

Prediction of the Effect of Chemical Composition of Electrolyte on the Thickness of Anodic Aluminium Oxide Layer

P. Michal, A. Vagaská, M. Gombár, J.Kmec, E. Spišák, M. Badida

Abstract—The paper describes some possibilities of control of technological process of anodic aluminium oxidation based on the experimental study and investigation of the influence of chemical composition of the used electrolytes on the thickness of the formed oxide layer. The influence of individual factors acting during the anodic oxide process has been investigated and based on the experimental results the prediction model was developed by the usage of neural networks, especially the cubic neural unit. The developed prediction model determines the layer thickness at surface current density $1 \text{ A}\cdot\text{dm}^{-2}$. The reliability of the developed model is 72.53 % with predetermined tolerance range of $\pm 2\cdot 10^{-3}$ mm.

Keywords—aluminium anodic oxidation, design of experiments, prediction model

I. INTRODUCTION

ALUMINIUM and its alloys belong to the materials with the highest annual increase in consumption nowadays. It is highly appreciated in almost every branch of industry for its excellent mechanical, electrical and chemical properties [1], [2]. Appearance and surface quality of parts made of aluminium and aluminium alloys is sufficiently high even before any surface treatment. To maximize service life of aluminium products, it is necessary to apply appropriate surface treatment.

The research is supported by the project VEGA 1/0738/14. Title of the project: “The Study of Corrosion Resistance of Coated Steel Sheets for Use in Automotive Industry”.

P. Michal, Technical University of Košice, Faculty of Manufacturing Technologies, Department of Mathematics, Informatics and Cybernetics, 08001 Prešov, Slovak Republic (e-mail: peter.michal@tuke.sk)

A. Vagaská, Technical University of Košice, Faculty of Manufacturing Technologies, Department of Mathematics, Informatics and Cybernetics, 08001 Prešov, Slovak Republic (e-mail: alena.vagaska@tuke.sk)

M. Gombár, University of Prešov in Prešov, Faculty of Management, Department of Management, 08001 Prešov, Slovak Republic (e-mail: gombar.mirek@gmail.com)

J. Kmec, Institute of Technology and Businesses in České Budějovice, The Department of Mechanical Engineering, Okružní 517/10, 370 01 České Budějovice, Czech Republic, (e-mail: doc.kmec@gmail.com)

E. Spišák, Technical University of Košice, Faculty of Mechanical Engineering, Department of Technologies and Materials, 042 00 Košice, Slovak Republic (e-mail: emil.spisak@tuke.sk)

M. Badida, Faculty of Mechanical Engineering, Department of Environmentalistics, Technical University of Košice, 042 00 Košice, Slovak Republic (e-mail: miroslav.badida@tuke.sk)

Anodic oxidation is the most frequently used but also the least explored method of surface treatment of aluminium profiles as means to increase corrosion resistance. [3], [4]. Its basis lies in enrichment of aluminium part surface with oxygen [5], [6] in acidic environment, under electric current, while a thin layer of AAO (Anodic Aluminium Oxide) is created. The most common component of electrolytes involved in the process of anodic aluminium oxidation is sulphuric acid [7], which has an influence on geometric structure of created oxide layer – observed by Tsangaraki et al. [8], Patermarakis [9], and Aerts et al. [10]. In contrast to previously mentioned authors, this article takes into account other components of electrolyte, especially oxalic acid, aluminium cations and their interactions.

II. EXPERIMENTAL METHOD

For the purposes of experiment, samples of alloy EN AW 1050 H24 were used. These samples were oxidized in electrolytes with different chemical composition (concentration of sulphuric acid in electrolyte $c_1= 0.34 \text{ mol}\cdot\text{l}^{-1}$ to $3.74 \text{ mol}\cdot\text{l}^{-1}$, concentration of oxalic acid in electrolyte $c_2= 1.65\cdot 10^{-2} \text{ mol}\cdot\text{l}^{-1}$ to $2.28\cdot 10^{-2} \text{ mol}\cdot\text{l}^{-1}$, concentration of aluminium cations in electrolyte $c_3=6.67\cdot 10^{-3} \text{ mol}\cdot\text{l}^{-1}$ to $6.23\cdot 10^{-1} \text{ mol}\cdot\text{l}^{-1}$) and with different operating conditions during the process of anodic oxidation of aluminium (electrolyte temperature $T=-1.78 \text{ }^\circ\text{C}$ to $45.78 \text{ }^\circ\text{C}$, oxidation time $t=6.21 \text{ min}$ to 57.77 min , connected voltage $U=5.24 \text{ V}$ to 14.76 V). Composition of electrolyte and the individual operating conditions were predetermined according to the central composite design of experiment.

