Using Neural Networks to Design Predictive Model of Creation of Aluminium Oxide Layer

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

Abstract—This paper shows an influence of amount of sulphuric acid in the electrolyte and an impact of electrolyte temperature on the thickness of aluminium oxide layer created with varying anodizing time and applied voltage. Impact of these variables is shown by using design of experiments methodology (DoE) for six factors (amount of sulphuric acid, oxalic acid, amount of aluminium cations, electrolyte temperature, anodizing time, applied voltage). Oxide layer was created with current densities of 1 A·dm^{-2} and 3 A·dm^{-2} respectively.

Keywords—anodizing, corrosion protection, layer thickness, neural networks

I. INTRODUCTION

PURE aluminium and its alloys, such as weight-saving materials, play an increasingly important role of technical, technological and economic terms [1] in the aerospace and automotive industries[2], where lightweight and rigid structure are preferred[3]. Anodic aluminium oxide (AAO) coating has recently attracted the scientists' attention because of its self-organizing nature of vertical (cylindrical) pores in the form of hexagonal arrays, which provides a 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 [4]. Anodizing is one of the most important processes in corrosion protection and colour finishes for aluminium [5].Anodizing of aluminium surfaces is carried out in a wide variety of plants for numerous uses in industries. It is an effective process applied to producing decorative and protective films on articles made from aluminium [6]. With the oxidation of aluminium, when forming the electrolyte, the most frequently used are sulphuric acid and oxalic acid,

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alternatively a combination of them, because of their environmental friendliness [7],[8]. The mechanism of an oxide layer formation when using sulphuric acid solution has been examined by Tsangaraki-Kaplanogloua et al.[9], Patermarakis [10], and Aerts et al.[11], who managed to design a mathematical model of local turbulences in the electrolyte and examine their influence on the geometrical dimensions of the pores. Aerts et al. were also dealing with the temperature effect on the growth of the oxide layer [12] and the layer porosity [4] of 99.50 % aluminium using the electrolyte comprising sulphuric acid based on which it followed that the structure of the layer, the layer porosity, its thickness and hardness are not so much under the influence of the temperature of the electrolyte compared to that of the electrode.

II. EXPERIMENT REALIZATION

Alloy EN AW 1050-H24 with dimensions 101x70x1 mm was used for specimens. Each applied specimen was degreased in a 38.00% solution of NaOH at 55.00 to 60.00 ° C for 2 minutes and stained in a 40.00% solution of NaOH at the temperature 45.00 °- 50.00 ° C for 0.50 min. Consequently, the specimen was immersed in a nitric acid bath (4.00% HNO$_3$) at the temperature from 18.00 to 24.00 ° C for 1.00 min. Between each operation, the sample was rinsed with distilled water.

Electrolyte for each anodizing sample was made from sulphuric acid, oxalic acid and aluminium cations (added like powdered aluminium oxide). Table 1 shows transfers of factors between nature scale and coded scale. Coded scale is used to prevent influence of the absolute value of the studied factors in evaluating the results of the experiment.

Table 1 table of transfers between natural scale 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}]	33.51	130.00	200.00	270.00	366.49
x_2	C_2H2O_4 [g.l^{-1}]	1.49	7.00	11.00	15.00	20.51
x_3	Al^{3+} [g.l^{-1}]	0.18	5.00	8.50	12.00	16.82
x_4	T [°C]	-1.78	12.00	22.00	32.00	45.78
x_5	t [min]	6.22	20.00	30.00	40.00	53.78
x_6	U [V]	5.24	8.00	10.00	12.00	14.76

III. PROBLEM SOLUTION

A higher-order neural unit (HONU), especially the 3rd order HONU based on the iterative Levenberg-Marquardt (LM) algorithm [13],[14],[15] was used to determine the influence of input factors on the thickness of the final AAO layer. This algorithm is often used for training technique of the neural unit [16]. It is a process of updating individual weights in a predetermined number of steps to achieve a minimum difference between the actual and calculated values of observed variable [17], [18], [19]. The equation describing the investigated model is the characteristic equation of given type of neural unit (1st order HONU, 2nd order HONU a 3rd order HONU) for observed factors $x_1, x_2, x_3, x_4, x_5, x_6$.

IV. RESULTS AND DISCUSSION

After the learning process of neuron unit is done, we get a prediction model that describes the thickness of AAO layer. The final thickness of oxide layer, α is preliminary thickness of oxide layer is expressed in $mm \cdot 10^{-3}$.

