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EFFECT OF ELECTROLYTE TEMPERATURE ON THE THICKNESS OF ANODIC ALUMINIUM OXIDE (AAO) LAYER

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Effect of electrolyte temperature on the thickness of resulting oxide layer has been studied. Unlike previous published studies this article was aimed to monitor the relationship between electrolyte temperature and resulting AAO layer thickness in interaction with other input factors affecting during anodizing process under special process condition, i.e. lower concentration of sulphuric acid, oxalic acid, boric acid and sodium chloride. According to Design of Experiments (DOE) 80 individual test runs of experiment were carried out. Using statistical analysis and artificial intelligence for evaluation, the computational model predicting the thickness of oxide layer in the range from 5 / µm to 15 / µm with tolerance ± 0,5 / µm was developed.

Key words: anodic aluminium oxide (AAO), layer thickness, electrolyte, temperature, oxidation

INTRODUCTION

Anodic oxidation of aluminium is the oldest and most widely used surface treatment of aluminium parts, carried out in order to improve the anti-corrosion properties and for the purpose of improving the aesthetics of the surface. It is about the process of enrichment of the surface of the material with oxygen forming a layer of porous alumina (AAO – Anodic Aluminium Oxide) [1]. The history of electrochemical aluminium oxidation dates from 1923, when using Bengough-Stuart process was patented as the anti-corrosion protection of aluminium.

This process used an electric current to enhance the surface layer of aluminium oxide in chromium acid solution. With a great number of studies involving use of acids such as sulphuric, oxalic and boric acid have made the whole process of anodic oxidation of aluminium more economical and much safer for human health [2]. Therefore, today the most commonly used electrolytes consist of sulphuric acid, oxalic acid and, to a certain extent, boric acid. It also extended the number of ways in which it is possible to create a layer of AAO. These methods differ from each other not only by composition of the electrolyte, the size of the connected voltage, temperature of the electrolyte used in which the oxidation of the surface takes place, oxidation time, but also by features of layer of oxidation [3]. In the context of the overall research of technological process of anodic oxidation of aluminium mostly the relationship between the temperature of the electrolyte and the geometrical dimensions of pores is studied. Another very populous group of studies follows the relationship between the geometrical dimensions of the pores but in relation to used electrolytes. Aerts et al. were also dealing with the temperature effect on the growth of the oxide layer and the layer porosity of 99,5 % aluminium using [3] the electrolyte comprising of sulphuric acid, based on which, it followed that the structure of the layer, the layer porosity [4], its thickness and hardness are not so much under the influence of the temperature of the electrolyte compared to that of the electrode [5].

Experimental work

Used samples were cuts from a sheet of alloy EN AW 1050 H24 with dimensions 100x70x1 / mm. Each sample was degreased and stained before oxidation in Hull bath. Electrolyte for each anodizing sample was consisting of sulphuric acid, oxalic acid, boric acid and sodium chloride. Standard values for concentration of chemical components of electrolyte intended for process of anodic oxidation are shown in Table 1, along with standard operating conditions for the process of aluminium oxidation.

In order to determine the relationship between the electrolyte temperature and resulting thickness of oxide layer, the experiment with 80 test runs was carried out. Based on design of experiments (DOE) seven input factors for the process of anodic oxidation of aluminium were considered. Table 2 shows conversion of factors between nature scale and coded one and five factor levels of each factor. Comparison of Table 1 and Table 2 shows that concentration of electrolyte components used during the experiment reached values that are 10 %

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to 50 % lower than standard concentrations of electrolyte components. Operating conditions for the process of anodic oxidation of aluminium have stayed at standard levels during the experiment.

At the end of oxidation a map of measuring points was created on each sample, the thickness of aluminium oxide layer was measured at each point. Measuring points were placed on a sample 1 to 9 cm from left edge with 1 cm spacing and 1 to 4 cm from bottom edge with 1 cm spacing. Measured values of oxide layer thickness on measurement points 5 cm from left edge of the sample were used to create a prediction model presented in the article.

