

THE SIMULATION OF THE TEMPERATURE EFFECTS ON THE MICROHARDNESS OF ANODIC ALUMINA OXIDE LAYERS

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Preliminary Note – Prethodno priopćenje

In order to improve the mechanical properties of the layer deposited by anodic oxidation of aluminum on the material EN AW-1050 H24, in the contribution was investigated the microhardness of the deposited layer as a function of the physico-chemical factors affecting in the process of anodic oxidation at the constant anodic current density $J = 3 \text{ A.dm}^{-2}$ in electrolyte formed by sulfuric acid and oxalic acid, with the emphasis on the influence of electrolyte temperature in the range – 1,78 °C to 45,78 °C. The model of the studied dependence was compiled based on mathematical and statistical analysis of matrix from experimental obtained data from composite rotation plan of experiment with five independent variable factors (amount of sulfuric acid in the electrolyte, the amount of oxalic acid in the electrolyte, electrolyte, anodizing time and applied voltage).

Key words: anodizing of aluminium, microhardness, simulation, design of experiments

INTRODUCTION

The surface properties of anodic alumina oxide (AAO) films render anodized aluminium products suitable for a wide range of applications, not only in the standard fields of machinery, transport and building industry, but also for the potential use in the area of magnetic storage [1] photo voltaic solar cells [2], filters [3] chemical sensors [4], photonics [5], and metallic nanowires [6, 7].

In many of these applications a key role is played by the mechanical properties such as the microhardness, wear resistance and corrosion resistance.

Depending on the considered anodizing conditions these properties can be varied to a wide extent, hence the research of the process conditions influence of chemical, physical and technological factors on the resulting AAO layers has received extensive attention. The basic information concerning this matter is available in the literature [8 - 10].

Most experimental studies in the field of microhardness have been performed under hard anodizing conditions, which comprise the use of low electrolyte temperatures and often special chemical composition of electrolytes, with the primary purpose to achieve anodic oxide layers with high values of microhardness [11]. According to Scott [12], who considered anodizing in a sulphuric acid electrolyte at a constant applied current density of 4 A.dm^{-2} with the varied electrolyte temperature in the

range from -5 °C up to +15 °C, the microhardness and abrasion resistance related with it is influenced only in a small extent under such anodizing conditions.

Another study by Koizumi et al. [13], dealing with galvanostatic anodizing at current densities from 1 to 8 A.dm^{-2} in a mixed sulphuric acid - oxalic acid electrolyte at temperatures, varied between - 5 °C to + 20 °C, report an almost constant microhardness and wear resistance in the temperature range - 5 °C to + 5 °C, regardless of the applied current density. Furthermore, this study predicate that the value of microhardness gradually decreases with increasing electrolyte temperature, with the effect being more pronounced for the lower applied current densities. This latter declaration should be handled with care because the anodizing time during this experiment process was always constant 45 min., regardless applied current density. As a result, there were formed and afterward evaluated anodic oxide films with larger film thickness, which influences the final value of microhardness and wear resistance [14 - 16].

According to some authors [17, 18], the anodic oxides with a thickness of 25 μm or more, formed in a sulphuric acid electrolyte at temperatures between + 15 °C and + 30 °C under different applied current densities (from 1 up to 4 A.dm^{-2}), are characterized by a softer outer layer which reduces the transparency and wear resistance of the layer. According to the above-mentioned works, the similar effect has been observed on the level of the microhardness.

Based on the review of published studies on the mechanical properties of anodic oxide layers, focusing particularly on the microhardness, we can state that there is very often an emphasis on the influence of electrolyte temperature and applied current density without

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considering other factors. Therefore, in this study is observed not only the influence of electrolyte temperature but also the influence of other chemical and physical factors affecting the thickness and also the mechanical properties of resulting anodic oxide films formed in the electrolyte containing sulphuric acid and oxalic acid, using the Design of Experiments and subsequent mathematical and statistical analysis.

In regard to the complexity of the anodizing process of aluminium and its alloys, it is necessary to monitor the temperature effect in interaction with other factors affecting at actual current density and not as the only factor influencing the observed parameter.

MATERIAL AND EXPERIMENTAL METHODS

Aluminium sheet EN AW-1050 A - H24 with chemical symbol Al 99,5 of thickness 0,5 mm was used as an experimental anode material.