Table 2 shows significant statistical indicator for compiled prediction models of surface AAO layer thickness for surface current densities $1\ A \cdot dm^{-2}$ and $3\ A \cdot dm^{-2}$. Those indicators are sum of square errors "SSE", mean square error "RMSE", correlation coefficient "R", coefficient of determination "R", standard deviation of errors "se", variation of errors "s^2e" and biggest error of prediction "maxe".

Table 2 significant statistical indicators for compiled mathematical models

	$1\ A \cdot dm^{-2}$	$3\ A \cdot dm^{-2}$
SSE	87.51	60.30
RMSE	1.90	1.31
R^2	0.93	0.96
R	0.97	0.98
se	1.38	1.15
s^2e	1.90	1.32
maxe	6.6	5.64

Fig. 1, Fig. 2, Fig. 3, Fig. 4 and Fig. 5 show the influence of factor x_1 (concentration of sulphuric acid in the electrolyte) and x_4 (temperature of the electrolyte) on the thickness of aluminium oxide created on sample surface. These graphs also demonstrate influence of factor x_5 (anodizing time) on the oxide thickness. The level of factor x_5 is set to level "-2.38" (6.22 min) Fig. 1, "-1" (20 min) Fig. 2, "0" (30 min) Fig. 3 "1" (40 min) Fig. 4 and "2.38" (53.78 min) Fig. 5. Aluminium oxide layer was created on the surface areas at $1.00 A \cdot dm^{-2}$ of current density. Factors x_2, x_3 and x_6 have zero factor level for all these graphs. Zero factor level for factor x_2 is 11 g.l⁻¹, for factor x_3 it is 8.5 g.l⁻¹ and for factor x_6 it is 10 V.

From these graphical characteristics it can be surmised that the thickness of AAO layer is proportional to concentration of sulphuric acid in the electrolyte (factor x_1). Thus we can state that with increasing amount of sulphuric acid in the electrolyte also rises an amount of dissociated ions. Increased ion amount in an electrolyte increase its conductivity. Oxygen, which is bound to a part of these ions, is used to create a layer of an aluminium oxide. Electrolyte temperature (factor x_4) influences

the speed of oxide layer creating and also the thickness of AAO layer. With increasing temperature also rises the speed of chemical reactions on metal-electrolyte interface. However, general claim that with increasing electrolyte temperature also proportionally increases the thickness of AAO layer is not true. This claim is true only in a specific case. It means that some others variables significantly influences the thickness of AAO layer, specifically, the time of oxidation (factor x_5). If the concentration of sulphuric acid in electrolyte influences the amount of ions in electrolyte and if electrolyte temperature influences the speed of chemical reactions on a metal-electrolyte interface, then not only does time of oxidation determinate time of chemical reactions between meal and electrolyte but also between electrolyte and already created oxide layer. Reactions between metal and electrolyte create new molecules of aluminium oxide on the surface of metal and thus contribute to the rise of oxide layer. However, reactions between oxide layer and electrolyte cause reduction in thickness of created oxide layer due to it dissolving in the solution. Thus with the increase in time of oxidation, the thickness of oxide layer decreases, due to increase in electrolyte temperature. After crossing a certain temperature threshold (factor level -1 for Fig. 2, factor level 0 for Fig. 3, Fig. 4, Fig. 5), the resulting oxide layer thickness increases. Speed of oxide layer creating is higher than speed at which it before it reaches the temperature of factor -1.
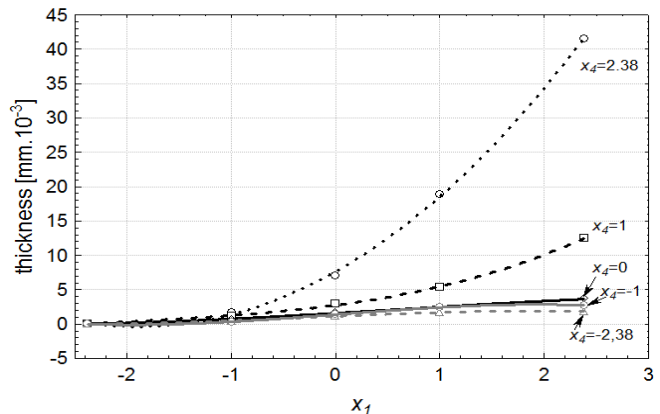

