

## STATISTICAL ELOXAL COATING MICROHARDNESS ANALYSIS

BADIDA, M[iroslav]; GOMBAR, M[iroslav]; KMEC, J[an] & SOBOTOVA, L[ydia]

**Abstract:** *In order to improve the mechanical properties of the excluded layer by anodic oxidation of aluminum on material EN AW-1050 H24, there was investigated the micro-hardness of excluded layers as a function of physical and chemical factors involved in the anodic oxidation process. The constant current density was  $J_A = 3 \text{ A.dm}^{-2}$  in the electrolyte, constituted by sulfuric acid and oxalic acid. The emphasis was put on the impact of all considered active factors and their interactions in this process. The model of studied dependence was designed based on mathematical and statistical analysis of matrix with experimental obtained data of composition rotation plan of experiment with five independent variables factors (amount of sulfuric acid in the electrolyte, amount of oxalic acid in the electrolyte, temperature of electrolyte, anodizing time and applied voltage). The experiment was carried out on 44 separate attempts with current change of values of individual factors under defined levels in each implementation.*

**Keywords:** *Aluminium anodic oxidation, microhardness, Design of Experiments*

### 1. INTRODUCTION

In many applications of structural components made of aluminum and its alloys, which are governed by anodic oxidation, have a key role in the mechanical properties, especially micro-hardness and wear resistance. Depending on the conditions of anodizing, these properties can vary widely, so research on the impact of chemical, physical and technological factors on the resulting AAO layers has gained much attention. Basic information related to these dependences we can find in the literature [1], [2], [3].

Most experimental works, in the field of (micro) hardness, are performed in the "heavy" anodizing conditions, under which we may include low temperatures of the electrolyte and also special chemical composition of the electrolytes. But their primary purpose is to identify the high-values of micro-layers [4]. According to Scott [5], the anodic oxidation in sulfuric acid at a constant current density  $4-2 \text{ A.dm}^{-2}$  was varied at temperature ranges from  $-5^\circ\text{C}$  to  $+15^\circ\text{C}$ , the micro-hardness is affected by such conditions on a small scale, with what is related to wear resistance.

Another study published by Koizumi [6], which deals with the anodic oxidation of aluminum in the galvanic-static mode at current densities of 1 to  $8 \text{ A.dm}^{-2}$  in the electrolyte, constituted by sulfuric acid and oxalic acid at electrolyte temperatures between  $-5^\circ\text{C}$  to  $+20^\circ\text{C}$ , claims that the examined interval is the micro-hardness and wear resistance nearly constant in the temperature range  $-5^\circ\text{C}$  to  $+5^\circ\text{C}$ , regardless of the applied current density. Furthermore, this study argues that in an increase

temperature of the electrolyte occurs gradually reducing the value of the micro-hardness. The decline is more pronounced at the using of lower current density values. This argument, however, should be taken with caution, because the anodizing time in this experiment was always constant, it means 45 minutes, regardless of used current density. As a result, there were created and then evaluated the layers with greater thickness, which one directly affects on the final value of micro-hardness and wear resistance [7] [8] [9].

The oxide layers with the thickness of  $25 \mu\text{m}$  or more, formed in the electrolyte, constituted by sulfuric acid at temperatures in the range  $+15^\circ\text{C}$  to  $+30^\circ\text{C}$  and at various applied current densities ( $1-4 \text{ A.dm}^{-2}$ ), according to some authors [10], [11], are characterized by a softer outer layer, which reduces the transparency of the layer and its resistance to wear. Such effects have been the similar on the value of micro-hardness according to mentioned works.

Regarding of the influence of electrolyte temperature on the microstructure of anodic formed layers at potentiostatic conditions, some authors argue that the increasing temperature of the electrolyte leads to a decreasing value of the ratio of the thickness of the barrier layer to the applied voltage together with the reduction of the pore diameter [12]. Recent studies show that the thickness of the barrier layer is independent on the electrolyte temperature and applied electric potential [13] [14]. Usually, there is received the concept of increased level of the chemical dissolution of created oxide layer, generated at elevated temperature of the electrolyte, which leads to the conical shape of pores with their increasing diameter towards to the surface [15], so the dissolution of the material of the walls of pores is resulting in increasing of layer porosity.

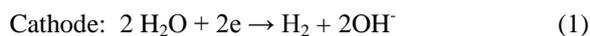
Based on the review of published papers from the area of the mechanical properties of anodic formed layers, focusing particularly on the micro-hardness, the emphasis is putting on the influence of electrolyte temperature and applied current density without considering of other factors. Therefore, in this study is, through a planned experiment and subsequent mathematical and statistical analysis, observed not only effect of the electrolyte temperature, but also recent influence of next chemical and physical factors affecting both on the thickness and on the mechanical properties of layers formed by anodic oxidation of aluminum in an electrolyte constituted by sulfuric acid and oxalic acid. The effect of temperature, due to the complexity of the anodizing process of aluminum and its alloys, should be monitored in interaction with other factors that were

considered in a particular current density and not alone as the only effect influencing an endpoint parameter.