The chemical composition of experimental material is shown in Table 1.

Table 1 **Chemical composition of experimental material / wt.%**

Si	Fe	Cu	Mn	Cr	Zn	Ti
0,25	0,40	0,05	0,01	0,01	0,07	0,05

The samples with dimensions $100 \times 70 \times 0,5$ mm were chemically degreased in solution containing: sodium bicarbonate < 20 %, sodium metasilicate pentahydrate < 5 %, phosphates < 30 %, borates < 40 % and surfactants, at the temperature 50 ± 2 °C for total exposure time 15 minutes. The samples were then rinsed thoroughly in deionized water and immersed in a 45 % sodium hydroxide solution at a temperature 55 ± 2 °C for 1 min. The anodizing was performed based on the Design of experiments methodology corresponding to the rotatable central composite design with 44 test runs. The individual runs were carried out according to the design of experiment as a combination of factor levels corresponding to Table 2.

After anodizing, the samples were immediately rinsed in cooled (approx. 10 °C) demi-water for 1 minute, followed by rinsing in running tap water for another 2 minutes to wash-out the electrolyte entrapped in the defects. The specimens were thereafter dried with compressed air and in an oven (at temperature 50 °C, for time 20 minutes).

In the field of surface treatment the Hull cell is mostly used to verify the electrolyte functionality and chemical composition of electrolyte.

RESULTS AND DISCUSSION

The temperature effect on the predicted value of microhardness of AAO layer in the wide temperature is from range 0 °C to 45 °C. Figures 1, 2, 3 show the change in microhardness value at a constant applied

Table 2 **Conditions of performed experiment**

EXPERIMENT GX5							
Anodic oxidation method			GX5				
Type of experiment design			The rotatable central composite design				
The number of factors:	5		The number of test runs:	44			
Controlled factors							
Factor code	Factor	Unit	Factor Level				
			-2,37	-1	0	+1	+2,37
x_1	m (H ₂ SO ₄)	g.l ⁻¹	9,19	85	140	195	270,81
x_2	m (C ₂ H ₂ O ₄)	g.l ⁻¹	5,80	12	16	21	27,20
x_3	T	°C	-1,78	12	22	32	45,78
x_4	t	min	1,22	15	25	35	48,78
x_5	U	V	6,43	8	10	11,5	13,57
Constant factors							
anode / cathode material:			AW - 1050A H24				

voltage 11 V, in the electrolyte containing 16,50 g.l⁻¹ of oxalic acid, throughout the study domain of the amount of sulphuric acid and anodizing time according to Table 2, at the electrolyte temperature 0 °C (Figure 1), at the electrolyte temperature 20 °C (Figure 2), at electrolyte temperature 45 °C (Figure 3).

Two areas with the maximum value of microhardness $HV_{0,01} = 266,449$ can be seen at the lower and upper interval limit of the amount of sulphuric acid at short periods of anodizing time (circa to 10 minutes). On the both of these limit intervals of the sulphuric acid concentration, the value of microhardness decreases with increasing the total anodizing time, what can be explained by low value of applied voltage and lower thickness of formed layer related with it. At sulphuric acid concentrations in interval from 90 to 160 g.l⁻¹, the increasing microhardness was recorded.

It should be noted that with increasing the electrolyte temperature up to 20 °C (Figure 2) the area of higher microhardness value is extended in two intervals of

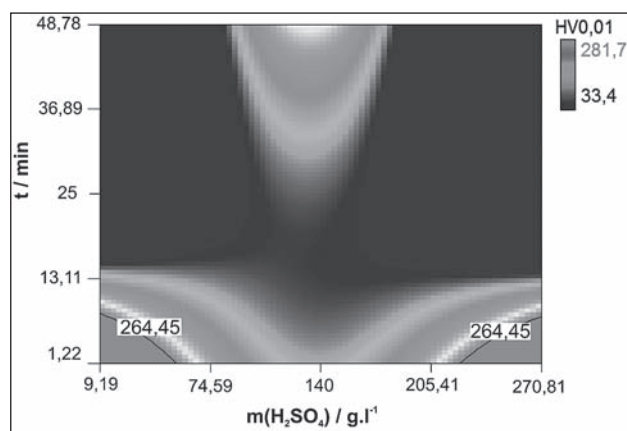


Figure 1 The simulated change in microhardness value of AAO layer in electrolyte at temperature 0 °C depending on the amount of sulfuric acid in the electrolyte and anodizing time