III. EVALUATION OF EXPERIMENT

Determine the relationship between the chemical composition of the electrolyte and the resulting AAO layer thickness created during the oxidation process consisted of two connected methods of experiment evaluation. Factors that have a significant effect on the thickness of the formed AAO layer and their interactions were identified in the first step. These factors and their interactions were used in the second step in order to create a prediction model by using methods of artificial intelligence. Specifically, a modified type of cubic neural unit, the 3rd order HONU (Higher Ordered Neural Unit)

based on adaptive optimization Levenberg–Marquardt algorithm, was used.

The application of a coded scale for the evaluation of experimental results prevents from distortion of the experimental results by absolute sizes of the individual factors. Table. I. presents the conversion of input factors between coded and natural scale.

Table. I Influence of input factors

Coded scale	x_1	x_2	x_3	x_4	x_5	x_6	
Natural scale	H ₂ SO ₄ [mol·l ⁻¹]	C ₂ H ₂ O ₄ [mol·l ⁻¹]	H ₃ BO ₃ [mol·l ⁻¹]	T [°C]	U [V]	t [min]	
Factor levels	-2.37	0.34	1.65·10 ⁻²	6.67·10 ⁻³	-1.78	5.24	6.21
	-1	1.33	7.77·10 ⁻²	1.85·10 ⁻¹	12.00	8.00	20.00
	0	2.04	1.22·10 ⁻¹	3.15·10 ⁻¹	22.00	10.00	30.00
	1	2.75	1.66·10 ⁻¹	4.45·10 ⁻¹	32.00	12.00	40.00
	2.37	3.74	2.28·10 ⁻¹	6.23·10 ⁻¹	45.78	14.76	55.77

Table. II shows the influence (expressed in percentages) of individual significant input factors and their interactions on the resulting AAO layer thickness. There are presented only such input factors and their combinations which have been identified as significant based on statistical analysis. The level of statistical significance was set at $\alpha=5\%$.

Table. II Influence of input factors

Factor	Influence[%]	Factor	Influence [%]
x_1	8.55	$x_4 \cdot x_5$	1.65
x_2	0.18	$x_4 \cdot x_6$	1.70
x_3	3.00	$x_5 \cdot x_5$	1.94
x_4	3.44	$x_5 \cdot x_6$	0.59
x_5	4.56	$x_6 \cdot x_6$	3.02
x_6	9.52	$x_1 \cdot x_1 \cdot x_1$	5.86
$x_1 \cdot x_1$	5.79	$x_1 \cdot x_1 \cdot x_2$	0.20
$x_1 \cdot x_2$	2.73	$x_1 \cdot x_1 \cdot x_3$	1.96
$x_1 \cdot x_3$	0.84	$x_1 \cdot x_1 \cdot x_4$	3.86
$x_1 \cdot x_4$	2.60	$x_1 \cdot x_1 \cdot x_5$	1.12
$x_1 \cdot x_5$	0.02	$x_1 \cdot x_1 \cdot x_6$	3.70
$x_1 \cdot x_6$	2.38	$x_1 \cdot x_2 \cdot x_3$	2.86
$x_2 \cdot x_2$	1.63	$x_1 \cdot x_2 \cdot x_4$	1.65
$x_2 \cdot x_3$	2.14	$x_1 \cdot x_2 \cdot x_5$	0.55
$x_2 \cdot x_4$	0.82	$x_1 \cdot x_2 \cdot x_6$	1.96
$x_2 \cdot x_5$	0.55	$x_1 \cdot x_3 \cdot x_4$	0.42
$x_2 \cdot x_6$	0.15	$x_1 \cdot x_3 \cdot x_5$	0.75
$x_3 \cdot x_3$	4.10	$x_1 \cdot x_3 \cdot x_6$	0.40
$x_3 \cdot x_4$	0.73	$x_1 \cdot x_4 \cdot x_5$	1.85
$x_3 \cdot x_5$	2.75	$x_1 \cdot x_4 \cdot x_6$	1.12
$x_3 \cdot x_6$	0.86	$x_1 \cdot x_5 \cdot x_6$	2.00
$x_4 \cdot x_4$	3.50		

The influence of 83 combinations of factors and their interactions has been investigated, but only 43 combinations of factors and their interactions have significant influence on the AAO layer thickness, as we can see in the Table. II. It means that effect of 40 factor combinations we can eliminate and still we can obtain sufficiently precise prediction model. It was possible to create a prediction model determining the resulting AAO layer thickness by usage 43 significant combinations of factors and their interactions. These factors were considered as inputs for neural unit. Also we can see that the influence of factor x_1 in combinations is significant 23 times. It means that factor x_1 has the most significant influence on the resulting AAO layer thickness.

