE PROCESS OF ANODIZING ALUMINUM

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The contribution researches and solves the suitability of utilize of electrolyte, consisting of the oxalic acid, boric acid, sodium chloride and aluminium cations in the process of anodizing aluminium in operating conditions of electrolyte $T = 22\text{ }^{\circ}\text{C}$, $t =$ time of oxidation and the size of at least 210 an applied voltage $U = 12\text{ V}$. The appropriate use of the electrolyte is judged by the thickness of the anodic aluminium oxide layer (AAO) formed on the basis of the monitoring and the resulting quality of the sample surface.

Key words: aluminium, elektrolit, deposition, chemical nickeling, surface protection

INTRODUCTION

The porous anodic alumina (PAA) film has recently attracted the attention of scientists because of its self-organizing nature of the vertical (cylindrical) pores in the form of hexagonal arrays, which provides controlled and narrow distribution of pore diameters and inter-pore distances in addition to the possibility of forming the pores with extremely high aspect ratio [1]. The anodization is one of the most important processes in the corrosion protection and colour finishes for aluminium [2]. The anodizing of the aluminium surface is carried out in a wide variety of plants for numerous uses in industries. It is an effective process for producing decorative and protective films on articles made from aluminium [3].

The contribution is primarily based on the work of H. Na [4], who, after 6 hours, oxidized alloy EN AW 1050 - H24 in the electrolyte of sulphuric acid and reached a thickness of AAO formed layers up to $230\text{-}284\text{ mm}\cdot 10^{-3}$ [5]. He studied the development of pore sizes formed oxide layer in an electrolyte 0,30 M oxalic acid at a temperature of $20\text{ }^{\circ}\text{C}$ for at least 60 min., 100 min., and 240 min. [6]. He determined the effect of additives NH_4Fe in the electrolyte 0,40 M oxalic acid for the formation of the barrier layer. The anodic oxidation in electrolyte of boric acid deals with [7] and [8]. Zhang [7] identified the relationship between the structure and composition of the electrolyte formed layer. Shih [8] evaluated the effect of the thickness of the electrolyte composition formed layer ($16\text{ - }35\text{ mm}\cdot 10^{-3}$) and the hardness (HV 162 - 481).

In contrast to these papers, this work does not specify how to explore the creation of layers in conventional

electrolytes constituted by oxalic acid and boric acid, but is also considering the possibility of adding of other additives to the electrolyte cations, such as aluminium and sodium chloride. Further, the in the work, is not considered, during the evaluation, only with the thickness of formed oxide layer, but also pursues a quality surface texture.

REALIZATION OF THE EXPERIMENT

Samples:

The impurities in aluminum could influence the results. That is why it is important to study the change in the growth mechanism of porous alumina films on pure aluminum [9]. For the experiment was used the sample of alloy, marked EN AW 1050 - H24 with the dimensions $101\text{ x }70\text{ x }1\text{ mm}$. Each applied sample was degreased in a 38 % solution of NaOH at a temperature of from $55\text{ to }60\text{ }^{\circ}\text{C}$ for 2 minutes and stained in a 40 % solution of NaOH at a temperature of $45\text{ -}50\text{ }^{\circ}\text{C}$, for time 0,50 minutes. Consequently, the sample was immersed in a brightness bath (40 % HNO_3) at the temperature $18\text{ - }24\text{ }^{\circ}\text{C}$ for 1,00 minute. Between each operation, the sample was washed with distilled water. The cathode was formed by aluminum with the purity 99,90 %.

Oxidation of samples:

The operating conditions of the oxidation process of the individual samples (the composition of the electrolyte, temperature of the electrolyte, an applied voltage of the size and duration of oxidation) followed the selected plan of experiment, as is illustrated in Table 1. During the oxidation process were done measurements and were written the values of flowing current, applied voltage and temperature of the electrolyte at regular intervals: 1/60

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min. in time from 0 to 2 min., 0,50 min. in time 2 - 60 min., 1,00 min. at the time 60 - 210 min. of oxidation. After the oxidation process, the samples were rinsed with distilled water and dried with compressed air.