Primary goal of the experiment was to study the relationship between electrolyte temperature and the resulting AAO layer thickness. Secondary goal of the experiment was to study the effects of interactions between electrolyte temperature and chemical composition of electrolyte on the resulting layer thickness. Evaluation of experimentally obtained data was performed by using neural network in conjunction with mathematical-statistical analysis. Specific significant input factors and significant interactions of input factors were determined at the chosen significance level of α = 10 %, served as a model for neural network schema. This combination of statistical methods and artificial intelligence techniques was chosen because of advantages these evaluation methods provide. Creation of prediction model using statistical methods is difficult, because even considering several input parameters leads to complicated analytical solution. However, statistical evaluation methods can explain relationships between inputs and outputs. Determination of relationship between inputs and outputs using only artificial intelligence is not acceptable, because these methods are used only to create „black box“ models. On the other hand, use of artificial intelligence for evaluation of data from experiment brings advantages, mostly for their ability to quickly create desired prediction model [6].

Figure 1 compares measured and calculated values of AAO layer thickness. It shows deviations of actual and calculated values of aluminium oxide layer thickness from the line of ideal prediction. Figure 1 shows that calculated values of aluminium oxide layer thickness follow a trend made by measured values of aluminium oxide layer thickness. Figure 2 shows that almost all deviations of measured and calculated values of aluminium oxide layer thickness lies on an ideal line of prediction. Thus, even by Figures 1 and 2, it is possible to consider the created prediction model as accurate even by Figures 1, 2.

Table 1 **Standard levels of observed factors**

Factor	Level
H_2SO_4	200 / g·l^{-1}
$C_2H_2O_4$	20 / g·l^{-1}
H_3BO_3	50 / g·l^{-1}
NaCl	0 / g·l^{-1}
T	22 / °C
U	10 / V
t	30 / min

Table 2 **Table of conversion between natural and coded scale of examined factors**

Factor		Factor level				
Coded scale	Nature scale	- 2,37	- 1	0	+ 1	+ 2,37
x_1	H_2SO_4/g.l^{-1}	12,57	40,00	55,00	70,00	97,43
x_2	$C_2H_2O_4$/g.l^{-1}	3,76	6,50	8,00	9,50	12,24
x_3	H_3BO_3 /g ·l^{-1}	4,51	10,00	13,00	16,00	21,49
x_4	NaCl /g·l^{-1}	0,12	0,30	0,40	0,50	0,68
x_5	T / °C	-5,46	11,00	20,00	29,00	45,46
x_6	U / V	2,34	6,00	8,00	10,00	13,66
x_7	t / min	1,72	40,00	30,00	40,00	58,28

x_1 - concentration of sulphuric acid, x_2 - oxalic acid, x_3 - boric acid, x_4 - sodium chloride, x_5 - electrolyte temperature, x_6 - applied voltage, x_7 - anodizing time