In the training process of neural units only 30 samples of total 46 samples were used. Samples which were not used during the training process of neural unit were used to verify the accuracy of prediction model. Fig.1 shows training process of neural unit and Fig. 2 shows the verification process of prediction model. As can be seen in Fig. 1, measured and calculated values are identical for almost every sample after the training. After the training process, the value of adjusted index of determination of the data variability was 98.75%. It During the verification process of prediction model there occurs a difference between measured and calculated values of formed oxide layer, as it is shown in Fig. 2. It is possible to set the tolerance range $\pm 2.00 \text{ mm} \cdot 10^{-3}$. The value of adjusted index of determination of the data variability was calculated after the verification process, it was 72.53%.

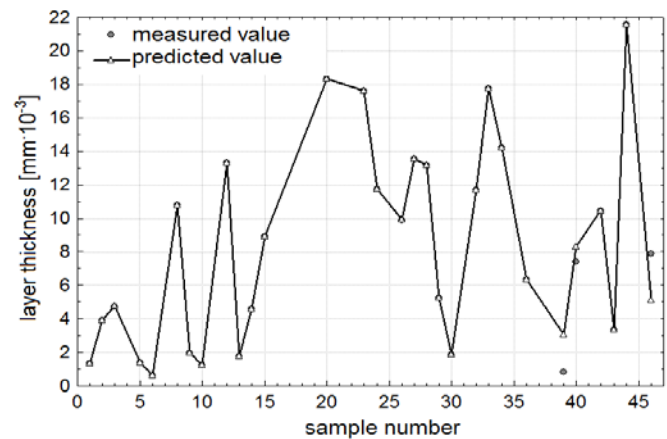


Fig. 1 Measured and calculated values for training processes

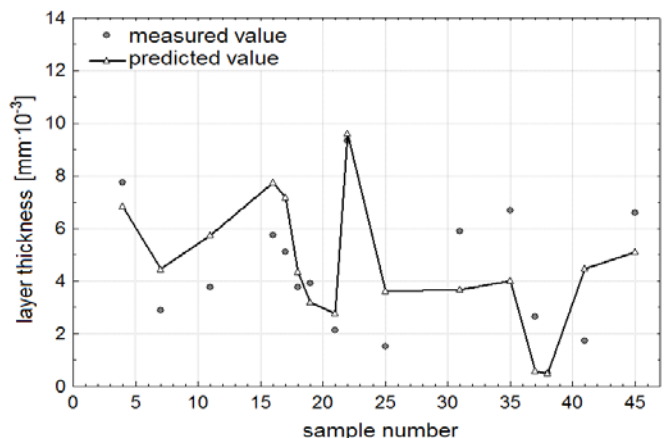


Fig. 2 Measured and calculated values for verification processes

IV. RESULTS AND DISCUSSION

Based on the developed prediction model, it was possible to determine the influence of chemical composition of electrolyte on the created oxide layer thickness. This influence is shown in the next figures, from Fig. 3 to Fig. 8. For all plotted relationships it was considered with the same values of factors x_4, x_5, x_6 , and their values were set to factor level "0".

Fig. 3 shows the effect of factor x_1 (concentration of sulphuric acid in the electrolyte) on the AAO layer thickness at different levels of factor x_2 and with constant level of factor $x_3="0"$. Fig. 4 shows the effect of factor x_1 (concentration of sulphuric acid in electrolyte) on the AAO layer thickness at different levels of factor x_3 with constant level of factor $x_2="0"$.