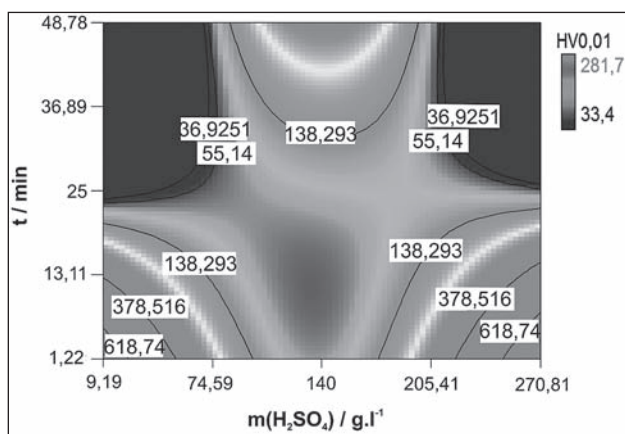


Figure 2 The simulated change in microhardness value of AAO layer in electrolyte at temperature 20°C depending on the amount of sulfuric acid in the electrolyte and anodizing time

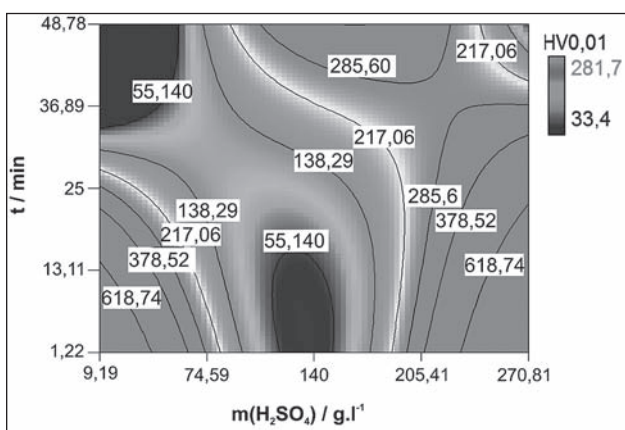


Figure 3 The simulated change in microhardness value of AAO layer in electrolyte at temperature 45°C depending on the amount of sulfuric acid in the electrolyte and anodizing time

used amount of sulphuric acid in the electrolyte, i.e. in the interval from 9,19 to 74,59 g.l⁻¹ and 205,41 – 270,81 g.l⁻¹ at simultaneously increasing of anodizing time to circa 17 minutes. Prolongation of anodizing time at the electrolyte temperature of 20 °C causes the dissolution of the layer and thus reducing of the thickness and consequently decreasing of the microhardness values in these limit intervals.

The increasing microhardness values can be seen in the middle interval of the sulphuric acid concentration (140 ± 20 g.l⁻¹) at anodizing time interval from 40 to 48,78 minutes. The increasing of the electrolyte temperature at lower value of DC voltage supply has resulted in increasing value of the observed response. However, it should be noted that the qualitative characteristics of the formed layers at lower and upper limit of used sulphuric acid concentration are very bad and the layers formed under these conditions are practically useless despite of higher microhardness value.

The increasing of the electrolyte temperature up to 45 °C at a constant anodic current density $J_A = 3 \text{ A.dm}^{-2}$ results in increase of the microhardness value of the

formed layer, in the range of used sulphuric acid concentration from 180 to 270,81 g.l⁻¹ throughout the study domain of anodizing time. At low sulphuric acid concentrations (from 9,19 to 74,59 g.l⁻¹), the creation of layer with a higher microhardness value is delayed until anodizing time of 25 minutes. The prolongation of anodizing time at a given temperature of 30 °C leads to the fast chemical dissolution of the formed layer, what results in decrease of its mechanical properties.