Fig. 1 Influence of factor x_1 and x_4 on AAO layer thickness at current density $1 \cdot A dm^{-2}$ and factor x_5 which is set to level -2.38
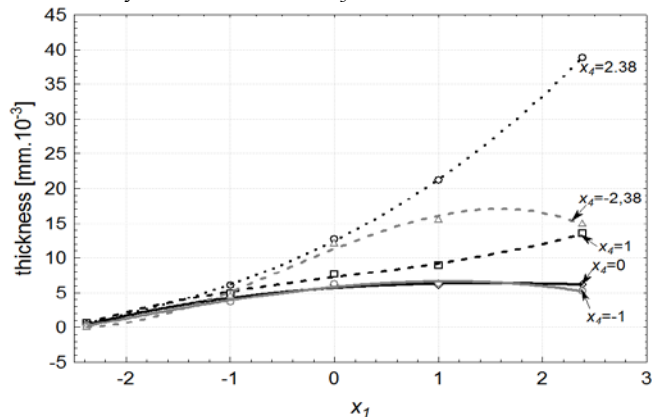

Fig. 2 Influence of factor x_1 and x_4 on AAO layer thickness at current density of $1 \cdot A dm$-2 and factor $x5$ which is set to level -1
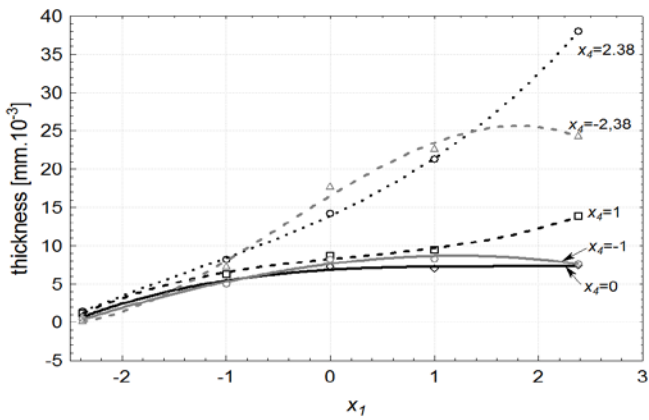
Fig. 3 Influence of factor x_1 and x_4 on AAO layer thickness at current density of $1 \cdot Adm^{-2}$ and factor x_5 which is set to level 0
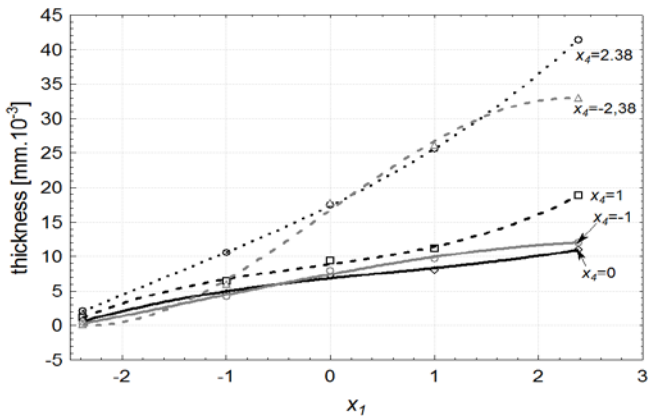

Fig. 4 Influence of factor x_1 and x_4 on AAO layer thickness at current density of $1 \cdot Adm^{-2}$ and factor x_5 which is set to level 1
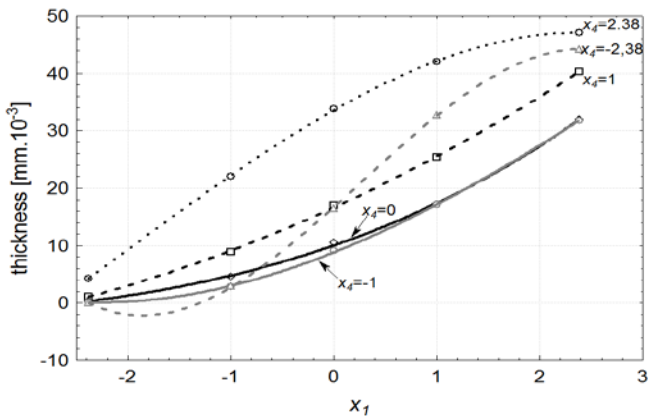

Fig. 5 Influence of factor x_1 and x_4 on AAO layer thickness at current density of $1 \cdot Adm^{-2}$ and factor x_5 which is set to level 2.38

Fig. 6, Fig. 7, Fig. 8, Fig. 9 and Fig. 10 shows influence of factors x_1(concentration of sulphuric acid in the electrolyte) and x4 (temperature of the electrolyte) on thickness of aluminium oxide created on sample surface These graphs also demonstrate influence of the factor x_5 (anodizing time) on the oxide thickness. Level of factor x_5 is set to level "-2.38" (6.22 min) Fig. 6, "-1" (20 min) Fig. 7, "0" (30 min) Fig. 8 "1" (40 min) Fig. 9 and "2.38" (53.78 min) Fig. 10. Aluminium oxide layer was created on $3.00 A \cdot dm^{-2}$ current density surface areas. Factors x_2, x_3 and x_6 have zero factor level for all these

pictures. Zero factor level for factor x_2 is 11 g.l^{-1}, for factor x_3 it is 8.5 g.l^{-1} and for factor x_6 it is 10 V.