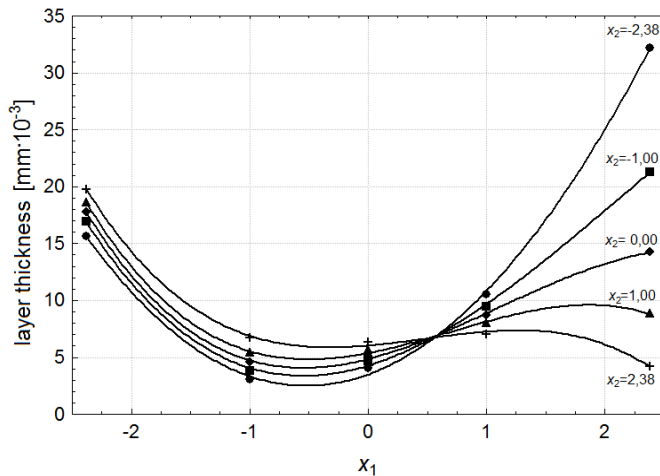


Fig. 3 Influence of factor x_1 on AAO layer thickness, $x_3="0"$

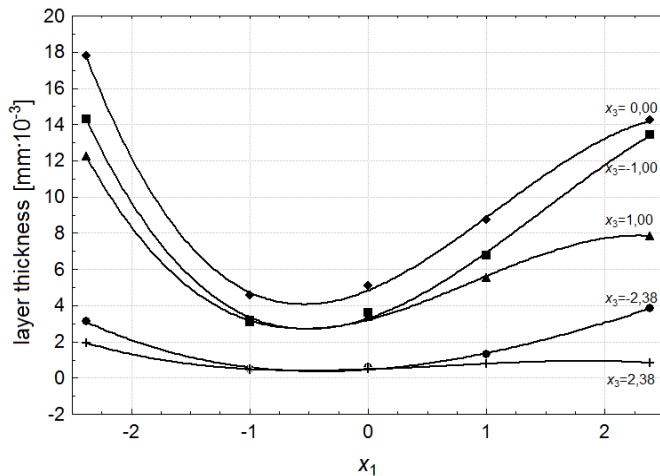


Fig. 4 Influence of factor x_1 on AAO layer thickness, $x_2="0"$

As it is shown in Fig. 3 and Fig. 4, with increasing level of factor x_1 (from its observed minimum to its zero value) the AAO layer thickness decreases for all shown levels of factor x_2 . Subsequently increasing of factor x_1 has positive effect on the AAO layer thickness. The thickness is growing faster at lower levels of factor x_2 than at higher levels of factor x_2 . This state is caused by the dissociated ions of used acids and aggressiveness of environment (used electrolyte) in which the sample resides during the oxidation. It is a state in which

increasing levels of factors x_1 and x_2 from their observed minimum to their zero values results in increasing of aggressiveness of the environment and it is increasing more rapidly than the number of dissociated ions in the electrolyte. When the level of factor x_1 crosses the zero level, the amount of dissociated ions in electrolyte begins to increase faster. Thus the speed of AAO layer build-up is higher as the speed in which the layer dissolves back into the electrolyte.

Fig. 5 shows the effect of factor x_2 (concentration of oxalic acid in electrolyte) on the AAO layer thickness with varying levels of factor x_3 and constant level of factor $x_1="0"$. Fig. 6 shows an influence of factor x_2 (concentration of oxalic acid in electrolyte) on AAO layer thickness with varying levels of factor x_1 and constant level of factor $x_3="0"$.