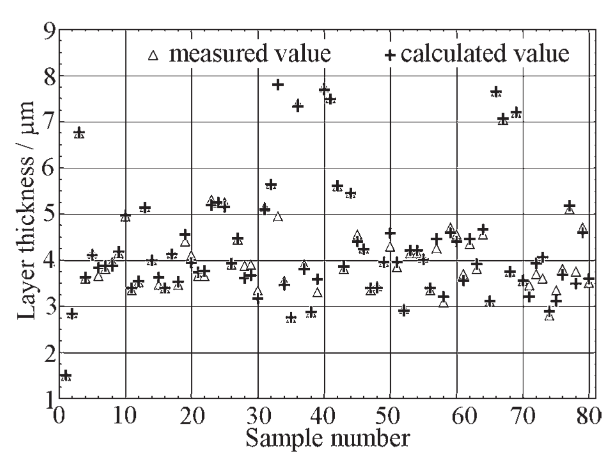

Figure 1 Measured and calculated values of aluminium oxide layer thickness

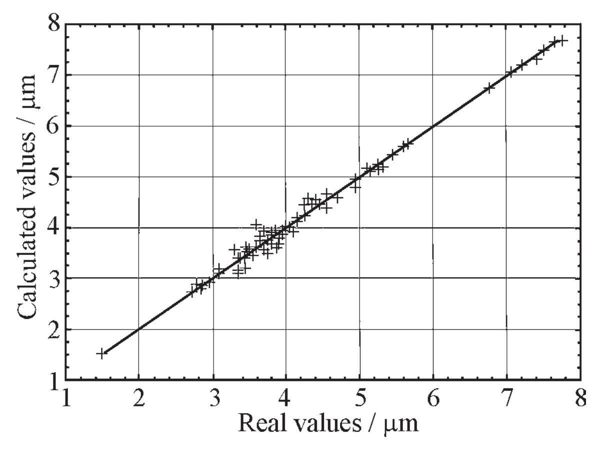

Figure 2 Verification of prediction model

RESULTS AND DISCUSSION

The Figures 3 to 5 show relationship between the temperature of electrolyte and final thickness of AAO layer at different concentrations of electrolyte components. Figure 3 shows relationship of electrolyte temperature and concentration of sulphuric acid on resulting oxide layer thickness. Factors x_2, x_3, x_4, x_6 and x_7 are set to factor level 0. Figure 4 shows relationship of electrolyte temperature and concentration of oxalic acid on resulting oxide layer thickness. Factors x_1, x_3, x_4, x_6 and x_7 are set to factor level 0. Figure 5 shows relationship of electrolyte temperature and concentration of boric acid on resulting oxide layer thickness. Factors x_1, x_2, x_4, x_6 and x_7 are set at level 0.

Comparison of graphs on Figures 3 to 5 evidently shows a positive effect of electrolyte temperature on the resulting aluminium oxide layer thickness. With increasing the electrolyte temperature also increases the resulting aluminium oxide layer thickness. Electrolyte temperature significantly influences electrolyte conductivity, and also speed of chemical reactions which occur on anode and cathode. With increase in electrolyte conductivity also drops the amount of energy needed for splitting the molecules containing oxygen. With constant amount of energy, which is supplied to the system, inevitably grows the number of free oxygen atoms in electrolyte. Subsequently, these free oxygen atoms are participating in chemical reaction on the surface of anode where the resulting products are molecules of aluminium oxide. These molecules of aluminium oxide primarily make up the oxide layer, and secondarily dissolve due to aggressive effects of electrolyte environment. Electrolyte aggression is closely related not only to its chemical composition but also to its temperature. Figure 3 shows how the electrolyte aggression changes in relation to concentration of sulphuric acid. In case the concentration of sulphuric acid is at level - 2,37 or - 1, the growth in resulting AAO layer thickness in relation to the increase in electrolyte temperature occurs. Layer thickness grows until the point in which factor level of electrolyte temperature reaches value 1. At this point the speed at which layer dissolves due to effects of electrolyte is greater than the speed at which the oxide layer grows. That is why a gradual decrease in resulting oxide layer thickness occurs. On the other hand, if the concentration of sulphuric acid is at factor level 1 or 2,37, at first, we can see a drop in resulting aluminium oxide layer thickness until the electrolyte temperature reaches factor level 1. At this point the speed at which layer dissolves drops and speed at which oxide layer forms grows. Thus we can observe a substantial growth in resulting aluminium oxide layer thickness.

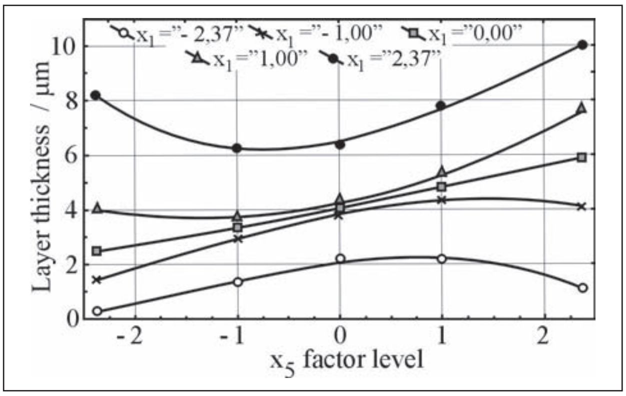

Figure 3 Effects of electrolyte temperature and sulphuric acid on oxide layer thickness