From comparison of thickness based on concentration of sulphuric acid in electrolyte, electrolyte temperature and time of oxidation for current densities of 1 A·dm^{-2} and 3 A·dm^{-2} (Fig. 1 - Fig. 10), it is evident that current density does not have a significant influence on the thickness of oxide layer if concentration of sulphuric acid is lower as at factor level 0. With its higher concentration, the thickness of oxide layer increases by approximately 5 mm·10^{-6} at current density of 3 A·dm^{-2}.
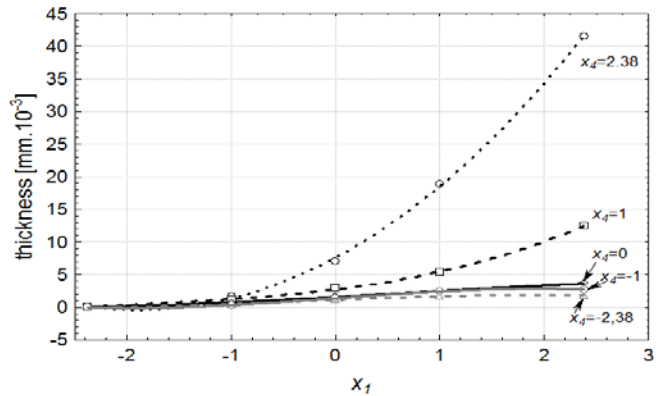

Fig. 6 Influence of factor x_1 and x_4 on AAO layer thickness for current density $3 \cdot Adm^{-2}$ and factor x_5 which is set to level -2.38
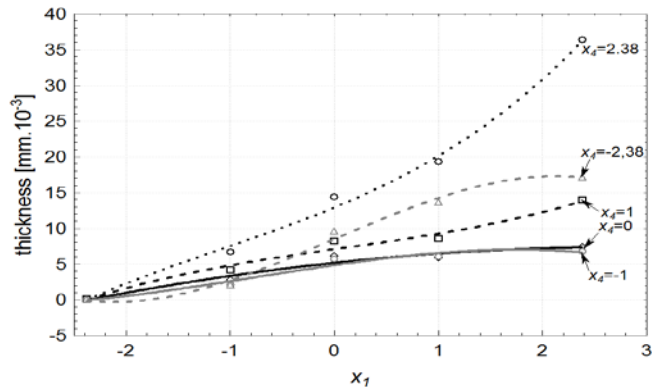

Fig. 7 Influence of factor x_1 and x_4 on AAO layer thickness at current density of $3 \cdot Adm^{-2}$ and factor x_5 which is set to level -1
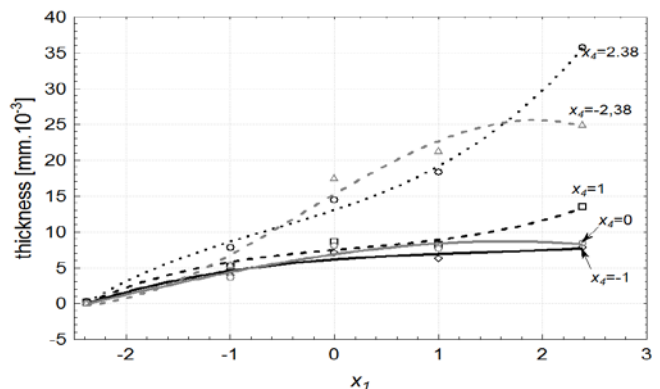