## 2. ALUMINIUM ANODIC OXIDATION

Anodic oxidation represents one of important methods of aluminium and its alloys surface finish. It represents an exceptional combination of scientific and natural aspects for one of the most effective kinds of surface finish creating. It is an electrochemical process which reinforces and firms up a naturally created oxidic layer. A surface microscopical structure as well as metal crystal structure changing near the surface is achieved by anodic oxidation. By final finishing procedure, the second hardest substance (after diamond hardness) is obtained. The surface layer is porous and it is a part of the metal. The layer also enables dyestuff or oil to penetrate and thus it is practicable to get various colour effects and to improve sliding properties.

The first hypothesis about anodic oxide layers forming mechanics was published in 1932. Till recent days no generally accepted theory totally clarifying this process has been developed. One of the theories [16] clarifies oxide layer formation. The theory is based on the fact that hydrogenium is produced on the cathode of insoluble metal and in the same time alkalinity grows due to hydroxyl anion concentration rising:



In the beginning of the process, some amount of aluminium is dissolved due to passing electric current, but with aluminium cations, and simultaneously a coating of insoluble aluminium hydroxide with electro-insulating properties is formed. This causes growth of electrical resistance and thus heating of layers. Following dehydration generates a layer of aluminium oxide. However, the anodic layer is not only the aluminium oxide one. It contains also water, anions of electrolyte, not oxidized impurities and alloy ingredients which the basic material may contain.

Since 1953 the Keller's, Hunters's and Robinson's theory has been known. According to it, the oxide layer consists of hexagonal prismatic cells with pores in their centres which are ended with approximately semi-globular bottom on the barrier layer, Fig. 1.

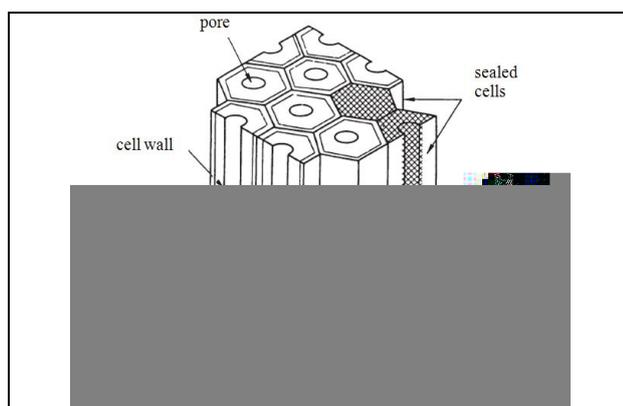


Fig. 1. Anodic oxidized layer structure [3]

More exact interpretation of anodic aluminium oxidation reaction mechanics theory is based on the assumption that aluminium is covered with aluminium oxide layer which creates a large amount of pores. During aluminium anodic oxidation process, a barrier layer is formed and thus a pore layer grows on it. Processes inside the layer are chemical and physical. Regressive dissolving of the layer at the bottom of pores is a process supported by electrical field; it is not case of simple chemical dissolving. Three components of current flow through the barrier layer: ion current, which causes layer porous part growth, ion current, which accompanies regressive layer dissolving process and electron current.

A base of another theory is existence of barrier layer planar inhomogeneity. This layer consists of areas with different electrical conductivity. Above low conductivity areas the oxide layer after reaching specific thickness cannot grow any more and pores begin being formed. On aluminium surface due to inserted voltage aluminium cations and oxygenium anions are formed. They move in counter movement. Their reciprocal reactions proceed near porous bottom.

## 3. EXPERIMENTAL PART

High-quality preparation, realization and analysis of scientific and research experiments in laboratory experiments area requires mastering and learning a certain complex of knowledge and methodology known as DOE – Design of Experiments.

A frequent task of experiments in technology practice is to find out relations and links among certain quantities of studied process. It is important in cases when the process is very complicated and there is no sufficiently suitable mathematical-physical-chemical model for it. Common aim of the experiment is to determine how some factors influence studied quantity often called a response. Required data for model design can be obtained by studied process quantities observing. [17],[18],[19] and [20].