Measurement of the thickness of the formed/created layer:

The thickness of the formed oxide layer was measured at the level of 25 mm from the lower edge of the sample. The distance between the points, in which the layer thickness was measured, was 5 mm. Such separation of points across the whole length of the sample indirectly represents the effect of the distance between the anode and cathode on the layer thickness.

RESULTS AND DISCUSSION

The Figures 1, 2, 3, 4 show the resulting surface of all the samples after the oxidation. The quality of created surface can be divided into four groups.

Group A, which covers the samples oxidized in an electrolyte 3, 4, 7 and 8 (Figure 2 - a, b, c and d) exhibits no significant abnormalities. The surface of the sample is homogeneous and smooth.

The electric current, which flowing in the circuit, ranges from 70 to 300 A · 10⁻³.

Group B, which covers the samples oxidized in the electrolyte 1, 6, 11 and 14 is characterized by large surface structures, which cause significant surface roughness of the sample. These structures are created from two reasons:

- In the first case (Figure 2 - e and f) there are occurred very small current densities that are close to zero. Due to the small current, which is flowing in circuit (3 to 5,8 A · 10⁻³), there is a significant slowing of surface oxidation. The unused oxygen anions are joining to form oxygen gas in the form of miniature bubbles established on the surface. In the place, where such a bubble

of oxygen gas is situated, there is occurring a complete stop oxidation of the surface. The oxidation of the surface is restarted after the removal of oxygen bubbles.

- In the second case (Figure 2 - g and h) is, at the start of oxidation, the size of the current flowing through device similar to those of samples 3, 4, 7 and 8. During the oxidation, there is occurred a massive increase of the current size (current flowing in circuit, at the end of oxidation, is reached up to 10 times of its initial value 1,30 – 1,50 A). The speed of the reaction between oxygen and aluminium increases proportionally with the current until it reaches a level that arising molecules of Al₂O₃ stop to form ties among themselves. Thus, self-isolated molecules of alumina pass into the aquatic environment of the electrolyte, where they dissolve to the ions. The aluminium cations are attracted to the cathode, where they take free electrons to form dispersed atoms of aluminium in the electrolyte. The oxygen anions travel to the anode, where they are involved in the creation of more isolated molecules Al₂O₃.

The surface of the samples 2, 5, 13 and 15 (**group C**) also form the surface structures. Such structures arise due to small current densities (Figure 3- i and j), and by influence of added sodium chloride (Figure 3- k and l). The chlorine anions in the electrolyte cause the pittings on the sample surface. As the result of the process, there is created the boundaries between the grains of the material substrate. The arising gaps are filled in at the same time by emerging alumina and therefore the sample surface after oxidation is smooth as well as the samples of the group A. In addition, the samples in group C have after painting decorative mosaic look.

Last **group D** (samples 9, 10, 12 and 16) is characterized by extensive weighing loss of the material substrate. The sample surface is covered with deep parallel grooves that go from the top edge of the sample to the lower edge of the sample. The material loss is caused by a high concentration of chloride anions in the electrolyte.

Table 1 The chemical composition of the electrolyte and the operating

s.	Al ³⁺ / mol.l ⁻¹	C ₂ H ₂ O ₄ / mol.l ⁻¹	H ₃ BO ₃ / mol.l ⁻¹	NaCl/ mol.l ⁻¹	T/°C ± 13,64 %	U/V ± 4,17 %	t/min
1	0,00	0,00	0,00	0,00	22,00	12,00	210,00
2	0,08	0,00	0,00	0,00	22,00	12,00	210,00
3	0,00	0,33	0,00	0,00	22,00	12,00	210,00
4	0,08	0,33	0,00	0,00	22,00	12,00	210,00
5	0,00	0,00	0,81	0,00	22,00	12,00	210,00
6	0,05	0,00	0,81	0,00	22,00	12,00	210,00
7	0,00	0,17	0,40	0,00	22,00	12,00	210,00
8	0,08	0,17	0,40	0,00	22,00	12,00	210,00
9	0,00	0,00	1,21	6,85·10 ⁻²	22,00	12,00	210,00
10	0,00	0,00	0,00	6,85·10 ⁻²	22,00	12,00	210,00
11	0,00	0,33	0,00	8,56·10 ⁻³	22,00	12,00	210,00
12	0,08	0,17	0,40	8,56·10 ⁻³	22,00	12,00	210,00
13	0,08	0,00	0,00	8,56·10 ⁻³	22,00	12,00	210,00
14	0,08	0,17	0,00	8,56·10 ⁻³	22,00	12,00	210,00
15	0,08	0,00	0,4	8,56·10 ⁻³	22,00	12,00	210,00
16	0,00	0,09	0,20	8,56·10 ⁻³	22,00	12,00	210,00