Fig. 8 Influence of factor x_1 and x_4 on AAO layer thickness at current density of $3 \cdot Adm^{-2}$ and factor x_5 which is set to level 0
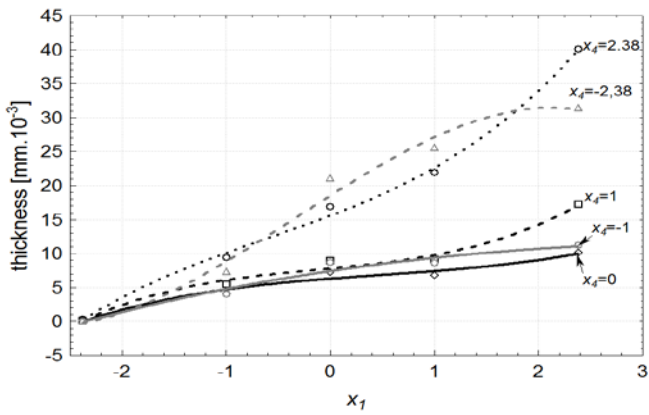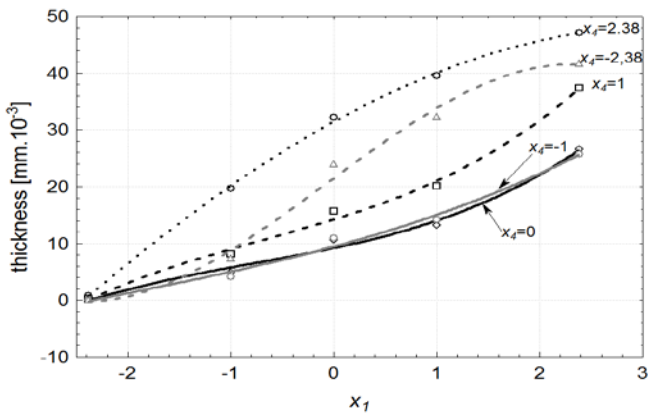
Fig. 9 Influence of factor x_1 and x_4 on AAO layer thickness at current density of $3 \cdot Adm^{-2}$ and factor x_5 which is set to level 1

Fig. 10 Influence of factor x_1 and x_4 on AAO layer thickness at current density of $3 \cdot Adm^{-2}$ and factor x_5 which is set to level 2.38

Just as figures Fig. 1 through Fig. 10 examine the relationship between the amount of sulphuric acid in electrolyte, electrolyte temperature, oxidation time and thickness of oxide layer, figures Fig. 11 through Fig. 20 show the influence of amount of sulphuric acid in electrolyte, electrolyte temperature and voltage levels in relation to the thickness of the oxide layer. Results are shown for cases of current densities 1 A·dm^{-2} a 3 A·dm^{-2}.

Fig. 11, Fig. 12, Fig. 13, Fig. 14 and Fig. 15 show the influence of factor x_1 (concentration of sulphuric acid in the electrolyte) and x_4 (temperature of the electrolyte) on the thickness of aluminium oxide created on sample surface. These graphs also demonstrate the influence of factor x_6 (the size of an applied voltage) on the oxide thickness. Level of factor x_6 is set to level "-2.38" (5.24 V) Fig. 11, "-1" (8 V) Fig. 12, "0" (10 V) Fig. 13 "1" (12 V) Fig. 14 and "2.38" (14.76 V) Fig. 15. Aluminium oxide layer was created at 1.00A·dm^{-2} current density surface areas. Factors x_2, x_3 and x_5 have zero factor level for all these graphs. Zero factor level for factor x_2 is 11 g.l^{-1}, for factor x_3 is 8.5 g.l^{-1} and for factor x_5 is 30 min.

Connected voltage levels are proportional to the electric potential. Electric potential is proportional to electrodynamics forces. These electrodynamics forces determine the force with which are positively charged ions attracted to the negatively charged electrode (cathode) and the force with which are negatively charged ions attracted to the positively charged electrode (anode). If we increase voltage, electric potential on

anode will also increase. Higher electric potential on anode will attract higher number of oxygen anions. Thus, the surface of aluminium sample will contain higher amount of oxygen anions and more molecules of aluminium oxide will be created on the surface of the sample. Through this, the thickness of AAO layer increases. It is possible to see this process on figures Fig. 11 through Fig. 20– same for current densities of 1 A·dm-2 (Fig. 11 through Fig. 15) and 3 A·dm-2 (Fig. 16 through Fig. 20), where the thickness of oxide layer increases faster with the increase of voltage.
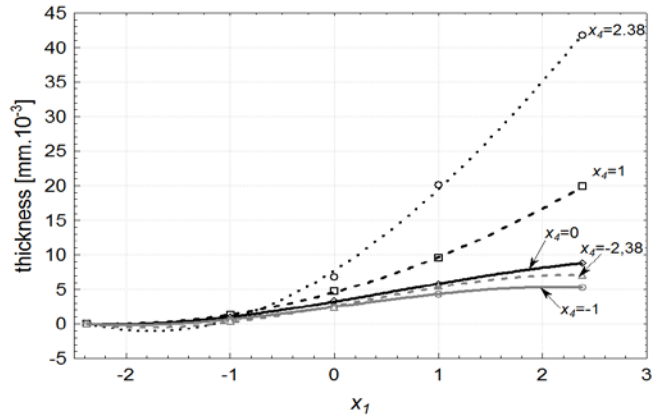