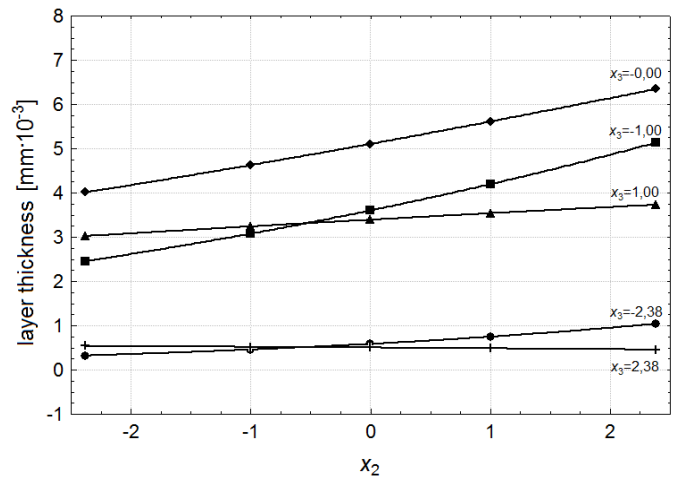


Fig. 5 Influence of factor x_2 on AAO layer thickness, $x_1="0"$

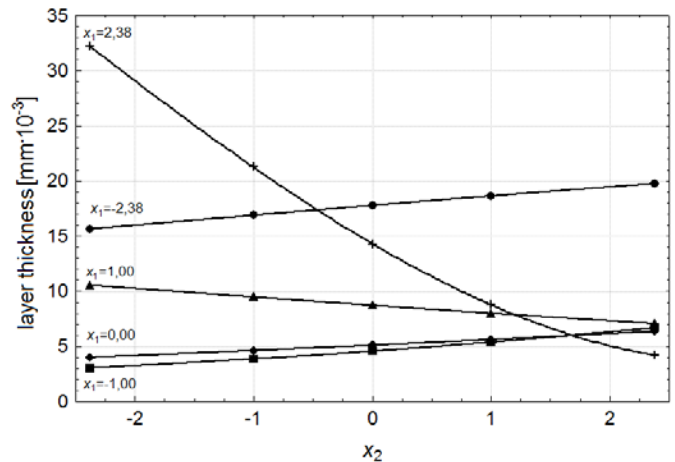


Fig. 6 Influence of factor x_2 on AAO layer thickness, $x_3="0"$

As shown in Fig. 5 and Fig. 6, with increasing level of factor x_2 the thickness of resulting AAO layer increases. This is caused by the number of dissociated ions that are involved in the formation of oxide layer (similarly to Fig. 3 and Fig. 4). Oxalic acid does not increase the aggressiveness of environment as significantly as does an increase in levels of sulphuric acid. That is why the speed in which the created oxide layer dissolves back into the electrolyte is significantly higher than speed in which it builds up. Based on this, it is

possible to create an AAO layer with greater thickness in lesser amount of oxidation time without a risk of decrease in quality.

Fig. 7 shows an influence of factor x_3 (concentration of added aluminium cations) on the AAO layer thickness with varying levels of factor x_1 and constant level of factor $x_2=0$. Fig. 8 shows an influence of factor x_3 (concentration of added aluminium cations) on AAO layer thickness with varying levels of factor x_2 and constant level of factor $x_1=0$.

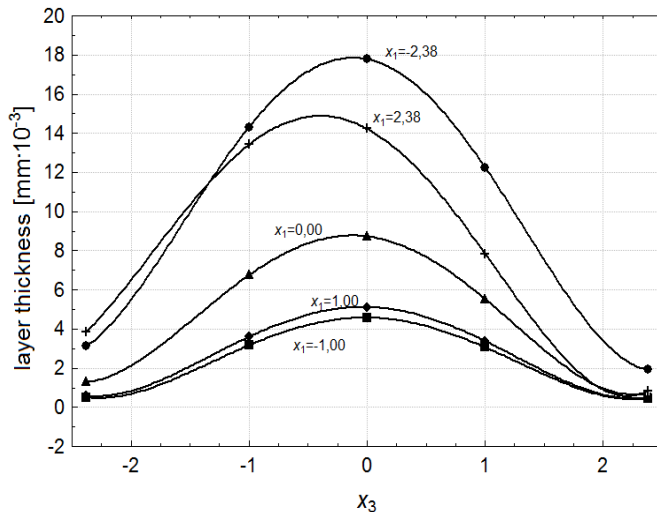


Fig. 7 Influence of factor x_3 on AAO layer thickness, $x_2=0$

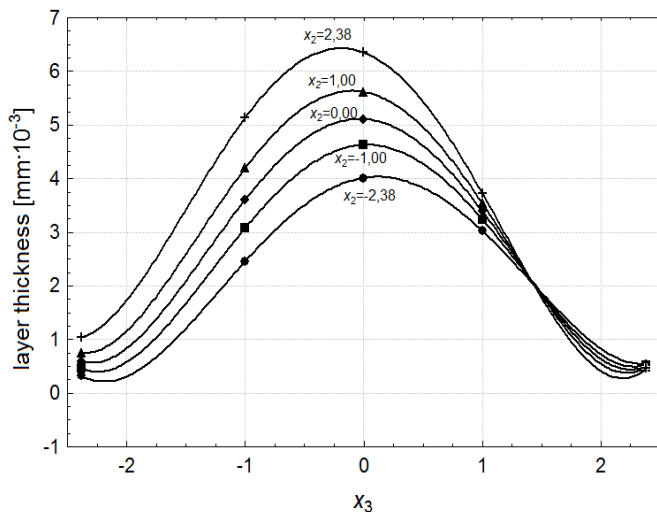


Fig. 8 Influence of factor x_3 on AAO layer thickness, $x_1=0$

Similarly to the influence of concentration of sulphuric acid (shown in Fig. 3 and Fig. 4) and oxalic acid (shown in Fig. 5 and Fig. 6) in the electrolyte, the concentration of added aluminium cations (factor x_3) also significantly influences the thickness of AAO layer. With gradual increase in factor level (from its observed minimum to its zero factor level) significantly increases the thickness of AAO layer. Electrolyte is trying to assume a state of equilibrium during an oxidation of a sample. In case there is an insufficient amount of aluminium cations ($x_3 < 0$), their number in electrolyte increases when aluminium atoms on anode transmit their