For experiment realization a central composite plan with 44 experiments has been used. The experiments itself consisted of complete factor experiment type  $2^k$  where  $k$  represents numbers of factors – input independent variables and this complete factor experiment represents a core of the plan. Also, so called **star-radial** points and two measurements in experiment schedule centre were used. Coded and natural intervals of individual factors are shown in Tab 1.

| Coded factor | Factor      | Unit                         | Factor level in natural scale |     |      |      |        |
|--------------|-------------|------------------------------|-------------------------------|-----|------|------|--------|
|              |             |                              | -2,37                         | -1  | 0    | +1   | +2,37  |
| $x_1$        | sulph. acid | $\text{g}\cdot\text{l}^{-1}$ | 9,19                          | 85  | 140  | 195  | 270,81 |
| $x_2$        | oxalic acid | $\text{g}\cdot\text{l}^{-1}$ | 5,80                          | 12  | 16,5 | 21   | 27,2   |
| $x_3$        | temperature | $^{\circ}\text{C}$           | -1,78                         | 12  | 22   | 32   | 45,78  |
| $x_4$        | time        | min                          | 1,22                          | 15  | 25   | 35   | 48,78  |
| $x_5$        | voltage     | v                            | 6,43                          | 8,5 | 10   | 11,5 | 13,57  |

Tab. 1. Experiment real conditions

Individual experiments were carried out in random order at current density  $3 \text{ A}\cdot\text{dm}^{-2}$ .



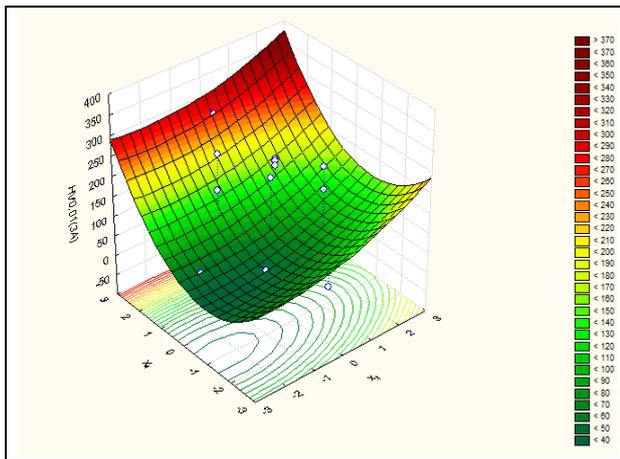


Fig. 5. Dependence between Factors  $x_1$  and  $x_4$

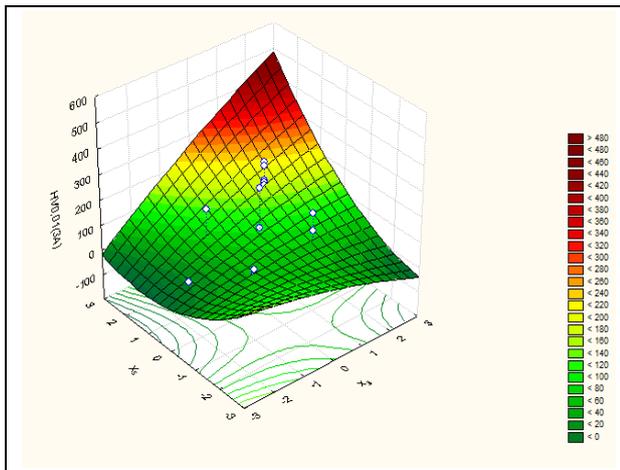


Fig. 6. Dependence between Factors  $x_3$  and  $x_5$

## 5. CONCLUSION

Anodic aluminium oxidation represents effective way of aluminium and alloy constructional parts surface finish. Apart from corrosion resistance and thermal insulation properties improvement, surface microhardness increases, too[21][22]. However, it would be a mistake to assume that anodic oxidation means substantial increase of material hardness and thus aluminium mechanical resistance, because anodic layer thickness is 0.01 – 0.05 mm. Coating microhardness increase itself depends on running conditions and especially on electrolyte composition, which is mostly sulfuric acid and water solution only. It depends also on time of anodic oxidation, electrolyte temperature and voltage. These general conclusions are supported by results of performed experiment whose results are valid only within intervals of used independent variable factors. This is the reason why it is necessary to carry out further experiments with extended intervals to obtain valid conclusions within complete scale of practically used working conditions.

The results of experimental research presented in this paper are rejected pilot study of research of mechanical properties of layers formed by anodic oxidation of aluminium and its alloys. The team of authors in the future plans to expand research for next practically used anodic current densities as well as to extend the interval of parameters engaged in the technological process of anodic

oxidation and to work with comparison of results at using of electrolytes with different chemical compositions.

## 6. ACKNOWLEDGEMENTS

The authors express their sincere thanks to Slovak Ministry of Education, Science, Research, project KEGA 049-TUKE- 4/2012 and project VEGA No. 1/ 0396/11.