Fig. 11 Influence of factor x_1 and x_4 on AAO layer thickness at current density of $1 \cdot Adm^{-2}$ and factor x_6 which is set to level -2.38
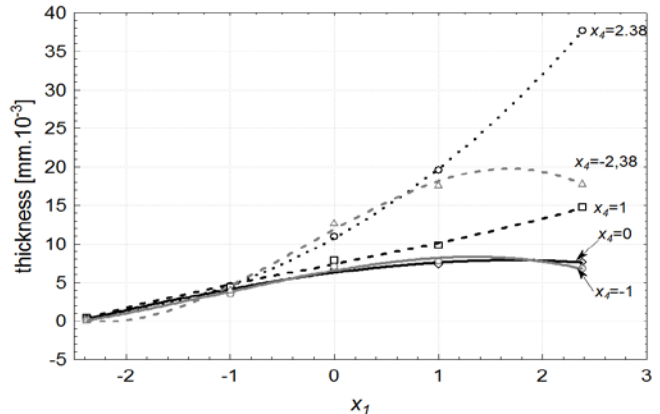

Fig. 12 Influence of factor x_1 and x_4 on AAO layer thickness at current density of $1 \cdot Adm^{-2}$ and factor x_6 which is set to level -1
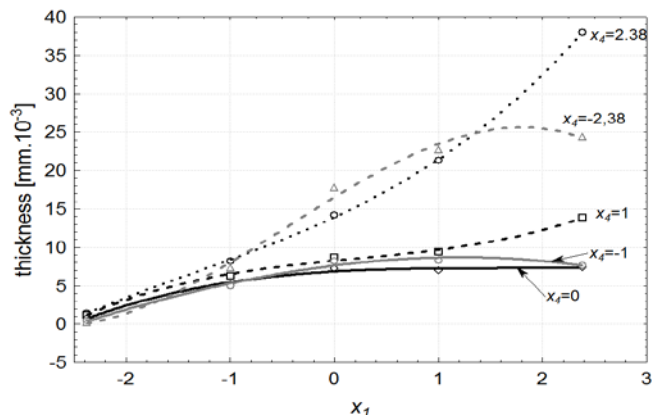

Fig. 13 Influence of factor x_1 and x_4 on AAO layer thickness at current density of $1 \cdot Adm^{-2}$ and factor x_6 which is set to level 0
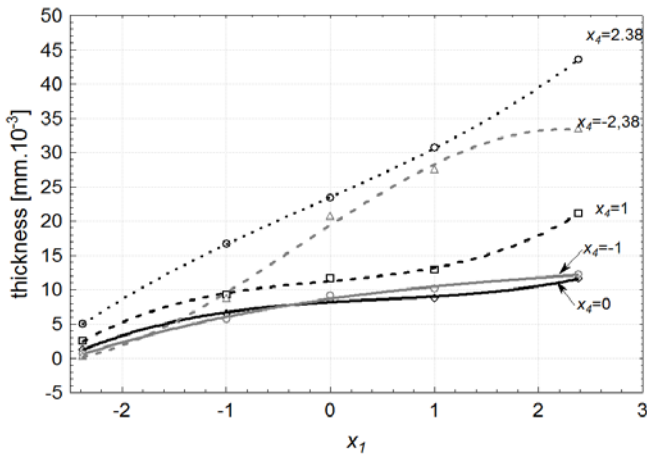
Fig. 14 Influence of factor x_1 and x_4 on AAO layer thickness at current density of $1 \cdot Adm^{-2}$ and factor x_6 which is set to level 1
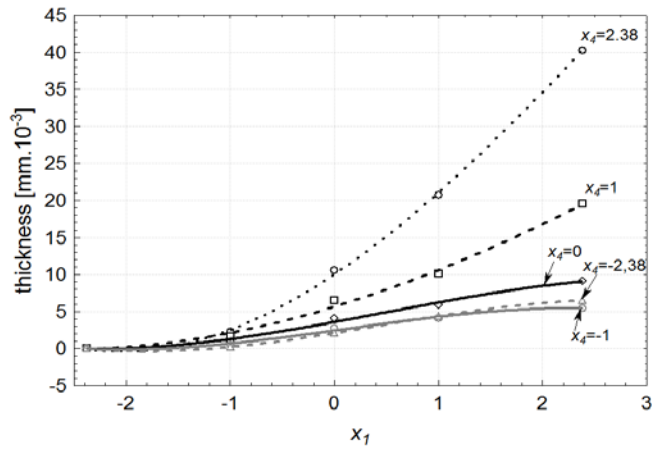