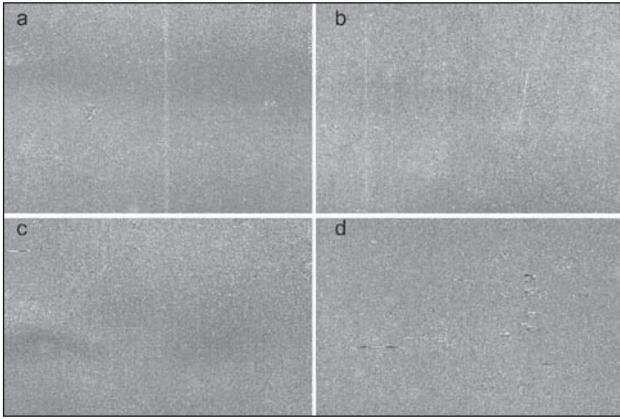


Figure 1 Surface of the samples, group A a) sample 3, b) sample 4, c) sample 7, d) sample 8

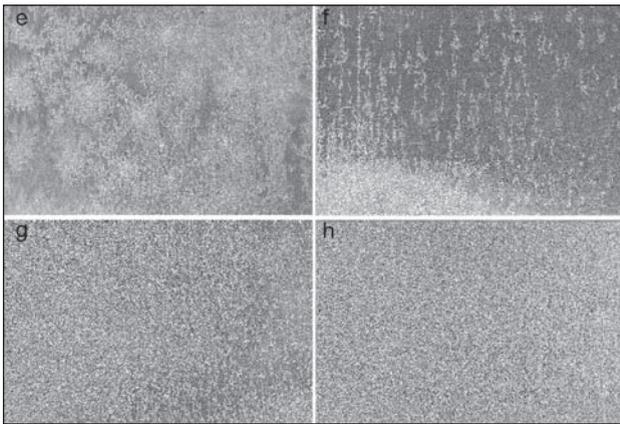


Figure 2 Surface of the samples, group B e) sample 1, f) sample 6, g) sample 11, h) sample 14

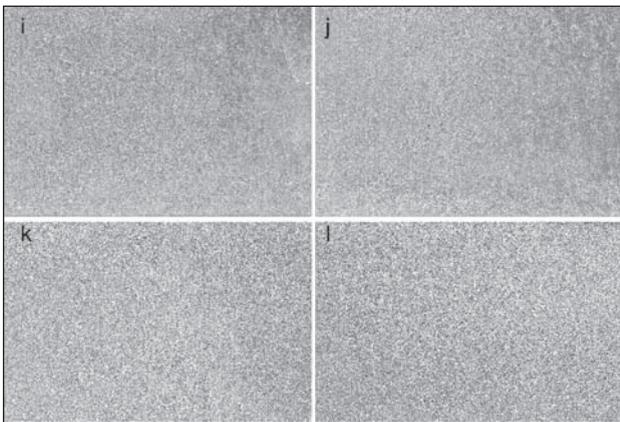


Figure 3 Surface of the samples, group C i) sample 2, j) sample 5, k) sample 13, l) sample 15

The Figure 4 shows the evolution of the thickness of the formed anodic aluminium oxide layer in electrolytes of samples 1 - 8. From the graph it can be seen that the created thickness is nearly constant along the sample.