valence electrons and seize to create anode material. In case AAO layer has already formed of the anode, aluminium cations get into electrolyte by dissolution of bonds in aluminium oxide molecules. This causes faster dissolution of the formed AAO layer. Otherwise, when an amount of aluminium cations is excess ($x_3 > 0$), electrolyte tries to expel them in a form of aluminium atoms on cathode. Aluminium cations on anode receive free electrons and become cathode material. This process blocks the creation of anions with bound oxygen that is necessary for the creation of aluminium oxide. This causes decrease in speed of oxide layer build-up on cathode.

V. CONCLUSION

Based on calculated values of AAO layer thickness by developed prediction model, it is possible to observe how chemical composition of electrolyte influences technological process of Prediction model created by a neural unit shows relatively high reliability of prediction in case without tolerances and 95.46 % prediction reliability with prediction tolerance $\pm 2.00 \cdot 10^{-3}$ mm. Such high prediction reliability level gives many opportunities to optimize the process of anodic aluminium oxidation in regards to time and material used. More research should expand the prediction model by adding larger spectrum of current densities and also, more precisely define an influence of physical parameters on resulting AAO layer thickness.

REFERENCES

- [1] M. Gombár, J. Kmec, M. Badida, L. Sobotová, A. Vagaská, P. Michal, "The simulation of the temperature effects on the microhardness of anodic alumina oxide layers", *Metalurgija*, vol. 53, 2014, pp. 59-62.
- [2] M. Badida, M. Gombár, J. Kmec, L. Sobotová, A. Vagaská, P. Michal, P "Štúdium vplyvu chemického zloženia elektrolytu na mikrotvrdosť vrstvy vytvorenej anodickou oxidáciou hliníka", *Chemické Listy*, vol. 107, 2013, pp. 973-977.
- [3] M. Badida, M. Gombár, L. Sobotová, J. Kmec, A. Vagaská, P. Michal, "The influence of sodium chloride on the resulting AAO film", *Advanced Materials Research*, vol. 816-817, 2013, pp 18-22.
- [4] P. Michal, M. Gombár, A. Vagaská, J. Pitel' J. Kmec, "Experimental study and modeling of the zinc coating thickness", *Advanced Materials Research*, vol. 712-715, 2013, pp. 382-386.
- [5] M. Gombár, A. Vagaská, J. Kmec, P. Michal, "Microhardness of the coatings created by anodic oxidation of aluminium", *Applied Mechanics and Materials*, vol. 308, 2013, pp. 95-100.
- [6] E. Evin, J. Kmec, E. Fehová, "Optimizing of Electric Discharge Texturing Parameters of Rolls of the Rolling Mill of Steel Sheets", *Applied Mechanics and Materials*, vol. 420, (2013), pp. 78-84.
- [7] A. Vagaská, M. Gombár, J. Kmec P. Michal, "Statistical analysis of the factors effect on the zinc coating thickness", *Applied Mechanics and Materials*, vol. 378, 2013, pp. 184-189.
- [8] I. Tsangaraki-Kaplanoglou, S. Theohari, Th. Dimogerontakis, N. Kallithrakas-Kontos, W. Yar-Ming, K. , Hong-Hsiang, K. Sheila, "Effect of alloy types on the anodizing process of aluminum", *Surface & Coatings Technology*, vol. 200, 2006, pp. 2634 – 2641.
- [9] G. Patermarakis, "Development of a theory for the determination of the composition of the anodizing solution inside the pores during the growth of porous anodic Al₂O₃ films on aluminium by a transport phenomenon analysis", *Journal of Electroanalytical Chemistry*, vol. 447, 1998, pp. 25–41.
- [10] T. Aerts, I. DeGraeve, G. Nelissen, J. Deconinck, S. Kubacki, E. Dick, H. Terryn, "Experimental study and modelling of anodizing of aluminium in a wall-jetelectrode set-up in laminar and turbulent regime", *Corrosion Science*, vol. 51, 2009, pp. 1482–1489.