Fig. 16 Influence of factors x_1 and x_4 on AAO layer thickness at current density $3 \cdot Adm^{-2}$ and factor x_6 which is set on level -2.38
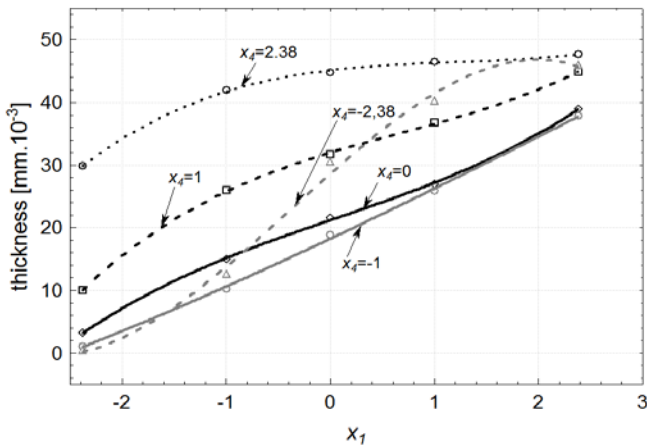

Fig. 15 Influence of factor x_1 and x_4 on AAO layer thickness at current density of $1 \cdot Adm^{-2}$ and factor x_6 which is set to level 2.38
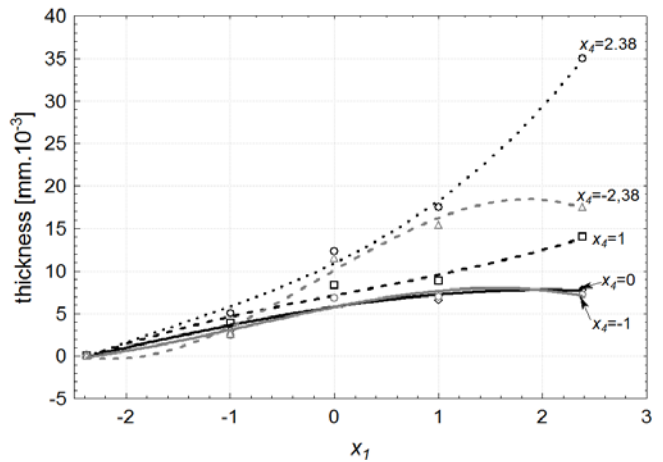

Fig. 17 Influence of factors x_1 and x_4 on AAO layer thickness at current density of $3 \cdot Adm^{-2}$ and factor x_6 which is set on level -1

Fig. 16, Fig. 17, Fig. 18, Fig. 19 and Fig. 20 show the influence of factors x_1 (concentration of sulphuric acid in the electrolyte) and x_4 (temperature of the electrolyte) on the thickness of aluminium oxide created on sample surface. These graphs also demonstrate the influence of the factor x_5 (anodizing time) on the oxide thickness. Level of factor x_5 is set to level "-2.38" (6.22 min) Fig. 16, "-1" (20 min) Fig. 17, "0" (30 min) Fig. 18 "1" (40 min) Fig. 19 and "2.38" (53.78 min) Fig. 20. Aluminium oxide layer was created at $1.00 A \cdot dm^{-2}$ current density surface areas. Factors x_2, x_3 and x_6 have zero factor level for all these pictures. Zero factor level for factor x_2 is 11 g.l^{-1}, for factor x_3 is 8.5 g.l^{-1} and for factor x_6 is 10 V. By comparing the effects of input factors x_1 (concentration of sulphuric acid in electrolyte), x_4 (electrolyte temperature) and x_6 (voltage level) at current density 1 A·dm-2 (Fig. 11 through Fig. 15) and at current density 3 A·dm^{-2} (Fig. 16 through Fig. 20) it is possible to surmise, that levels of surface current density have no influence on the resulting thickness of oxide layer. Differences in thickness of AAO layer are minimal – as is the case with input factors x_1 (concentration of sulphuric acid in electrolyte), x_4 (electrolyte temperature), x_5 (time of oxidation) for current density 1 A·dm^{-2} (Fig. 1 - Fig. 5) and at current density 3 A·dm^{-2} (Fig. 6 - Fig. 10).