CONCLUSION

In this study the microhardness of anodic alumina oxides (AAO), produced by anodizing of 99,5 % pure aluminium electrodes EN AW-1050 A - H24 at constant anodic current density $J_A = 3 \text{ A.dm}^{-2}$ under varied and controlled experimental conditions (listed in Table 2), were evaluated as a function of physical and chemical factors acting during the anodizing process. Based on the experimental analysis performed and evaluated according to the DoE methodology with 44 individual trials, the following can be concluded:

- the microhardness of deposited layer is influenced by the size of applied voltage and anodizing time,
- the electrolyte temperature is statistically insignificant as the main factor effect,
- the electrolyte temperature appeared to be significant as the factor effect only in interaction with other observed variables – factors; so the microhardness of deposited layers accordingly increase with increasing electrolyte temperatures,
- the increasing electrolyte temperature from 0 °C to 20 °C at a constant applied voltage and oxalic acid concentration in the electrolyte, results in increasing of microhardness value of deposited film of almost 233 %; but the increase of electrolyte temperature from 20 °C to 45 °C not affect the microhardness value so:
- with increasing the electrolyte temperature from 20 °C to 45 °C, the interval of higher value of microhardness is extended in relation to total anodizing time at a sulphuric acid concentration in the electrolyte in the range from 9,19 to 74,59 g.l⁻¹ for 25 minutes; at sulphuric acid concentration in the range from 180,00 to 270,81 g.l⁻¹ this area approximately extends to the whole interval of anodizing time.

The determination of dependency, at which are formed AAO layers of certain mechanical properties have a significant impact on the environment and also of the work environment, especially it is the result of the total quantity of the used sulfuric acid in the the electrolyte and electrolyte temperature at anodic oxidation.

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REFERENCES

- [1] D. AlMawlawi, N. Coombs, M. Moskovits, *J. Appl. Phys.* 70 (1991) 4421
- [2] N. Haberkorn, J.S. Gutmann, P. Theato, *ACS Nano* 3 (2009) 1415
- [3] G. Gorokh, A. Mozalev, D. Solovei, V. Khatko, E. Llobet, X. Correig, *Electrochim. Acta* 52 (2006) 1771
- [4] J. H. Holtz, S. A. Asher, *Nature* 389 (1997) 829
- [5] M. Deubel, G. von Freymann, M. Wegener, S. Pereira, K. Busch, C. M. Soukoulis, *Nat. Mater.* 3 (2004) 444
- [6] G. Sauer, G. Brehm, S. Schneider, K. Nielsch, R.B. Wehrspohn, J. Choi, H. Hofmeister, U. Gösele, *J. Appl. Phys.* 91 (2002) 3243
- [7] Santos, L. Vojkuvka, J. Pallarés, J. Ferré-Borrull, L. F. Marsal, *Nanoscale Research Letters* 4 (2009) 1021
- [8] T. Aerts, Th. Dimogerontakis, I. DeGraeve, J. Fransaeer, H. Terryn, *Surface & Coatings Technology* 201 (2007) 7310–7317
- [9] L. E. Fratila-Apachitei, J. Duszczuk, L. Katgerman, *Surface and Coatings Technology* 165 (2003) 309–315
- [10] L. Vojkuvka, A. Santos, J. Pallarés, J. Ferré-Borrull, L. F. Marsal, J.P. Celis, *Surface & Coatings Technology* 206 (2012) 2115–2124
- [11] P. G., Sheasby, R. Pinner, *The Surface Treatment and Finishing of Aluminium and its Alloys*, 6th Edition, ASM International, USA/ Finishing Publications Ltd, UK, 2001, 743.
- [12] B. A. Scott, *Trans. Inst. Met. Finish.* 43 (1965) 1.
- [13] S. Koizumi, S. Ninagawa, S. J. Ueda, *J. Metal Finishing Society Japan* 19 (1968) 504
- [14] K. Okubo, *Met. Finish.* 81 (1983) 63.
- [15] A. P. Gruar, D. R. Gabe, *Trans. Inst. Met. Finish.* 63 (1985) 1.
- [16] L. E. Fratila-Apachitei, J. Duszczuk, L. Katgerman, *Surf. Coat. Technol.* 165 (2003) 309.
- [17] J. Herenguel, R. Segond, *Rev. Met.* 46 (1949) 377.
- [18] R. W. Thomas, *Trans. Inst. Met. Finish.* 59 (1981) 97.

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