## 7. REFERENCES

- [1] T. Aerts , Th. Dimogerontakis , I. DeGraeve , J. Fransaeer , H. Terryn, *Surface&CoatingsTechnology* 201 (2007) 7310–7317
- [2] L.E. Fratila-Apachitei, J. Duszczyc, L. Katgerman, *Surface and CoatingsTechnology* 165 (2003) 309–315
- [3] L. Vojtkuvka , A. Santos , J. Pallarès , J. Ferré-Borrull , L.F. Marsal , J.P. Celis, *Surface&CoatingsTechnology* 206 (2012) 2115–2124
- [4] P.G., Sheasby, R., Pinner, *TheSurfaceTreatment and FinishingofAluminium and itsAlloys*, 6th Edition, ASM International, USA/ FinishingPublicationsLtd, UK, 2001, 743
- [5] B.A. Scott, *Trans. Inst. Met. Finish.* 43 (1965) 1
- [6] P.G. Sheasby, R. Pinner, *TheSurfaceTreatment and FinishingofAluminium and itsAlloys*, 6th Edition, ASM International, USA/ FinishingPublicationsLtd, UK, 2001, 761 (after S. Koizumi, S. Ninagawa, S.J. Ueda, *J. Metal Finishing Society Japan* 19 (1968) 504)
- [7] K. Okubo, *Met. Finish.* 81 (1983) 63
- [8] A.P. Gruar, D.R. Gabe, *Trans. Inst. Met. Finish.* 63 (1985) 1
- [9] L.E. Fratila-Apachitei, J. Duszczyc, L. Katgerman, *Surf. Coat. Technol.* 165 (2003) 309
- [10] J. Herenguel, R. Segond, *Rev. Met.* 46 (1949) 377
- [11] R.W. Thomas, *Trans. Inst. Met. Finish.* 59 (1981) 97
- [12] J.P. O'Sullivan, G.C. Wood, *Proc. R. Soc. Lond., A* 317 (1970) 511
- [13] Y.-C. Kim, B. Quint, R.W. Kessler, D. Oelkrug, *J. Electroanal. Chem.* 468 (1999) 121
- [14] P.G. Sheasby, R. Pinner, *TheSurfaceTreatment and FinishingofAluminium and itsAlloys*, 6th Edition, ASM International, USA/ FinishingPublicationsLtd, UK, 2001, p 368(after K. Ebihara, H. Takahashi, M. Nagayama, *J. Metal Finishing Japan* 33 (1982) 4)
- [15] F. Debuyck, M. Moors, A.P. VanPeteghem, *Mater. Chem. Phys.* 36 (1993) 146
- [16] Badia, M., Majerník, M., Šebo, D. & Hodolič, J., *Engineering and manufacturing environment (Strojárska výroba a životné prostredie)*. Viena, pp. 253. ISBN 80-7099-695-1: Košice, 2001
- [17] Zdravecká, E., Briančin, J. & Fecsu, Š., *Analysis of selected properties of PVD films*. Scientific Bulletins of University of Technology. No. 253, pp. 305-310. ISSN 0209-2689, Rzeszów, 2008
- [18] Štefko, R., Slusarczyk, B., Kot, S. & Kolmasiak, C., (2012). *Transformation on Steel Products Distribution in Poland and Slovakia*. *Metallurgija*, Vol: 51, pp. 133-136, ISSN 0543-5846, 2012
- [19] Pavlenko, S., Haľko, J., Maščenik, J. & Nováková, M., *Machine Parts Design with PC Support*, Vol: 1. FVT TU, pp. 347, ISBN 978-80-553-0166-2: Prešov, 2008
- [20] Maščenik, J. & Gáspár, Š., (2011). *Experimental Assessment of Roughness Changes in the Cutting Surface and Microhardness Changes of the Material S 355 J2 G3 after Being Cut by Non-Conventional Technologies* In: *Advanced Materials Research*. Vol. 314-316, pp. 1944-1947. ISSN 1022-6680: Prešov, 2011
- [21] Muránsky, J., Badida, M. & Hricová, B., *Ecodesign in Engineering (Ekodizajn v strojárstve)*. Elfa , pp. 198, ISBN 978-80-553-0788-6, Košice, 2011
- [22] Wessely, E., Kralikova, R. & Krupa, M., *Evaluation of work environment factors in mechanical engineering plants* 2010. In: *Annals of DAAAM for 2010 & Proceedings of the 21th international DAAAM symposium.: DAAAM International*, pp. 219-220. - ISBN 978-3-901509-73-5 - ISSN 1726-9679- , Vienna, 2010