Fig. 18 Influence of factors x_1 and x_4 on AAO layer thickness at current density of $3 \cdot Adm^{-2}$ and factor x_6 which is set on level 0

Fig. 19 Influence of factors x_1 and x_4 on AAO layer thickness at current density of $3 \cdot \text{Adm}^{-2}$ and factor x_6 which is set on level 1
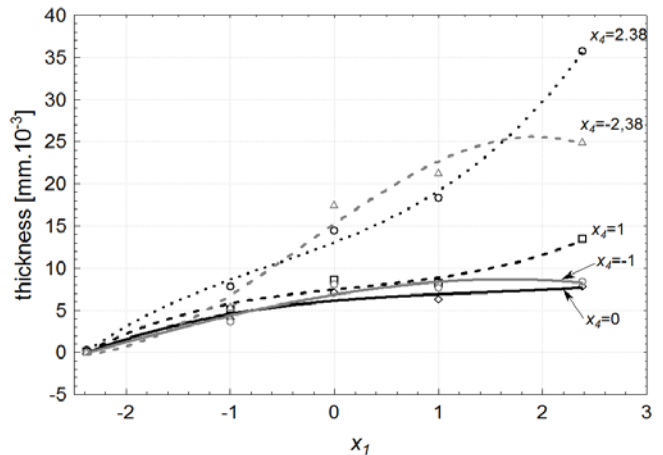

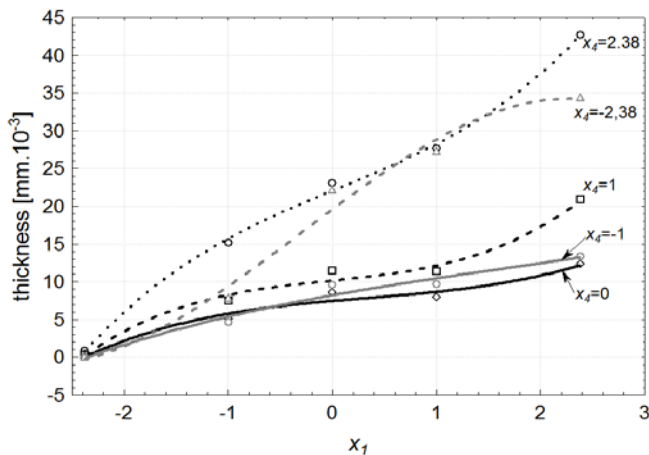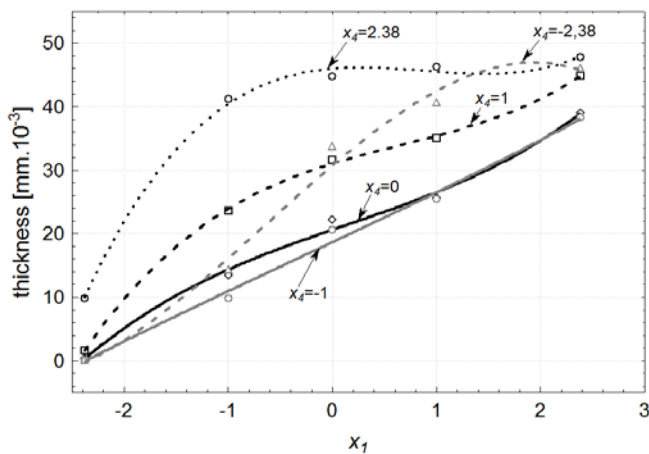Fig. 20 Influence of factors x_1 and x_4 on AAO layer thickness at current density of $3 \cdot \text{Adm}^{-2}$ and factor x_6 which is set on level 2.38

V. CONCLUSION

As shown by the evaluation process of experimental results presented above, the use of 3rd order neural unit based on the iterative Levenberg-Marquardt (LM) optimization algorithm provides a wide range of options to investigate influence of input factors on the final AAO layer thickness. By using of neural unit we can quickly and simply describe the behaviour of the monitored system. This neural unit allowed us to monitor the impact of input factors (concentration of sulphuric acid, electrolyte temperature, anodizing time and applied voltage) on the final thickness of the AAO layer at surface current density 1 A·dm^{-2} and 3 A·dm^{-2}. Also by using the neural unit of 3rd order HONU it was possible to describe the influence of input factors on the thickness of final AAO layer with confidence interval of 93.45% at surface current density 1 A·dm^{-2}, and with confidence interval of 95.60% of surface current density 3 A·dm^{-2}.

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