The distance between the anode and cathode (surface distribution of current density) has not a major impact on the thickness of the formed layer. In contrast, the thickness of the formed layer on samples 9 - 16 (Figure 5) is on the distance between the anode and cathode, and depends to a large extent. From the graph it can be seen that at the point where the smallest elec-

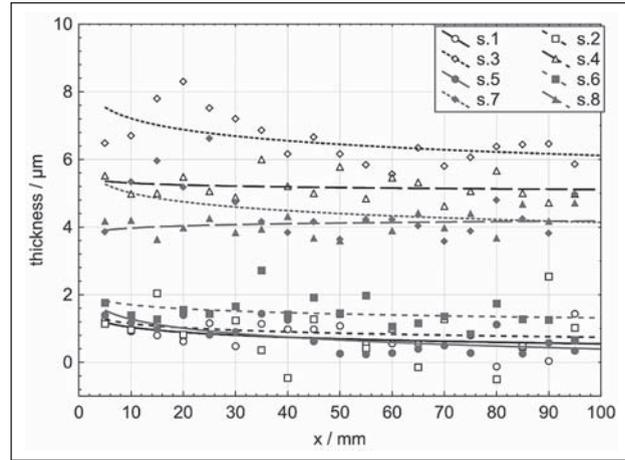


Figure 4 Thickness AAO layer, created in electrolytes without NaCl

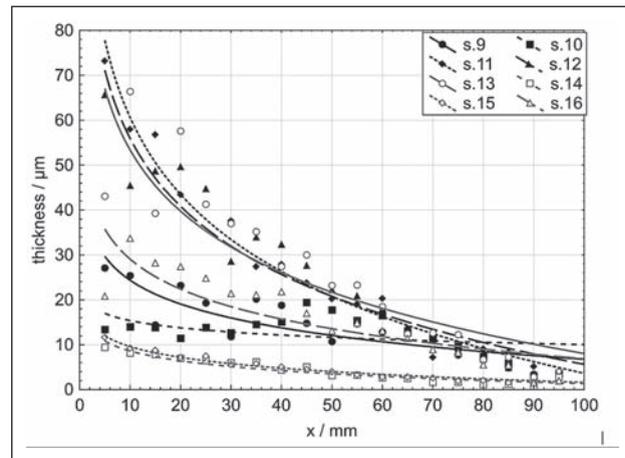


Figure 5 Thickness AAO layer, created in electrolytes with NaCl

trode spacing and surface current density in these areas reach their maximum values, here creates a layer up to 10 times thicker than the place, where the electrode spacing is the largest.

CONCLUSIONS

By monitoring of the resulting formed thickness AAO on the sample surface and monitoring of the surface quality of the sample can be used to assess the suitability of used electrolyte for technology of anodizing aluminum. From the results of the experiment show that at the operating conditions the electrolyte temperature $T = 22\text{ }^{\circ}\text{C}$, oxidation time $t = 210\text{ min}$. and the size of the connected voltage $U = 12\text{ V}$, provide the best protection against the corrosion protective of the oxide layer, formed in electrolytes $0,33\text{ M C}_2\text{H}_2\text{O}_4$; $0,33\text{ M C}_2\text{H}_2\text{O}_4$ and $0,08\text{ M Al}^{3+}$; $0,17\text{ M C}_2\text{H}_2\text{O}_4$ and $0,40\text{ M H}_3\text{BO}_3$; $0,17\text{ M C}_2\text{H}_2\text{O}_4$, $0,40\text{ M H}_3\text{BO}_3$ and $0,08\text{ M Al}^{3+}$. For atypical mosaic surface design with less corrosion protection are suitable the electrolytes $0,81\text{ M H}_3\text{BO}_3$; $0,08\text{ M Al}^{3+}$, $0,08\text{ M Al}^{3+}$ and $8,56 \cdot 10^{-3}\text{ M NaCl}$; $0,08\text{ M Al}^{3+}$, $0,40\text{ M H}_3\text{BO}_3$ and $8,56 \cdot 10^{-3}\text{ M NaCl}$; anodic oxidation in the distilled water, which creates a very decorative

surface, but makes almost no corrosion protection. To further aim of the research in the determined area will be monitoring of the thickness of the formed anodic aluminium oxide layer and surface quality at the changed concentrations of components of electrolytes as also at the various operating conditions.

Knowing of the possibilities of the anodic oxidation of aluminum and its alloys in various types of electrolytes have from a perspective of technological applications in workplaces of surface finishes, as well as in impact of the environment and working environment.

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