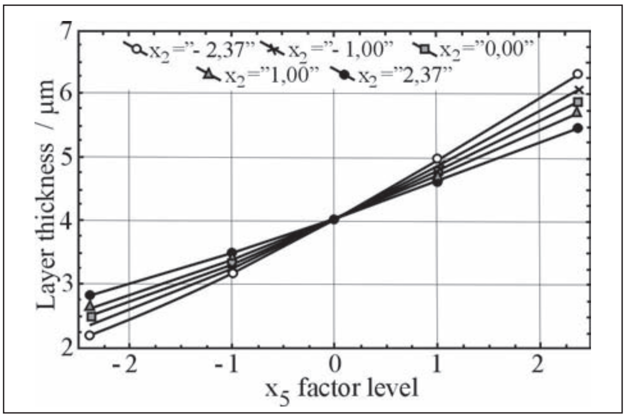

Figure 4 Effects of electrolyte temperature and oxalic acid concentration on oxide layer thickness

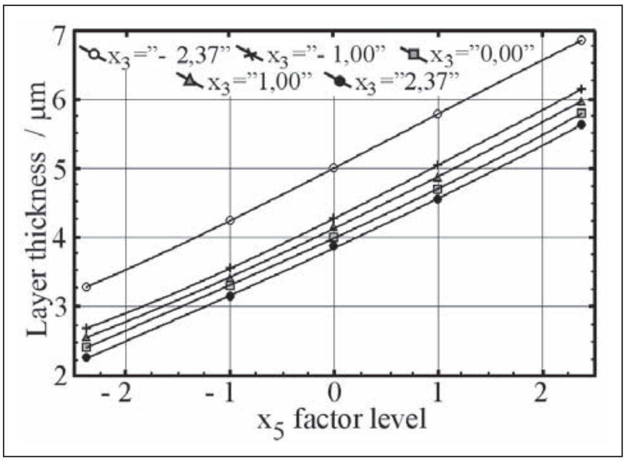

Figure 5 Effects of electrolyte temperature and boric acid on oxide layer thickness

In case of interaction between electrolyte temperature and concentration of oxalic acid in electrolyte have on resulting layer thickness (shown in Figure 4), the effects are not as significant as the effects of concentration of sulphuric acid (shown in Figure 3) In case of oxalic acid concentration in electrolyte (Figure 4), there is an observable difference in speed at which the resulting oxide layer forms in relation to electrolyte temperature. If oxalic acid concentration in electrolyte reaches lower levels (factor levels - 2,37 and - 1) the speed at which oxide layer forms decreases in relation to the increase in electrolyte temperature. That is why the oxide layer is thicker at higher temperatures. At higher concentrations of oxalic acid in electrolyte (factor levels 1 and 2,37), the layer thickness grows faster at higher electrolyte temperatures. That is why the resulting oxide layer is thicker at lower electrolyte temperatures. In case of effect between electrolyte temperature and concentration of oxalic acid in electrolyte on resulting aluminium oxide layer thickness (Figure 5), we can observe a completely negative effect of oxalic acid concentration in the whole studied range of temperatures. That is why, in case the highest possible layer thickness is desired, it is necessary to keep the concentration of boric acid to minimal possible factor levels.

CONCLUSION

In regard to the complexity of the anodizing process, it is necessary to monitor the temperature effect in interaction with other factors affecting the thickness of final AAO layer and not as the only factor influencing the observed parameter. In this study the thickness of AAO layer was evaluated as a function of chemical and physical factors acting during anodizing process. Based on the experimental analysis according to the DOE methodology with 80 individual trials, subsequently evaluated by statistical methods and artificial intelligence techniques, the computational model predicting the thickness of the formed layer has been created. The model with laboratory proven reliability of 96,23 % can predict the thickness in tolerance range from 5 / μm to 15 / μm, tolerance limit ± 0,5 / μm. Regarding experimentally obtained values of final thickness and values of thickness calculated by prediction model, it can be stated that the electrolyte temperature significantly affect the AAO layer thickness, especially in interactions with chemical factors, as it is mentioned above.

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